Theory and Computer Simulations of Solvation and Chemical Reactions at Liquid Interfaces

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1. Introduction

Many important chemical processes occur at the interface between a liquid and a second phase. The uptake of pollutants by water droplets involves solvation and ionization of small inorganic compounds at the water/air interface.[1] Corrosion and the operation of electrochemical cells represent important electron transfer reactions at the water/metal interface.[2] The transfer of solute across the interface between an organic phase and water is a critical element of phase transfer catalysis.[3] Charge transfer (ions and electrons) across and at the interface between two immiscible liquids has been the focus of intense interest of electrochemists[4,5] and is also relevant for studies of the function of biological membranes.[6]

In addition to the obvious practical importance of liquid interfaces, an understanding of the behavior of solute molecules and their chemical reactivity in the highly inhomogeneous media is both interesting and important at a fundamental level. The asymmetry in the intermolecular forces experienced by the molecules, the steep variation in the density and dielectric properties, and the unique dynamical behavior of the liquid at the interface may influence chemical reactivity and selectivity in ways that are quite different from those in bulk liquids.

Thus, studies of the structure and dynamics of liquid interfaces and of the behavior of chemically active species in these environments have been the focus of intense research activity. In recent years, the macroscopic (theoretical and experimental) approaches used to probe these systems[7] have been complemented by techniques that are more sensitive to the microscopic detail of the systems. This has been possible thanks to major advances in spectroscopic techniques (such as second harmonic generation and sum frequency generation[8]) that are sensitive to interfacial phenomena, as well as to advances both in theories of liquid structure and in our available computational tools. As a result, a better understanding of the factors that influence the interaction of a solute molecule with the relatively poorly understood inhomogeneous region of the liquid interface is beginning to emerge.

Several review articles have been published regarding these new experimental approaches and their application to the study of liquid interface structure and chemical reaction at the interface.[9,10] In this Account, we will focus on the insight gained from theoretical work on the behavior of reactive species which reside at the interface. Our goal is to highlight some general aspects of the effect of the inhomogeneous environment on several relaxation and reactive processes at different liquid interfaces.

In the following sections, we consider some general characteristics of liquid interfaces which are particularly relevant and are expected to influence the solvation, relaxation, and chemical reactivity of solutes at liquid interfaces. We demonstrate how these characteristics manifest themselves in the behavior of reactive solute at the interface, using as examples isomerization reactions, electron transfer reactions, and ionic solvation and transport. In particular, we concentrate on the effective density, the dielectric properties, and the roughness of the liquid surface as unique characteristics that are expected to influence the solvation thermodynamics of a solute, and thus reaction free energy and activation free energy, as well as the dynamics of relaxation and transport processes. Of course, there are other interesting properties of the interfacial region, such as molecular orientation and reorientation dynamics. These are in part responsible for the unique dielectric behavior of the interface region and in part have a direct bearing on the properties of active solutes. Some comments regarding these aspects will also be mentioned.

In order to discuss the properties of a solute molecule at the interface, we will make extensive use of the progress made in recent years in understanding the properties of the neat (free from solute) interfacial system. There is an extensive literature on the

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properties of liquid interfaces, and the reader is referred to several review articles for details.[11-14]

2. Density and Viscosity Effects

One of the relatively well understood properties of the liquid interface region is the so-called density profile. It is the density of the liquid(s) as a function of the distance along the normal to the interface. Experimental data,[9,12] mean field approximations,[11] analytical and computational statistical mechanical theories,[11,13] and computer simulations[14] all give a reasonably consistent picture of this property with results that can be summarized as follows:

(a) There is a monotonic change in the density profile of a liquid in equilibrium with its own vapor. The density varies by about 3 orders of magnitude over a distance of 4–10 Å for most liquids far below their critical point.[12] The width is determined by the superposition of thermally excited density fluctuations (capillary waves) and increases with a decrease in the surface tension.[11]

(b) The same holds for the interface between two immiscible liquids. There is evidence from molecular dynamics computer simulations[14,15] that on the bulk side of the interface region the density profile exhibits dampened oscillations, but it is not yet clear if these are artifacts of the finite system size and/or the short simulation time.

