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Ion transport through water – organic solvent

liquid-liquid interface: a simulation study

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Abstract

Ion interactions and partitioning at the water-organic solvent interface and the solvation characteristics have been characterized by molecular dynamics simulations. More precisely, we study sodium cation transport through water-cyclohexane, water-1,2-dichloroethane, and water-pentanol interfaces providing a systematic characterization of the ion interfacial behavior including barriers against entering the apolar phase, as well as, characterization of the interfaces in the presence of the ions. We find a sodium depletion zone at the apolar interface and persistent hydration of the cation when entering the apolar phase. The barrier against the cation entering the apolar phase and ion hydration depend strongly on specific characteristics of the organic solvent. The strength of both barrier and hydration shell binding (persistence of the cation hydration) go with the applarity and the surface tension at the interface, that is, both decrease in order cyclohexane-water > 1, 2-dichloroethane-water >pentanol-water. However, the size of the hydration shell measured in water molecules bound by the cation entering the less polar phase behaves oppositely with the cation carrying most water to the pentanol phase, and a much smaller in size, but very tightly bound water shell to cyclohexane. We discuss the implications of the observations for ion transport through the interface of immiscible, or poorly miscible liquids, and for materials of confined ion transport such as ion conduction membranes or biological ion channel activity.

Keywords: molecular dynamics, hydration, ion interactions, thermodynamic integration.

Introduction

The interface between two immiscible liquids remains a region on which very little is known at the microscopic level.^{1–3} Besides the interfacial microstructure, understanding transport through the interface remains a major unsolved problem of electrochemistry, despite both the fundamental and practical importance of the interface formed by two liquids. E.g., ion transport through membranes, ion selective electrodes, protein folding, biological ion channels, salting in and out of biological macromolecules, and emulsification processes all depend on immiscible liquids, their interfaces, and ions at the interfaces. In particular, in all of these, free energy of transfer through the interface of water and different non-polar, organic liquids and the size and persistence of the hydration shell of the transported ion are the key factors in understanding the transport. Here, we tackle the topic by molecular simulations of ion transport through organic-water interfaces of varying degree of polarity and the molecular behavior at the interface providing a systematic characterization of the interfacial behavior as a function of immiscibility of the two liquids toward the purpose of understanding better barriers for electrochemical transport at interfaces and especially in porous systems such as ion conduction membranes.

Whereas the structure of bulk liquids can, at molecular level, be characterized by, e.g., scattering techniques, the molecular level interface of two immiscible liquids, and charge interactions there, remain challenging for experimental techniques. Only recently, experimental techniques with molecular level resolution have matured sufficiently to provide specific information about the aqueous interface. The basic understanding obtained by second harmonic generation (SHS),^{4–6} vibrational sum-frequency generation (VSFG),^{1,7–11} and photoelectron spectroscopy^{12–15} is that the interfaces have ion-type and interface specific, active interactions with the ions. Molecular simulations, on the other hand, readily provide information of such interfaces providing coinciding information, which presents the interfaces as rather active and showing ion specificity in their interactions. For recent reviews, see for example refs 2, 16, and 17. In particular, the binding strength of the ion hydration shell has direct consequences for their interfacial behavior; small hard ions that form a strong hydration shell, such as alkali cations or fluoride, are depleted from the interface, whereas large polarizable ions, for example heavier halides and hydronium, may show propensity for the interface.^{2,5,18–21}

The possibility to characterize the liquid-liquid interface on a microstructural level and

the detailed dynamics information readily available have raised significant interest on molecular dynamics simulations of ions and their interactions at immiscible water - organic solvent interfaces since 1990s,^{4,22–33} but only recently molecular simulations have reached the system sizes and timescales sufficient to describe interfacial coarsening and transport through the interface in atomistic detail.^{32,34} The approaches taken are dominantly classical, point-like partial charge models although the need for polarizable, or quantum mechanical models, has been argued.^{17,35} Polarizable models have been used for the study of ions at the water - vapor interface^{17,36–38} but also for ion interactions at liquid-liquid interfaces in, e.g., refs 39–43, and ion transport in, e.g., refs 40,44–46. These studies show that accounting for polarization in the model affects the ion-interface behavior, especially when large, polarizable anions are considered; whereas for sodium, a small and hard ion, the effect is reduced.

We probe the ion transport through water - organic solvent interface by a set of basic laboratory systems representing interfaces from aqueous-strongly apolar interface (watercyclohexane) to partially miscible aqueous-polar liquid interface (water-pentanol). Intermediate interface is provided by water and a slightly polar organic solvent (water-1, 2dichloroethane). In agreement with earlier related studies,^{32,37,40,43,47} we find an interfacial depletion zone corresponding to the hydration of the sodium cation. Furthermore, we report persistent hydration of the cation when entering the apolar liquids. For the more polar pentanol, the remaining hydration shell includes more water molecules but their dynamics are faster and the hydration is less persistent with some of the water molecules replaced by alcohol groups dynamically every now and then. Moreover, the observed barrier against entering the less polar phase depends strongly on specific molecular characteristics of the liquid with the barrier decreasing with changing the organic solvent from cyclohexane to dichloroethane to pentanol in this order.

To our knowledge, with the exception of Benjamin's^{48,49} pioneering comparisons of interfaces of water and an apolar, a weakly polar, or a polar solvent, this is the first time a series of liquid interfaces with varying polarity difference has been studied; the existing studies are typically limited to a specific aqueous interface at each time which makes comparison of different interfaces difficult. The present work provides significant new microscopic understanding of the differences of the interfaces as here the interfaces are characterized in atomistic detail both in water and the organic solvent with dynamics included. Additionally, to our knowledge, this is the first time a series of system sizes and time scales sufficient to characterize the interfacial coarsening and its dynamics are presented. We relate the barrier height, interfacial coarsening, and ion hydration between the different systems enabling comparison. Furthermore, to provide an estimate on the effects of polarizability, we perform comparative simulations with a fully polarizable force field using the cyclohexane-water system. Finally, we discuss the implications of the observations, especially the barrier and the persistent hydration.