(c) There are well-defined density oscillations at the interface between a liquid and a solid surface. The oscillations decay to the bulk value of the density in about 2–4 molecular diameters for water near a metal surface[16,17] or a hydrophobic wall,[18] but can be somewhat longer range for nonpolar liquids.[13] Depending on the interaction between the liquid and the solid and on the bulk density of the liquid, the density near the wall can be several factors larger than the bulk density.

Numerous experimental and theoretical studies of reaction thermodynamics and dynamics in *bulk* nonpolar liquids have shown that the liquid density can have a major effect on reactions involving significant change in the volume occupied by the reactant and products.[19] Thus, given the universal nature of the density changes at liquid interfaces noted above, an important issue to examine is how these density variations affect reactions at interfaces. A 3 orders of magnitude change in the density at the liquid vapor interface could significantly alter the reaction free energy and activation free energy of a reaction! A change in the density is strongly correlated with the change in the viscosity of the liquid. The viscosity of the vapor is much lower than that of the bulk liquid, and the viscosity of liquid near a solid surface could

be significantly higher than the bulk viscosity.[20] Again, it is known from studies of reactions in bulk liquids that viscosity can play a significant role in affecting the rate of the reaction as reflected by a transmission coefficient different from unity.[21] Can solvent effects on reactions at interfaces be understood using the "macroscopic" values of the effective viscosity and density at the interface, or is a local, microscopic description necessary?

There are some clues from recent experiments that suggest that these are indeed relevant issues. For example, an increase by a factor of 2.5 in the rate of a cis–trans isomerization reaction at the air/water interface relative to the rate in the bulk was interpreted by Eisenthal and co-workers to be the result of the reduced friction at the air/water interface.[22] The photoisomerization of stilbene at the aluminum oxide/hexane interface was studied by Scott et al. using a picosecond multiple light scattering technique and was found to be hindered relative to the reaction in the bulk.[23] The photoisomerization of malachite green at the diethyl ether/quartz interface, studied by Meech and Yoshihara using picosecond second harmonic generation, was also found to be slower than in the bulk liquid.[24]

Experimental studies of density effects on chemical reaction rates are complicated because it is almost impossible to disentangle the solvent contribution to the equilibrium free energy from the contribution to the transmission coefficient, which reflects a dynamical correction to the transition state theory rate constant.[21] In many cases, one assumes that one of the effects is small or can be approximately accounted for by a study of the reaction in a series of chemically similar solvents. The advantage of a molecular dynamics study is that the equilibrium and dynamic effects can be rigorously separated, as has been shown in many studies of reactions in bulk liquids.[21,25-28]

In order to examine density effects on both the equilibrium and dynamic behavior of chemical reactions at liquid interfaces, we have chosen to study a particularly simple case of an isomerizing diatomic molecule that is located at the liquid/vapor interface of a Lennard-Jones fluid and at the interface between a Lennard-Jones liquid and a flat wall. Isomerization reactions are some of the simplest reactions used to elucidate solvent effects, and thus they have been extensively studied in bulk liquids both experimentally and theoretically. Many studies have shown that both equilibrium and dynamic solvent effects on the rates and equilibrium constants of the reactions can be significant, and therefore this type of reaction

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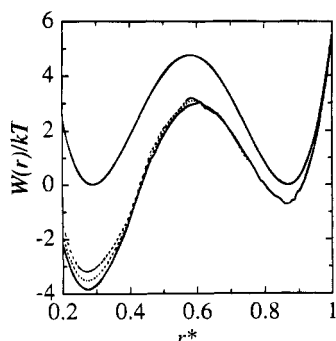
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Figure 1. The reaction free energy for an isomerizing diatomic in the gas phase (top solid line), in the bulk of a Lennard-Jones liquid (bottom solid line), at the Lennard-Jones liquid/wall interface (bottom dotted line), and at the Lennard-Jones liquid/vapor interface (top dotted line). In all cases, $T^* = 0.9$.

represents an ideal starting point for elucidating interfacial effects.