Methods

Computational Model

The Gromacs 4.5.6 simulation package⁵⁰⁻⁵² with GROMOS43A1⁵³ united atom force field with the corresponding ions were employed for the atomistic molecular dynamics (MD) simulations. GROMOS43a1 is parametrized based on the reproduction of molecular volumes and heats of vaporization of small chemical species. Cyclohexane and dichloroethane (DCE) are rather well within the parametrization regime but the pentanol results depend delicately on the exact miscibility of the two liquids here, as the extent and width of water fingers penetrating into the alcohol phase (interface raggedness) depend on the mutual solubility of the alcohol and water molecules within the simulation model. Therefore, for comparison, in addition to the GROMOS43a1 simulations, we performed the pentanol-water interfacial study also with pentanol described within the OPLS-aa⁵⁴ force field which is based on optimizing organic liquid properties (however, not specifically alcohol-water partitioning). The OPLS-aa simulations use the standard Åqvist sodium⁵⁵ and Chandrasekhar chloride⁵⁶ parameters. In compliance with the GROMOS43a1 force field, the SPC water model⁵⁷ is used for the water phase in the simulations. With the exception of the cyclohexane system, the SPC/E⁵⁸ variant, which introduces a minor polarization change to the water partial charges correcting for density and diffusion, has been used. The same water model is used for consistency also with the OPLS-aa comparison of pentanol despite not being the recommended OPLS-aa water model.

The liquid-liquid interface in all systems was constructed by first creating separate cubic slabs of organic solvent and water. These slabs were first energy minimized using the steepest descent method and initially relaxed by very short 0.1 ns NVT and 1.0 ns NPT simulations on individual slabs. Next, the two slabs were united to create the liquid-liquid interface. The relaxed final system sizes varied between $4.24 \text{ nm} \times 4.24 \text{ nm} \times 8.47 \text{ nm}$ (cyclohexane water) to $4.75 \text{ nm} \times 4.75 \text{ nm} \times 9.51 \text{ nm}$ (pentanol - water). These correspond to 2178 -3844 water molecules in the aqueous phase. The variation in final system sizes result from differences in initial organic liquid component density. The GROMACS genion algorithm was used to generate Na⁺ and Cl⁻ ions in an amount corresponding to an initial 4 M total ion concentration in the water slab in all systems. Depending on the water slab size, the number of ions varied between 192 and 300. Consequently, a bi-interfacial periodic liquidliquid system was created with ions spread out in the aqueous phase, see 1 for the resulting cyclohexane-water system. For calculating the interfacial tensions between the liquids, the individual slabs were simulated separately in the absence of ions. To ensure that the high salt concentration or the system size do not affect the physical results, identical cyclohexanewater simulations were performed at 2 M and 1 M NaCl concentrations, as well as, using a system where the thickness of the cyclohexane phase was doubled (at NaCl concentrations of 2 M and 30 mM) and a system where the interfacial surface area was increased by a factor of 9 (at a NaCl concentration of 2 M). No observable change in ion transport behavior was observed with the exception of ion pairing behavior, see 4, which is concentration dependent.

Following initialization, all simulations were performed in the NPT ensemble at p = 1 bar



Figure 1: The bi-interfacial cyclohexane-water system. At left, a surface plot of water phase plotted as its accessible surface area using a 0.3 nm in diameter probe. The water-cyclohexane interface is molecularly sharp with some fluctuations. Cyclohexane and the ions are omitted in the surface visualization. At right, the corresponding molecular detail visualization of the cross section with both water and cyclohexane phase visualized. Ions are enlarged in the visualization with sodium represented in black and chloride in green. The snapshots correspond to 80 ns.

and T = 300 K using the stochastic rescaling thermostat of Bussi et al.⁵⁹ and isotropic Parrinello-Rahman barostat⁶⁰ for a total of 80 ns. The coupling times were set to 2.0 ps for pressure and 0.1 ps for temperature, and the temperatures of the organic molecules were controlled independently of those of the water and ions. From the beginning of each simulation, 10 ns were disregarded as initial relaxation in the analysis. The bond lengths of organic molecules were constrained by the LINCS algorithm⁶¹ and those of water molecules by SETTLE.⁶² A time step of 2 fs was used in all reported simulations. The full particlemesh Ewald method⁶³ was employed for the long-ranged electrostatic interactions; not fully accounting for these interactions has been shown to lead to serious artifacts in the simulations of amphiphilic molecules.^{64,65} The Lennard-Jones interactions and the real-space part of the Ewald summation were cut off at 1 nm with Fourier spacing of 0.12 nm. We are aware the GROMOS force field has been parametrized with a longer Lennard-Jones cut-off and typically it is strongly advised to use the original parametrization values for the cut-offs. To ensure this choice did not affect the energy profiles, we run comparison against 1.4 nm cut-off, and neither the liquid density profiles nor the interfacial interactions data of the ion were affected.

The GROMOS Na⁺ and Cl⁻ ion models have a tendency to form artificial microcrystals or clusters at concentrations much lower than experiments.⁶⁶ This aggregation propensity has been addressed in a related study³² where comparison with Kirkwood-Buff ions⁶⁷ resulted in similar interfacial behavior providing confidence in the ion model performance under these conditions. Regardless, we monitored for persistent clustering or crystallization but did not observe occurrence beyond short time correlations.

Furthermore, the force field, water model and the ion model used in the work are with fixed intramolecular partial charges, although polarizability with molecular charge distribution has been called for in relation to ion behavior at the liquid-liquid interface.^{17,35} Nonpolarizable molecular models in general result in weaker interfacial interactions than when calculated with polarizable models when the ions are soft.³⁹ The ions in this work are small, hard ions, and they remain solvated by a water shell crossing the interface. This reduces the magnitude of expected polarization changes. However, to evaluate the significance of polarizability here, we performed comparative simulations for the cyclohexane-water system using the CHARMM-based, Drude-polarizable force field⁶⁸ at an ion concentration of 40 mM. The cyclohexane-water system was chosen for these comparison simulations because cyclohexane has the largest polarizability of the studied organic molecules. The corresponding non-polarizable reference data were obtained with the regular CHARMM36 force field.⁶⁹ Additional details regarding these comparison simulations are reported in the Supporting Information.