The particular reaction system we study consists of two atoms moving in a double well potential between a compact and an extended state. The interaction potential of the liquid, the liquid–solute, the wall–liquid, and the wall–solute are all given by the same Lennard-Jones potential. The solvent contribution to the free energy of the reaction along the reaction coordinate (the distance between the two atoms), the transmission coefficients for the rate of the reaction, and the friction exerted by the liquid on the reaction coordinate for different orientations relative to the interface, were calculated using standard techniques,[21,28-30] and the details are given elsewhere.[31,32] Figure 1 summarizes the equilibrium free energy calculations of the reaction profile as a function of the reaction coordinate (given in reduced units: $r^* = r/\sigma$, where σ is the Lennard-Jones size constant).

The symmetric double well potential corresponding to the bare potential energy surface (the "gas phase" reaction profile) becomes asymmetric in the bulk liquid. This just reflects the well-understood[19] negative solvent contribution at interatomic distances that are smaller than the typical equilibrium interatomic distance in the neat liquid (which is near $r^* = 1.1$ for a Lennard-Jones liquid in the liquid/vapor coexistence region). The profile at the two interfaces is quite close to the one in the bulk. However, it represents a different physical situation: At the liquid/vapor interface, the diatomic solute is restricted to be near the Gibbs dividing surface, which is approximately the distance at which the average density drops to 50% of the bulk value. The contribution of the reduced density solvent to the solute potential of mean force becomes less negative (by about kT), which is the expected effect. However, when the solute is adsorbed at the wall/liquid interface, the reaction profile includes contributions from the liquid and from the adsorption at the solid surface. Because the wall contribution can be calculated independently, one finds that both of the contributions are about half the contribution of the bulk liquid for this weakly physisorbed solute.[33]

The surprising result of a *less negative* liquid contribution, even though the effective solvent density near the wall is about 3 times the bulk value, could be explained by noting that when the solute is adsorbed at the surface, approximately 50% of the configuration space does not have any liquid molecules. Thus, the large effective density is "not available" to solvate the solute to the same extent that one might expect if the solute were in a bulk liquid with 3 times the normal density.

The free energy profile can be used to obtain the effect of the interfacial region on the equilibrium and rate constant of the reaction. In both interfacial systems, the transition to the surface destabilizes the compact reactant state. The activation free energy for the transition to the extended state is reduced at the interface relative to the bulk liquid (but it is larger than that in the gas phase). Thus, the transition state theory rate constant will be reduced. The actual rate will also depend on any deviation from this theory due to barrier recrossings of the transition state, as quantified by a transmission coefficient value less than unity. These barrier recrossings represent a dynamic solvent effect which is related to the friction exerted on the reaction coordinate on the time scale of the motion over the barrier.[21,26] We find that in both interfacial systems the friction is reduced. Depending on the details of the reaction systems' intramolecular potential and masses, this results in an acceleration of the rate over that in the bulk liquid by up to a factor of 2, with the effect being more noticeable at the liquid/solid interface.

Since details about the particular values of the transmission coefficient as a function of system parameters can be found elsewhere,[31,32] we focus here on the general physical origin of the reduced friction. At the liquid/vapor interface, the reduced density results in less frequent collisions between the liquid atoms and the reaction system, which results in fewer recrossing events. At the liquid/solid interface, the frequency of collisions with significant force along the reaction coordinate is similar to the frequency in the bulk when the diatomic bond is parallel to the wall, but it is less than the bulk value when the bond is perpendicular to the wall. This is consistent with the picture discussed above of limited solvent access to the solute at the interface being an important issue even for a weakly physisorbed solute.

Although the quantitative details of the above study will necessarily be system-specific, we expect a wider qualitative applicability of the conclusions about what type of effect on the equilibrium and rate constants one should expect for reactions that involve nonpolar solutes at the liquid/vapor and liquid/solid interfaces. Isomerization reactions that involve a change in the dipole moment introduce the issue of dielectric interfacial effects.[34] These effects will be considered next in the context of ionic solvation and electron transfer reaction.

3. Dielectric Effects

Although the density and viscosity effects discussed in the last section can be found in most reactions, they are completely dwarfed in many cases by the stronger

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electrostatic effects involved in reactions between ionic and/or polar molecules in polar liquids.[21,35] A large part of physical chemistry and physical organic chemistry is devoted to a quantitative account of these effects. However, much less is known about electrostatic and dielectric effects on properties of the solute at liquid interfaces. Most of the developments in this area have been limited to a dielectric model of the interface, which views the system as two bulk continuum media separated by a mathematically sharp interface.[7,36] An important issue which we focus on in this section is understanding the limitations of the continuum picture and learning about dielectric interfacial effects from the success and failure of the continuum dielectric approach. We choose to demonstrate the range of behaviors one encounters by considering the solvation of ions at the water surface and electron transfer at the water/1,2-dichloroethane interface.

Solvation Thermodynamics and Dynamics at the Water Liquid/Vapor Interface. Understanding the solvation of charged and polar species at the liquid/vapor interface is an important first step in the study of reactions that involve charged and polar molecules. Experiments on this type of reaction have recently been reported at the water liquid/vapor interface.[10,22,37–39] Although most treatments of the solvation thermodynamics and dynamics of charged solutes at the water liquid/vapor interface (and at other liquid interfaces) have been limited to continuum models,[36] some studies based on microscopic solvent models have recently appeared. Wilson, Pohorille, and Pratt calculated the free energy of adsorption of small inorganic ions at the water surface,[40,41] and Benjamin and Pohorille similarly considered the adsorption of phenol and pentylphenol at the water surface.[42,43]

We consider here both the equilibrium thermodynamics and dynamics associated with the solvation of ions, with particular attention given to the adequacy of the continuum electrostatic picture. The free energy cost of moving any solute from the bulk liquid to the liquid/vapor interface region is a function of the distance along the surface normal. This equilibrium quantity will determine the distributions of solute molecules in the interfacial region and thus the surface potential of the system. Because of interionic interactions and many body effects, the computation of the free energy profile under conditions of finite ionic concentration using microscopic solvent models is, as of yet, an intractable problem. We thus limit ourselves to the problem of the transfer of a single ion,

which should be useful for dilute solutions and could be used as an ideal test of continuum models.

The quantity of interest, sometimes called the potential of mean force, is given by

$$A(Z) = -\beta^{-1} \ln\langle \delta(z_i - Z)\rangle \qquad (1)$$

where $\beta = 1/kT$, δ is the Dirac δ function, z_i is the location of the ion along an axis normal to the interface, and $\langle ...\rangle$ is the equilibrium ensemble average. Note that in a homogeneous fluid, because of translational invariance, $A(Z)$ is a constant, independent of Z. Unfortunately, despite significant progress in the statistical mechanics of inhomogeneous fluids,[13] we do not have a statistical mechanical theory for this quantity. Thus, we must resort to simulational techniques for its accurate determination. This can be accomplished in a straightforward manner using standard sampling techniques with biasing potential in order to obtain the free energy in regions of phase space that are infrequently visited.[29] Details about the particular implementation of this technique can be found elsewhere.[41,44,45] The calculations are performed on a system which includes 512 water molecules, modeled using a flexible simple point charge (FSPC) potential[44,46] and a single Cl^- ion whose interaction with the water is modeled using the sum of the Coulomb and Lennard-Jones potentials. The calculations are also done for an ion which has the same Lennard-Jones parameters as Cl^-, but with a charge of +1, which we will label as "Cl^+". Figure 2 shows the results for the free energy of transferring these two ions from bulk water to the water liquid/vapor interface. The increase in free energy as the ions approach the interface is consistent with the tendency of small ions to be repelled from the surface, where their solvation is much less favorable than in bulk water. Note that the positive ion experiences larger resistance to being pushed into the interface. A detailed analysis of a similar case investigated by Pohorille and Wilson[41] shows that this is due to the slight tendency of surface water dipoles to point toward the bulk. It is interesting to note that even more dramatic behavior has been observed for the adsorption of small ions at the water/metal interface,[47] where the tendency of water dipoles to slightly point toward the bulk is more pronounced.