Simulation methods and analysis

To extract an approximation of the effective free energy landscape the cation observes in an immiscible system of water and apolar organic solvent, we determined the potential of mean force observed by the cation. In practice, a Na⁺ ion residing in the bulk water phase was randomly selected and moved slowly stepwise with a constant rate toward and through the interface into the organic phase. The ion degrees of freedom on the plane parallel to the interface were unconstrained during the translation through the interface. The resultant force magnitude and direction on the ion being slowly moved from one phase to another fluctuates between consequent steps but provided the ion movement is slow enough, and allows sufficient sampling of configurations at each averaging step to provide accurate values, the mean force on the ion corresponds to the effective energy landscape observed by the ion. We determine this mean force computationally and in this work, the averaging is done over 5000 steps (10 ps).

The ionic solvation was determined by calculating the number of water molecules within a radius corresponding to the second solvation shell of the ion. For Na in water, this is determined to be 0.53 nm based on the minimum after the 2nd peak in the radial distribution function of water solvating Na. For an ion in the organic solvents, this radius is ambiguous, and depends on the system. In order to maintain comparability of the results within different systems, the same 0.53 nm cut-off was used also in the organic solvent phases for the hydrated ions. The sensibility of using the second solvation shell as the cut-off was verified by analyzing the final solvation clusters around Na ions in the cyclohexane and dichloroethane phases; these contain water in 1st and 2nd solvation shell but beyond that, only the organic solvent is present. In the partially miscible alcohol systems, frequent exchange of water molecules and alcohol groups in the solvation shell takes place; also here the same cut-off is used for comparability.

Molecular stability of the solvation shell was characterized by determining the persistence time the molecules typically remained in this solvation shell of the ion. The density profiles were calculated slabwise using an equal division of the simulation box into 100 bins in the direction perpendicular to the interface.

Simulated system

2 shows the chemical structures, as well as, the employed simulation model atom types and partial charges for the organic molecules in this study. No partial charges were assigned for cyclohexane molecules making cyclohexane completely apolar. The partial charges of 1,2-dichloroethane and pentanol are based on the partial charges of refs 70 and 54 with the all-atom charges of the non-polar hydrogens and the neighboring heavy atom combined in the united atom parametrizations. For pentanol, the counter charge of the alcohol group is divided between the two closest carbons to the group, see 2. In addition to the pentanolwater interface, we also run comparison simulations with the even more miscible butanolwater interface with an analogous model. However, as this system did not equilibrate within the simulation time scale due to high degree of miscibility and formation of extensive water channels into the butanol phase, the results were deemed quantitatively inconclusive and are included only at cursory level.

The water molecules follow the SPC^{57} and SPC/E^{58} models depending on the system.

All parameters not explicitly specified are according to the standard force field interactions in GROMOS 43a1.⁵³ The molecular topologies were generated using the PRODRG server.⁷¹



Figure 2: The structures of the simulated organic molecules; cyclohexane (top left), 1,2dichloroethane (top right), pentanol in GROMOS43a1 united atom description (bottom left), and pentanol in OPLS-all-atom description (bottom right). In addition, the force field specific atom type labels and assigned values of partial charges, δ , used in the simulations are shown. The values shown for individual hydrogens apply to each hydrogen connected to the same atom.

Results

Water-cyclohexane interface

The water-cyclohexane interface was chosen as a model interface for two immiscible liquids, see 1. In the simulations of joint water and cyclohexane slabs, both the water and the cyclohexane phase quickly equilibrate to form the uniform density profiles presented in 3 at left. The symmetric dual-interface results from the usage of periodic boundary conditions. The graphs show the interface to be molecularly sharp with practically non-existing interpenetration of one liquid phase to the other. This is further visualized in 1 where the surface plot shows equal roughness at the interface as on the simulation box faces corresponding to periodic boundary conditions, i.e., continuous water phase directions. Upon introduction of NaCl into the system, the density profile changes. This is presented in 3 at right. Most notably, 3 shows the interfacial region remains devoid of ions at a region corresponding to Na hydration shell. Related to this, the interfacial pure water density has a peak highlighted in the inset in 3: the actual salt water density here is water+ion density, and plotted together, the aqueous phase density remains flat. The overall ion concentration is high which could have an influence on the results: by decreasing the concentration of NaCl down to 2.0 M and 1.0 M in the water slab, we verified that the behavior persist independent of concentration. However, as expected, the decreasing ion concentration causes the peak of pure water density to become less pronounced in the interfacial region.

In our simulations of the ion free water-cyclohexane system, the water has 994 kg/m³ density while the cyclohexane phase corresponds to a density of 793 kg/m³. These values are in excellent agreement with experimental values of water 997 kg/m³ and cyclohexane 779 kg/m³.⁷² The calculated value also complies very well with the SPC water density of 985 kg/m³ at 298 K⁷³ with the slight variation resulting from interfacial fluctuations influencing determining the water slab volume. In the simulations, the density of the 4 M NaCl water solution is 1071 kg/m³. Experimentally, this density is 1152 kg/m³.⁷² The density of the cyclohexane phase remains constant in the presence of salt in the water phase, as expected.

Water-cyclohexane interface: estimating the ion energy based on molecular simulations

To further investigate the influence of the interface on the ions, Na ions residing in the bulk water phase were pulled through the water-cyclohexane interface. 4 shows the resulting



Figure 3: Cyclohexane and water density profiles in the absence of ions (left) and in the presence of 4.0 from interface (nm) interface (nm)

mean force vs. distance from the interface and the corresponding energy vs. distance data for pulling trajectories of different randomly picked ions including data of system size and ion concentration effects, as well as, comparison data with the Drude-polarizable and CHARMM non-polarizable force fields. Ion pulling rates varying from 2.0 m/s to 0.1 m/s were tested and 0.5 m/s was chosen as the rate for production runs due to this and slower rates producing rateindependent data. The pulling rate testing data is presented in the Supporting Information.