The general observation of negative adsorption of small ions at the water surface, and more so for cations than for anions, has been known qualitatively from surface tension measurements in dilute salt solutions.[36] However, the only other quantitative estimate given to the free energy change has been based on a continuum electrostatic model. A frequently used model is that of a spherical charged cavity embedded in a system which consists of two dielectric slabs whose dielectric constants are fixed at the bulk value of liquid water and the value of the vacuum (1). The free energy of charging an ion can be obtained from a numerical solution of the Poisson equation, given the dielectric constants of the two media and the size of the ion. In order to compare this calculation with the molecular dynamics data, one

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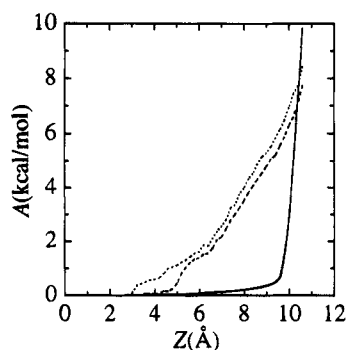(47) Rose, D. A.; Benjamin, I. *J. Chem. Phys.* **1991**, *95*, 6856.

Figure 2. The adsorption free energy of an ion as a function of the distance along the normal to the water liquid/vapor interface at $T = 300$ K. The Gibbs dividing surface is at 11.5 Å. Solid line: continuum model calculations based on a sharp dielectric model. Dashed line: molecular dynamics calculations for Cl⁻. Dotted line: molecular dynamics calculations for an ion with the same Lennard-Jones parameters as Cl⁻, but with a charge of +1.

must also specify the location of the dielectric discontinuity. The results for Cl⁻ are shown in Figure 2. We use 2.3 Å as the cavity radius (a value which reproduces the solvation free energy in bulk FSPC water) and 82.5 for the water dielectric constant (corresponding to the FSPC model), and we assume that the sharp jump in the dielectric constant is located at the Gibbs dividing surface. It can be seen that the continuum model underestimates the free energy far from the interface and overestimates it when the cavity begins to cross the interface. Other choices for the location of the interface will only shift the curve along the Z-axis.

The continuum model may be improved by realizing that the dielectric constant of water at the surface must be Z-dependent. One may obtain some crude information about this dependence from ellipsometric measurements.[48] In fact, we can find a dielectric profile $\epsilon(Z)$ which exactly reproduces the molecular dynamics free energy profile, although this improvement does not help in explaining the different behavior of negative and positive ions.

A much more serious problem with the Z-dependent dielectric model has to do with its prediction regarding the time-dependent dielectric response at the interface. This response can be measured by following the time-dependent shift in the emission spectra from a photochemically excited solute,[49,50] and it is given by

$$S(t) = [\nu(t) - \nu(0)]/[\nu(\infty) - \nu(0)] \qquad (2)$$

where $\nu(t)$ is the emission maximum at time t. Numerous experiments have been conducted in bulk liquids which suggest that although continuum models are not very accurate, they do provide a reasonable picture and can be improved by taking into account some aspects of the solvent molecular structure.[51,52] A particularly simple continuum electrostatic model for the response $S(t)$, which is the basis of many later models, is given by the Debye relaxation formula[53]

$$S(t) = e^{-t/\tau_L}, \quad \tau_L = \epsilon_\infty \tau_D/\epsilon_0 \qquad (3)$$