In the simulations, the ion observes the interface from a distance of 0.75 nm, see 4. The repulsion of the interface increases 1.0 nm beyond the equilibrium interface level, after which it decays over a region of 0.5 nm. The observations are consistent with the 0.53 nm hydration shell of the sodium ion but also indicate the water structure at the apolar interface to be more ordered than in bulk water, and that the ion hydration shell interacts differently with the interfacial water layers than with bulk water. At the level of the interface, in the simulations, the ion has an energy of 20 kJ/mol in comparison to an ion in bulk solution. This value characterizes the strength of repulsive barrier inducing the ion depletion region at the interface. In total, the energy barrier mean is 150 kJ/mol (1.55 eV) with individual pulling trial barriers ranging 120 - 190 kJ/mol. These fluctuations are purely stochastic, as 4 shows that the barrier mainly depends on the location of the point of maximum force and

the environment surrounding the ion at the interfacial boundary.

Most of the pulling trajectories at water-cyclohexane interface involve a Cl ion pairing with the pulled Na ion. 4 shows that this ion pairing reduces the extent of the water drag into the cyclohexane phase and correspondingly reduces the energy barrier related to the process. However, increasing the system size or changing the ion concentration in the water



Figure 4: At top left, the mean force versus distance from the interface for randomly picked Na ions pulled through the water-cyclonexane (CHX) interface using the GROMOS43a1 force field. Different lines correspond to different pulling trials. At top right, the corresponding integrated energy graphs showing the energy barrier height for the ions entering into the cyclohexane phase. At bottom, comparison energy graphs for assessing the influence of system size, ion concentration, and polarizability. Force curve maxima correspond to the maximum repelling force and the pulled Na ion typically spontaneously forms a contact ion pair with a Cl ion. The horizontal line in the bottom figure separates simulations where no ion pairing occurs (in addition to the polarizable simulation). Pulling direction is from right to left with the negative distances from the interface corresponding to the cyclohexane phase. The pull rate is 0.5 m/s which was verified to produce rate-independent data, see Supplementary Information.

slab, have little effect on the force and energy values, see 4. Furthermore, our simulation model has a van der Waals interaction cut-off coinciding with the observed repulsion region. To verify whether the extent of the repulsion region, or the outcome, is dependent on the van der Waals cut-off, comparison simulations with a longer cut-off of 1.4 nm were performed; the results remained intact and we conclude that the result is not related to interaction cut-off.

The results obtained with the CHARMM non-polarizable force field are analogous to GROMOS43a1, see 4, showing similar barriers and extent of the water drag regardless whether ion pairing occurs during pulling. In the fully polarizable simulation, no ion pairing is observed but the force maximum corresponds to energy levels of the majority of the pulling curves. Consequently, we find that polarization decreases the energy barrier for the transport of the naked ion to the level of the ion pair in non-polarizable simulations, thus, conserving the overall barrier. Moreover, analogous to non-polarizable simulations, the interface remains repulsive to the cation as the ion energy at interface level is 10 kJ/mol. Unlike the non-polarizable simulations, the polarizable force field pulling trajectory is terminated at the point of maximum force, which corresponds to most of the total energy barrier, because beyond this level the ion is fully surrounded by cyclohexane (although in water shell) and the overpolarization caused by the water shell reorganization around the Na causes the model to become unstable under these conditions. The stability difficulties are likely to be caused by a lack of damping of the short-range interactions between the ion and cyclohexane, which falls beyond the parametrization scheme of the force field.⁷⁴ For additional methodological discussion, see Supplementary Information. All in all, the polarizable force field results suggest that polarization has only a minor influence on the overall transport energy of Na, so the other systems, which are less polarizable than the examined cyclohexane, are studied only with a non-polarizable treatment.

The extent of the retracting force on the ion deep beyond the water-cyclohexane interface in 4 results from the ion dragging water into the cyclohexane phase. This is presented in 5. Here, a cone-like water wedge forms and penetrates into the cyclohexane region pushing away cyclohexane. The wedge grows as the ion is pulled further from the equilibrium interface, and finally breaks at an elongation dependent on the surface tension. The width of the lagging tail of the cone varies between 9 and 3 water molecules. 6 shows the corresponding temporal evolution of the ion solvation shell when the ion is pulled into cyclohexane. As the graph shows, upon cone breakage, the ion being pulled keeps carrying with it a small number of water molecules (between 7 and 14), and occasionally an other ion. These form a cluster in the cyclohexane phase.



Figure 5: Sample structure of the water cone formed by water dragged into the cyclohexane phase by the penetrating ion. The sodium ion being pulled is presented by the black dot at the tip of the cone. A solvation shell persists around the ion being pulled in all directions, that is, the size of the ion being pulled has been increased for visualizing it at the surface. In the visualization, the simulation box is shown by a wireframe, cyclohexane is omitted for clarity, and water is plotted as surface plot using an accessible surface probe diameter of 0.3 nm. In comparison, 1 shows the unperturbed interface and its molecular sharpness.



Figure 6: Number of **waster** and dyclohexane molecules within 0.53 nm of the sodium ion being pulled through the water-cyclohexane interface in different pull trials. Once the penetrating wedge breaks, the size of the partial solvation cluster of the ion remains constant (no water molecules escape) but the form of the cluster fluctuates.

Water-cyclohexane interface: estimating the ion energy based on interfacial tension and solvation calculations

The energies of ion penetration at a liquid-liquid interface can also be qualitatively estimated from the interfacial tension between the two liquids as this dictates the energetic penalty related to the increased surface area when the cation is pulled across the boundary. The interfacial tension in the simulation can be calculated as the energy per interface area when interface is created into the system. Hence, to calculate the interfacial tension within the simulated system, separate simulations of pure water and cyclohexane slabs were performed and the energetic contributions subtracted from the energy of the ion-free, biphasic system. Assuming the interface to be flat and diving the energy by the interfacial area, an estimate of 74 mN/m was obtained for the computational surface tension between water and cyclohexane within these models. This value is independent of the size of the liquid-liquid interface, as a similar calculation using the system with a larger interfacial area yielded a 71 mN/m surface tension. Alpbaz et al.⁷⁵ have measured the surface tension of the cyclohexane-water interface using an improved drop-weight method obtaining an interfacial tension over a range of temperatures. Their best fit linear relationship with interfacial tension and temperature results in water-cyclohexane system at room temperature to have a ca. 48 mN/m interfacial tension. Furthermore, the addition of NaCl has been reported to cause an increase by 1.5 mN/m (1 M NaCl concentration) or by 2.8 mN/m (1.5 M NaCl concentration).⁷⁶ The value calculated based on the used simulational model is 1.5 times larger than the measured values of surface tension.