where τ_L is the so-called longitudinal relaxation time, τ_D is the Debye relaxation time, which is related to the total dipole relaxation time of the liquid, and ϵ_∞ and ϵ_0 are the infinite frequency and static dielectric constants of the liquid. For the FSPC water model, $\epsilon_0 = 82.5$, $\epsilon_\infty = 1$, and $\tau_D = 11$ ps, which gives $\tau_L = 0.13$ ps in bulk water. Molecular dynamics simulations of $S(t)$ for the case of switching the charge on the Cl⁻ ion to zero in bulk water,[44] as well as for many other charge and dipole jump cases in water,[54] show a very fast initial component, which is attributed to inertial solvent motion,[55,56] followed by a tail which is slower than the one predicted by the Debye model by a factor of 2−3. Better agreement with the simulations and the experiments (mainly with other solvents) can be obtained by improving the Debye model by taking into account the size of the solvent molecules.[51,52]

We are interested here in the response of interfacial water to the charge-switching computer experiment. The results of the molecular dynamics calculations, described in detail elsewhere,[44] are that the interface and surface response are nearly identical! From the reorientation time of the water dipole at the surface, we estimate τ_D for water at the liquid/vapor interface to be 9 ps, a value which is very close to the bulk value of 11 ps. Thus, we can "explain" the interfacial relaxation data if we use the sharp interface model (with ϵ_0 still equal to 82.5[57]) and the Debye model. However, with the Z-dependent static dielectric constant (which we found earlier to be necessary for reproducing the equilibrium solvation free energy), the Debye model gives relaxation which is an order of magnitude slower than the one observed in the simulations. This discrepancy does not disappear by taking into account the finite size of the solvent molecule, as is done in the improved models, and thus it represents a problem with the continuum model that is surface-specific. An examination of the detailed structure of the ion/water solvation complex and the contribution of the first solvation shell to the total solvation energy at the interface shows that they are very similar to those in the bulk. This feature needs to be incorporated into the Z-dependent continuum model in order to bring it into agreement with both the equilibrium and dynamic simulation results.

The continuum electrostatic model has been enormously useful and successful in estimating solvation properties in bulk solution, and even in reasonably approximating time-dependent solvation. The discussion above clearly shows that these models need to be significantly modified by including some aspects of the liquid interface structure in order to correctly capture in a quantitative way both the equilibrium and dynamics of the interfacial solvation.

Electron Transfer at the Water/1,2-Dichloroethane Interface. A liquid interfacial system that has been the subject of many studies, and in which dielectric effects are of fundamental importance, is the

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(57) In this case, there is a contribution from image effects due to the sharp boundary, but they can be shown to be negligible. See: van der Zwan, G.; Mazo, R. M. *J. Chem. Phys.* **1985**, *82*, 3344.

interface between immiscible liquids of significantly different polarity. One such system is the interface between water and 1,2-dichloroethane (DCE), which has been extensively used in the study of electrochemical charge transfer. In contrast with the example given in the previous section, we examine in this section a system where a simple continuum model is in reasonably good agreement with the microscopic results, despite the fact that this model is based on some clearly flawed assumptions regarding the structure of the interface. In addition to the insight gained about the nature of the interface, this example also provides additional clues about the adequacy of continuum electrostatic models at interfaces in general.

The specific example we consider is the solvent free energy that governs outer-sphere electron transfer (ET) reactions at the interface. Experimental difficulties prohibited detailed kinetic studies of this type of reaction until recently, but reports on ET at the water/ DCE interface are beginning to be available.[58-60] Theoretical treatments of this problem to date include a continuum electrostatic model calculation of the reorganization free energy[61-63] and the rate constant,[64,65] and molecular dynamics calculations of free energies[66] and dynamics[67] in a model polar/nonpolar liquid/liquid interface and at the water/DCE interface.[68] The electron transfer reaction considered by all of the above treatments is an outer-phase transfer between a redox couple located at the interface. The reorganization free energy is defined as the free energy difference between the minimum of one electronic state and the free energy of the nonequilibrium polarization one gets after a "vertical" transition from the minimum of the other state. The continuum electrostatic calculations of this quantity involve a computation of the electrostatic free energy of a nonequilibrium solvent orientational polarization produced by an instantaneous electron jump between the two sites at the interface.[63] The interface is represented by two dielectric media A and B, with static dielectric constants of ϵ_{A0} and ϵ_{B0} and optical dielectric constants of $\epsilon_{A\infty}$ and $\epsilon_{B\infty}$. The result for the reorganization free energy λ, for the special case where the center of the line connecting the two centers is located exactly at the sharp boundary, is[63]