To obtain the energetic penalty related to the increased surface area when the ion passes through the interface, the interface deformation is modeled as a cone. The height of the water cone is determined from the cation distance to the original interface level at the point of maximum force, since beyond this point the cation and surrounding solvation shell begin departing the cone, see 4. The maximum force on the cation corresponds to a distance of 0.9 nm from the interface so the water cone is approximately 1.2 nm in height (at cone tip, the cation is covered by a monolayer of water 0.3 nm thick). The radius of the cone is less precise due to fluctuations; visually we estimated the mean radius to be 1.4 nm. Therefore, the extra surface area due to cone formation is 0.95 nm² assuming an ideal cone form. This corresponds to a surface energy of 86 kJ/mol (here, we use the earlier computed surface tension of 74 mN/m). The calculated surface tension does not include the effect of ions, however, the effect should be minor due to the low concentration of ions within the cone.

To estimate the magnitude of the reduced solvation of the cation within the cone, we estimated the solvation energy of the Na⁺ ion using the quantum chemical software package ORCA⁷⁷ and the COSMO model.^{78,79} The Na⁺ ion hydration was modeled as Na⁺ hexahydrate Na(H₂O)⁺₆ and nonahydrate Na(H₂O)⁺₉. The hexahydrate models the first solvation layer of the ion and the nonahydrate represents the final solvation cluster observed in our simulations. The solvation energies were calculated in water, cyclohexane and dichloroethane. In the ORCA calculations, the standard dielectric constant, ϵ , and refractive index of the solvent, η , were used for water. For cyclohexane, values of $\epsilon = 2.02$ and $\eta = 1.4262$, and for dichloroethane, values of $\epsilon = 10.36$ and $\eta = 1.4448$ were used. The resulting solvation energies

gies for Na(H₂O)⁺₉ were 2.571 eV (248.1 kJ/mol), 1.024 eV (98.8 kJ/mol) and 2.240 eV (216.1 kJ/mol) for water, cyclohexane, and dichloroethane, respectively. If we assume that 1/4 of the ion environment at the cone tip is water, and 3/4 consists of the organic solvent, the values above result in a solvation energy reduction of 112 kJ/mol, at the water-cyclohexane interface, and 24 kJ/mol, at the water-dichloroethane interface, for the ion at the cone tip. This reduction is insensitive to the number of waters, that is, the reduction obtained using hexahydrate as the hydrated ion, is essentially the same.

Water-cyclohexane interface: ion hydration shell

4 provides comparison between the trajectories where pairing occurs and those where a lone Na⁺ moves across the interface. In the mean force curves of 4, the maximum repelling force corresponds to the maximum extension of the water wedge dragged by the ion into the cyclohexane phase. When the water cone breaks, the force required to pull the ion forward rapidly decreases, and equilibrates to a constant value corresponding to dragging the remaining small ion solvation cluster through the cyclohexane phase. Such a small solvation cluster remains as direct exposure of the Na ion to the cyclohexane is energetically extremely unfavorable due to unavailability of ion-dipole bonding; the water molecules form a shielding barrier for the ion lowering its energy in the cyclohexane phase.

When the ion penetrates further into the cyclohexane phase, the exchange frequency, i.e., how often one water molecule in the solvation shell is replaced by another from outside the solvation shell, goes down. This is expected because a more extended water wedge dragged by the ion has less water molecules readily available for exchange diffusion to the solvation shell. Once the water wedge breaks into the small cluster shielding the ion in the cyclohexane phase, no exchange with bulk water is observed, that is, the cluster size remains constant.

Water-1,2-dichloroethane interface

Next, we examined an analogous water-1, 2-dichloroethane interface. These two liquids are also immiscible but unlike cyclohexane, the dichloroethane molecules have some polar character which can contribute to interactions with the sodium ion. Similarly to the cyclohexanewater interface, a distinct ion depletion zone exists in the interfacial region between water and dichloroethane as shown in 7. The density of pure dichloroethane in the simulations 1128 kg/m^3 is low in comparison to the experimental value of 1253 kg/m^3 ,⁷² whereas the density of water 1004 kg/m^3 is in agreement with both the experimental value of 997 kg/m^{372} and the SPC/E water density of 998 kg/m^3 at 306 K.⁵⁸ The small difference to literature value results from ambiguity in the interface location causing uncertainty in determining the bulk liquid volumes, and hence densities.



Figure 7: Dichloro@thane2and water density profiles in the absence of ions (left) and in the presence of 4.0 M NaCl concentration in the water slab.

Analogous to the water-cyclohexane system, sodium ions were pulled through the interface. The appropriate pulling speed was examined to be 0.25 m/s. As 8 shows, the energy barrier decreases to 120 kJ/mol with values ranging 110 - 130 kJ/mol in comparison to the mean barrier of 150 kJ/mol in water-cyclohexane system. The behavior remains analogous to the water-cyclohexane system with the required pulling force being zero in bulk water, increasing approaching the interface, reaching a maximum value when the wedge of water is about to rupture, and after the extended wedge ruptures, quickly saturating to a constant drag force. However, whereas in the the Na ion tended to pair with a chloride ion when entering cyclohexane, here the Na ion typically enters dichloroethane without the anion. This difference occurs despite the Na ion being shielded by a water shell, see 9, and thus not directly interacting with the dichloroethane phase.