$$\lambda = \kappa_1/\sigma_1 + \kappa_2/\sigma_2 - (4\kappa - \kappa_1 - \kappa_2)/(2R \cos \theta) - 2\kappa/R \quad (4)$$

where R is the distance between the two centers, θ is the angle between the interface normal and the line connecting the two centers, σ_i is the diameter of charge

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i, $\kappa_\nu = (\Delta q)^2(1/\epsilon_{\nu\infty} - 1/\epsilon_{\nu0})$ for $\nu = A, B$, $\kappa = (\Delta q)^2[1/(\epsilon_{A\infty} + \epsilon_{B\infty}) - 1/(\epsilon_{A0} + \epsilon_{B0})]$, and Δq is the size of the charge transfer. The molecular dynamics calculations for the reaction AD $\rightarrow$ A$^+$ + D$^-$ at the water/DCE interface are described in detail elsewhere.[68] They involve computation of the free energy[66,69-71] associated with the change in the solvent polarization from the one corresponding to the ion pair to the one corresponding to the neutral pair. The two charge centers are 5 Å apart and interact with the two liquids by the same Coulomb plus Lennard-Jones potentials (ϵ_{LJ} = 0.1 kcal/mol and σ = 5 Å), with the center of the pair of atoms fixed at the (water) Gibbs dividing surface. The molecular dynamics calculations give, in addition to the reorganization free energy, the geometry of the ion and neutral pairs relative to the interface and thus allow for a direct comparison with the continuum electrostatic model. Using ϵ_0 = 82.5 and 10 for water and for DCE, respectively (the values obtained from the molecular dynamics calculations of the bulk liquids), ϵ_∞ = 1 for both liquids (consistent with the electronically nonpolarizable nature of the model potentials), and the average value of θ obtained from the simulations, we obtain λ = 74 kcal/mol compared with the value of 80 ± 2 kcal/mol obtained from the molecular dynamics calculations. This represents excellent agreement between the two models. In addition, the full shape of the free energy curve as a function of the solvent polarization is a perfect parabola, again in agreement with the basic assumption on which the continuum model calculations are based. Similarly, quite reasonable agreement has been found for one other liquid/liquid interfacial system[66] and for ET at the liquid/metal interface.[72,73]

Since reasonable agreement between the microscopic and the continuum model calculations of the reorganization free enrgy has also been found for a number of outer-sphere ET in bulk liquids,[70,71] the success of the continuum model for interfacial liquid/ liquid ET would be expected. However, an examination of the detailed molecular dynamics results reveals that the basic assumption of a flat liquid/liquid interface that is central to the continuum model calculations is flawed. The surface appears to be very rough, as shown by a statistical analysis of the amplitude of capillary waves[15] or, more relevant to the ET case, by the fact that the angular distribution of the ion pair is significantly wider than the distribution one would predict on the basis of a flat interface. Given that the reorganization free energy calculated from the continuum model is quite sensitive to the angle θ in eq 4, the agreement between the two methods begins to look fortuitous.

An even more critical test of the continuum model is offered by an examination of the electrostatic potentials induced by the liquids at the sites of the charge centers as a function of the charges on the sites. These charges are varied continuously during the continuum model Born charging procedure and nearly continuously in the molecular dynamics sampling procedure.[71] Figure 3 shows the results for the electrostatic potentials induced by the water and the

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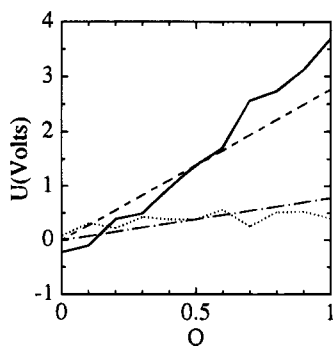(73) Rose, D. A.; Benjamin, I. *J. Chem. Phys.* **1994**, *100*, 3545.