The difference in the ion pairing behavior between the water-cyclohexane and the waterdichloroethane interfaces is due to the differences in the screening length of the apolar phases, that is, dichloroethane has a significantly shorter screening length than cyclohexane. In particular, the ion-ion interaction force magnitude in a solute with a dielectric constant ϵ is $F_{12} = \frac{1}{4\pi\epsilon\epsilon_0} \frac{Z_1 Z_2}{R}$, where ϵ_0 is the permittivity of vacuum, Z_1 and Z_2 are the ion charges, and R the inter-ion separation. As the apolar solvents have much lower dielectric constants than water, the ion-ion interactions are much stronger. The difference is, however, more pronounced for cyclohexane than dichloroethane. Near the interface, the situation is more complicated than in bulk but as the ion approaches the interface, the ion-ion interaction becomes stronger for two reasons. First, part of the interaction will pass through the apolar phase. Second, the dielectric constant of water decreases near the interface due to fluctuations of the interface. Both these effects enhance the ion-ion pairing in the cone, and for cyclohexane the influence is significantly larger. Consistently, our simulations show enhanced pairing propensity for ions at the water-cyclohexane interface.

The solvation shell of the ion penetrating into the dichloroethane phase behaves differently to the cyclohexane system as shown in 9; the number of water molecules keeps decreasing further from the interface indicating the formation of a longer neck with more molecular exchange. Also, the number of water molecules carried into the dichloroethane phase is lower. The number of water molecules equilibrates at the level of 4-8 molecules depending on the specific run. Here, as before, the cut-off for defining the second solvation shell is 0.53 nm, and determined from the radial distribution function. In dichloroethane, the number of water molecules bound by the ion is significantly smaller than in the cyclo-



-2Figure 8:1 At left, the mean force versus distance from the interface for randomly picked Na ions pulled through the water-dichloroethane interface at 0.25 m/s constant rate verified to produce rate-independent data, see Supplementary Information. At right, the corresponding integrated energy graph showing the barrier height of the ions entering into the dichloroethane phase.

hexane system, mainly, due to the lack of the chloride ion. In principle, the slightly polar characteristics of the dichloroethane molecule should make carrying water molecules across the interface easier but this difference is so small our simulation data does not show it.

Closer examination of the solvation shell of the Na ion in the dichloroethane phase reveals the water molecules in the first solvation shell to be, as expected, highly ordered with oxygens pointing toward the ion. The water molecules, residing in the 2nd solvation shell have significantly less orientation and also fluctuate further into dichloroethane. Quite expectedly, and analogous to the water-cyclohexane system, the exchange dynamics of the solvation shell slow down the further the ion is pulled into dichloroethane. Due to the slight polarity of dichloroethane, water molecules within the solvation shell are more mobile and faster to reorganize around the cation in comparison to water in the solvation shell in the apolar cyclohexane.

The energy of ion penetration into the dichloroethane phase was estimated based on interfacial tension employing the same procedure as depicted for the cyclohexane system. An interfacial tension of 63 mN/m was obtained by pure dichloroethane and water simulations. This is twice the experimental value of 28 mN/m measured electrochemically in the presence



Figure 9: Number of 2water and dichloroethane (DCE) molecules within 0.53 nm from the sodium ion being pulled through the water-dichloroethane interface in different pull trials. Once the penetrating wedge breaks, the size of the partial solvation cluster around the ion remains constant (no water molecule exchange with bulk water phase) but the form of the cluster fluctuates.

of minute concentrations of supporting electrolytes.⁸⁰The appropriate cone size parameters for this system were determined to be a height of 1.3 nm and a radius of 1.4 nm. Therefore, the formation of the ion-water wedge results in a 2.25 nm² excess surface area corresponding to an excess energy of 86 kJ/mol. While for the cyclohexane-water system the corresponding calculation resulted in a value equating to approximately 60 % of the total energy barrier obtained from the pulling simulations, this estimate for the transfer energy accounts for a larger portion, 70 %, of the total transfer energy calculated from molecular simulations.

Water-pentanol interface

The water-pentanol interface provides a comparison to somewhat miscible liquids and their interfaces. Water-butanol forms an even more miscible interface. Both were studied analogous to the water-cyclohexane and the water-dichloroethane interfaces but as the butanol-water results in a transient, partially mixed system which does not equilibrate within the simulation time scale (80 ns) due to the high solubility of butanol in water (9 g butanol / 100 g water at 15 °C⁷²), the butanol interface is discussed only qualitatively in comparison

with pentanol below. All data shown corresponds to the pentanol-water interface system. Pentanol forms a better defined interface due to the longer apolar hydrocarbon chain and the liquid-liquid interface equilibrates within the employed simulation time and ion pulling speeds. In these alcohol-water systems, the alcohol group forms hydrogen bonds with the ion, and transport through the interface is significantly aided by the polar nature of the molecules.

In the simulations, butanol slowly mixes with the aqueous phase with water forming fingering channels into the butanol phase but remaining out of equilibrium. The channel formation reminds of the initial steps of microemulsion formation. The formation of fingering water channels renders the barrier against the cation moving from the aqueous phase to the butanol phase ambiguous because there is no well-defined interface and the fingering aqueous regions enable easier penetration into the dominantly butanol phase. The partial miscibility also allows the ion to carry significant, loosely bound water shell with frequent molecular exchange with the bulk liquids with it to the dominantly butanol phase. We conclude there is a non-zero interfacial barrier but the barrier is very low compared to the truly immiscible interfaces examined earlier. The attempted ion pulling rates for butanol were fast compared to the water fingering reorganization time scales in the water-butanol system, and therefore the pulling runs correspond to a nearly static interface (an interface with little or no structural reorganization). In conclusion, the butanol interface is discussed only qualitatively concluding the existence of a finite barrier but otherwise inconclusive with respect to the interfacial behavior.

For pentanol, in comparison to the strongly intermingling water-butanol interface, a welldefined interface but with some fingering penetration of the water phase to the pentanol phase is observed. To evaluate the significance of the chosen force field, we performed the waterpentanol interface studies with both GROMOS43a1 and OPLS-aa force fields, see Methods. We do, indeed, observe some difference in the interfaces and in the ion pulling data between the two tested force fields, see 10 and 11. First, even though slowly equilibrating, the graphs of 11 are symmetric indicating compositional equilibrium. Pentanol is more soluble in the GROMOS43a1 model than in the OPLS-aa model which shows as more pentanol entering into the water phase and larger, more extended fingering. In comparison to butanol, however, the magnitude is much smaller.