Figure 3. The electrostatic potentials induced by water and DCE at the location of the water-soluble charge transfer center for a redox pair located at the water/DCE interface. Solid and dotted lines: water and DCE contribution, respectively, calculated from the molecular dynamics. Dashed and dashed–dotted lines: water and DCE contribution, respectively, calculated from the continuum electrostatic model.

DCE at the location of the charge center which is located in the aqueous phase. The continuum model predicts that the electrostatic potentials will vary linearly with the charge on the ion. We see that the model underestimates the rate by which the water contribution increases with the ion charge, but overestimates the DCE contribution. This behavior has a simple microscopic interpretation: As the charge on the ion is increased, the water solvation shell tightens around it at the expense of the DCE molecules, which are further expelled from the region. The "flexibility" of the interface between the two liquids makes this possible with no significant cost. Note, finally, that the electrostatic potential used to "charge" the ion to its final charge is the sum of the contributions from the two liquids, and this varies nearly linearly with the charge!

4. Surface Roughness

We conclude our selection of liquid interfacial characteristics by briefly examining the important role played by interface roughness in affecting solute behavior and chemical activity at liquid interfaces. Solid surface roughness has been the focus of numerous experimental and theoretical studies, but the roughness of the liquid surface, and in particular its relevance to interfacial processes, is just beginning to be explored. Recent experiments on X-ray scattering of the water/vapor interface,[74] on atomic scattering of complex liquid surfaces,[75] and on neutron reflections off the water/oil interface[76] are beginning to probe the structure of liquid interfaces using techniques that are sensitive to local roughness (rather than the macroscopic roughness implied by the surface tension). The implication of the local, microscopic roughness for understanding solute reorientation at the water/alkane interface has also been examined recently using fluorescence depolarization experiments.[77]

The contribution of interface roughness to the ability of an electron donor and acceptor to approach each other over a wide angular distribution at the water/DCE interface has already been discussed in the last section. The direct influence of surface roughness on the electron transfer process is also evident in the observation of the large contribution of water to the electrostatic potential at the location of the water-insoluble charge center.

The microscopic examination of the solvation thermodynamics and dynamics of ions at the water liquid/vapor interface discussed above is another demonstration of the critical importance of surface roughness. The ion at the interface tends to keep its solvation shell intact, and as the ion approaches the surface, it necessitates the creation of a bulge at the surface.[41]

Perhaps the most dramatic manifestation of surface roughness is in the process of ion transfer across the interface between two immiscible liquids. Water capillary distortions facilitating the transport of ions into the aqueous phase have been observed in molecular dynamics trajectory calculations.[78] Of a similar nature is the dragging of water molecules into the organic phase as a result of potential-driven ion transport, observed in the molecular dynamics simulations[78] and in experiments.

5. Conclusions and Outlook

We have examined several properties of liquid interfaces and their manifestation in several chemical systems. Although in many cases solvent effects on reactions at interfaces can be understood using the modified "macroscopic" values of the effective viscosity, density, or dielectric constants at the interface, in some cases, the detailed molecular structure of the interfacial region, and more specifically of the solvation complex, are of crucial importance for a quantitative account. In particular, the local interface roughness, which does not have a bulk counterpart (like the density or the dielectric constant), plays an important role.

The studies described above show the need for progress in two different directions. First, on the theoretical side, the improvement of continuum models by incorporating some aspects of surface roughness and the stability of the first solvation shell of small ions in many interfacial systems seems both worthwhile and feasible. Second, on the experimental side, the direct observation of microscopic solvent effects at interfaces is needed. The contribution of these experiments to understanding the interfacial region could be as invaluable as the contributions made in recent years to our knowledge of bulk solutions. Both of these research directions will continue to benefit from the ability of the molecular dynamics calculations to test theoretical models and provide microscopic insight.

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