In the water-pentanol systems, the appropriate ion pulling speed was examined to be 0.25 m/s. In accordance to the interface profile data of 11, the ion pulling force curves of 10 corresponding to GROMOS43a1 data have more noise due to larger variance in the environment observed by the cation being pulled. However, both force fields indicate the pulling barrier decreases to approximately 45 kJ/mol with a variation range of 20-70 kJ/mol, which is about two fifths of the water-dichloroethane barrier and one third of the water-cyclohexane barrier. Here, the barrier is more sensitive to the environment observed by the ion as the interface is less smooth than for the more immiscible liquids.

The solvation shell of the ion being dragged into the pentanol phase encompasses 7 - 10 water molecules and an equal amount of pentanol molecules, see 12. The number of waters forming the solvation shell oscillates with some of the water being replaced by pentanol molecules occasionally, that is, water and pentanol number count are highly correlated in 12. In comparison to the apolar solvents, the solvation shell is extended due to stronger interactions between water and pentanol. Correspondingly, the exchange of solvation shell molecules with the bulk phase molecules is more frequent in the slightly mixing alcohol-water system studied here.

Discussion

Here, we used a simple ion probe and molecular simulations to characterize the interface and interfacial dynamics of water and a set of organic solvents differing in their immiscibility with water. Using a small, hard cation as a probe, we are able to measure the barrier against ion transfer to the apolar organic liquid, the hydration behavior, and the liquid-liquid inter-



-2. Figure 10: At top, the mean force versus distance2 from the interface for randomly3 picked Na ions pulled through the water-pentanol interface at 0.25 m/s constant rate verified to produce rate-independent data, see Supplementary Information, in GROMOS43a1 (left) and OPLS-aa (right) simulations. At bottom, the corresponding energy graphs showing the energy barrier height for the ions entering into the pentanol phase.

facial region molecular structure between liquid interfaces of varying degree of immiscibility. The significance of the work is that by studying a series of liquid-liquid interfaces with the organic components differing in their immiscibility with water, and comparing the resulting interfaces with similar ion probing, we get systematic data of aqueous interfaces and their ion response which allows further deductions of behavior of the aqueous interface with different but analogous immiscible liquids. We go beyond the comparable prior studies^{32,40,81,82} by using a model and system sizes able to provide detailed molecular level description including hydration and interfacial dynamics, as well as, resulting interface coarsening in a series of interfaces with varying polarity difference between the liquids.



Figure 11: -Density profiles of the water-pentanol-interface with GROMOS43a1 force field (at left) and OPLS-aa force field (at right).

For the immiscible liquid interfaces of water-cyclohexane and water-dichloroethane, we observe a well-defined, molecularly sharp interface with capillary effects all in agreement with prior simulational works, see e.g. refs 48, 49, and 83. For the partially miscible interface of water-pentanol (and even more so for the transient water-butanol interface), significant fingering and interfacial roughening is observed, again as expected. In our modeling, we observed the energy barrier against the cation entering the apolar phase decreasing systematically with the apolarity of the organic solvent and the interfacial tension between the two liquids. For cyclohexane, we report a molecular simulations based barrier of 150 kJ/mol, for dichloroethane 120 kJ/mol, and for pentanol 45 kJ/mol. For water-butanol, we conclude the existence of a small barrier but the slow equilibration of the system does not allow determining the magnitude exactly.

It is well-known that classical sodium and chloride ion parametrizations vary,^{66,84} and this affects the potential of mean force results in individual systems. However, as the models here are the same between the different systems, the trend and comparable energy differences persist. Indeed, these values are in excellent agreement with prior experimental and theoretical studies for sodium in dichloroethane. For example, ref 31 reports the free energy of transfer at 298 K to be approximately 70 kJ/mol (17 kcal/mol) in clusters of Na surrounded



-2. Figure 12: Number tof water and pentanol molecules within 0.53 mm from the sortium ion being pulled through the water-pentanol interface in different pull trials. At left, GRO-MOS43a1 force field and at right OPLS-aa force field data is presented.

by 4 water molecules. Experimental values have been reported in the range between 49 and 64 kJ/mol.^{85–89} The values are in reasonable agreement with our result of 120 kJ/mol given that the interface tension is overestimated in our simulations. For ion partitioning at cyclohexane-water interface, experimental data is scarce because of the strongly apolar nature of the organic solvent. A thorough review of ion behavior at various interfaces is provided by Marcus.⁹⁰ Furthermore, Zhao and Abraham⁹¹ provide extensive characterization of partitioning between ions in water and solvents including dichloroethane and alcohols of varying tail length below and above pentanol.

Polarization has been shown to affect ion partitioning at liquid-liquid interfaces; refs 39, 42, and 43 report anions to have an increasing propensity towards the interface with growing polarizability of the ion, which also causes a charge compensating peak in the density of the cation near the interface. Furthermore, for the highly polarizable iodide, Wick and Dang⁴⁶ report polarization introduces a free energy minimum for the ion at the water-CCl₄ interface and this minimum is not present in non-polarizable simulations. However, it remains unclear whether this influences the total barrier observed by the ion. For ions with lower polarizability, the influence seems less pronounced, as Darvas et al.⁹² report a 55 kJ/mol barrier for chloride transfer from water to 1,2-dichloroethane in line with results from polarizable.

izable simulations.⁴⁰ Similarly, in this work, the Drude-polarizable force field resulted for the cyclohexane-water system in a reduction of the transfer energy of the unpaired Na to level of the paired ion obtained with non-polarizable force fields. This suggests that polarization compensates for the energetic penalty, as the ion penetrates into the apolar cyclohexane phase without a charge neutralizing counterion, so that the overall barrier remains unaffected. Furthermore, since here the other studied organic molecules are more polar and less polarizable, the effect of polarization should diminish in the order cyclohexane i_{c} 1,2-dichloroethane i_{c} pentanol. Consequently, polarization might have a quantitative influence on the transfer energy of Na but it should not change the observed ordering of the energy barriers.

Besides molecular simulations, we estimated the ion transfer energy based on interfacial tension between cyclohexane and water and dichloroethane and water. For cyclohexane, the computed transfer energy accounted for approximately 60% of the total energy barrier obtained in the molecular simulations and for dichloroethane approximately 70%. This crude model seems to indicate that the numbers our molecular simulations provide for the barriers are an overestimate. In line, the simulations based interfacial tension clearly overshoots the experimental interfacial tension between the immiscible liquids. Jointly, these factors result in the molecular modelling overestimating the barrier of ion transfer. Deviations from the absolute values, when using empirical force fields to predict quantities outside their original parametrization region, are expected. In this work, GROMOS43A1 force field was chosen for the main simulations as the GROMOS parametrization relies on reproduction of condensed phase properties of alkanes, ideally partitioning between apolar and water phases. This provides a founded basis for expecting phenomenological accuracy, and the force field performance was qualitatively checked by comparison simulations with OPLS-aa, CHARMM36, and polarizable force field simulations in the systems where most critical. Furthermore, ion pulling rates were chosen such that the results are independent of the rate (slow enough rates) and the observed phenomenology remained insensitive to simulation box size in finite size tests. However, the partially miscible alcohol systems have interfacial fingering which causes variation in the observed environment, and the simulation results of individual pulling trials unavoidably reflect this variation. In summary, all the comparison simulations provided comparable behavior and transfer energy barriers in the studied systems. As said above, the molecular modelling seems to overestimate the barriers. Further quantitative accuracy might be achieved by force fields derived to represent specifically partitioning, such as TraPPE,⁹³ but the force field testing here already shows the observed phenomenology to be universal in empirical force fields of a variety of parametrization basis including a polarizable model. However, it is interesting to note that if we used surface tension values corresponding to the experimental values (about half of the computational values) in calculating the analytical estimate for the transfer energy, the value obtained for dichloroethane would be very close to experimentally measured values even though the analytical estimate we made is very crude.

The characteristics of the ion transfer are affected by the polarity difference between the two liquids. Whereas in water-cyclohexane system the sodium probe being pulled across the interface typically pairs with a chloride ion, in dichloroethane, and pentanol, the sodium is more probable to enter the less polar liquid without the neutralizing counterion contact ion pair in its hydration shell. This is because the apolar cyclohexane is ineffective in screening the hydrated sodium ion charge. This increases the sodium probe visibility also in the polar liquid and increases the probability of counterion pairing. Dichloroethane, although also apolar, has more effective charge screening properties, and thus the hydrated sodium probe entering into the dichloroethane, is less likely to attract a counterion to pair with it. In our simulations, the pairing propensity is also affected by the ion concentration and the simulation time scale, i.e., if the ion pulling is slower, or there are more ions in the system, a higher probability for a chloride ion to diffuse close enough the sodium being pulled across the interface to pair with it exists. The ion pulling speed and the high ion concentration in the simulation act in opposite directions the former reducing the pairing probability and the latter increasing. Prior calculations on NaCl pairing propensity at liquidliquid interface include NaCl at water-dichloroethane interface. Whereas Schweighofer and Benjamin⁹⁴ observe an increased stability of the ion pair relative to bulk water, Wick and Dang⁹⁵ report the organic dichloroethane interface destabilizes the pair in comparison to bulk water. We argue the ion pairing, or lack of pairing depends on charge screening (ion hydration), the dielectric constants of the liquids, and interface form (surface tension) when the ion is penetrating the interface.

For the water-cyclohexane system, the size of the observed hydration shell is the joint hydration shell of also the chloride ion being dragged with the sodium. Dichloroethane has some polar character, and here the sodium frequently enters without the pairing chloride ion in our simulations. Therefore, even though it is energetically easier to drag water into dichloroethane, the actual solvation shell is smaller than the joint solvation shell of the NaCl pair in cyclohexane. Pentanol and butanol receive a large hydration wedge, with only a minor part of the second solvation shell being lost when the ion penetrates the less polar phase. Our observations of the magnitude of hydration, and the consistent partial loss of the second solvation shell are in excellent agreement with prior studies; dos Santos and Gomes⁸¹ report cesium, and Chorny and Benjamin⁹⁶ sodium losing comparable amounts of its second solvation shell when entering nitrobenzene, but persistent first shell hydration. Furthermore, refs 33 and 97 discuss similar water wedge formation and encapsulation of cation K⁺ at water-dichloromethane interface.

The observed water necking and persistent hydration behavior have significance in biology in, e.g., ion channel activity⁹⁸ and protein pumps such as bacteriorhodopsin,⁹⁹ as well as, in technology in ion transport in nanoporous materials, for example, ion exchange or separation membranes, as well as, electrochemical capacitors.^{100,101} Here, the persistence of the hydration and the dragged water wedge size are controlling factors in ion transport. The present work relates these quantities to the type of interfaces and shows how sodium ion hydration persistence differs between immiscible interfaces of a variety of nature, and discuss the dragged water wedge changes showing how molecular simulations can be used as tools to understand these systems.

Conclusions

In conclusion, we presented a molecular detail characterization of the liquid-liquid interface as a function of interfacial immiscibility, and demonstrated the significance of ion hydration and its persistence in ion transfer through such immiscible, or poorly miscible interfaces. The results show interfacial tension has a significant role in the ion transfer and energy barriers involved. Furthermore, the energy barrier against penetration is sensitive to polarity difference between the two liquids with a larger polarity difference resulting in larger barrier against penetration. Hydration shell behaves the opposite way with more water being carried, and more easily, into the liquids with less polarity difference to water. All in all, the current study is one of the first molecular detail studies addressing ion transport through immiscible and partially miscible interfaces. The results show modern molecular simulations are a powerful and a versatile tool in obtaining detailed interfacial information of ion interactions and the immiscible interface including the interfacial dynamics.

Supporting Information Available

The simulations of the water-cyclohexane system with the Drude-polarizable and CHARMM force fields are described in the Supporting information. Additionally, the convergence tests on the appropriate ion pulling rate are reported. This material is available free of charge via the Internet at http://pubs.acs.org/.

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Graphical TOC Entry

