Mechanism and Dynamics of Ion Transfer Across a Liquid-Liquid Interface

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A detailed molecular model for ion transfer across the interface between water and 1,2-dichloroethane provides insight into the mechanism of the transfer across the interface between two immiscible liquids. Extensive molecular dynamics computer simulations underscore the roles of surface roughness and capillary distortions in this process, demonstrate that ion transfer is an activated rather than a simple diffusive process, and provide a test for the applicability of theoretical models.

Ion transport across the interface between two immiscible liquids is a fundamental process in electrochemistry (*1*) and catalysis (*2*), and it is relevant to the study of ion-exchanging biological membranes (*3*). Despite numerous experimental studies and theoretical modeling, the mechanism by which ions cross the interface is not well understood. Experimental data have been interpreted in terms of widely differing theoretical approaches in which ion transfer has been described as a simple diffusion process (*1*), as a thermally activated chemical reaction (*4*), and even as similar to an electron transfer at the solution-metal interface (*5*). This situation is the result of a lack of direct knowledge about the structure of the interface and the difficulty of experimentally monitoring the process on the relevant time and distance scale (*6*).

There are several fundamental questions in this area that current models are silent about and that available experimental data are unable to clearly resolve. For example, if the process by which the ion crosses the interface requires an activation energy, what is the nature of the corresponding barrier? Does the process have to do with oriented solvent molecules at the interface or with the possible need to switch the members of the solvation shell? What is the role of the interface structure in this process? There is indirect evidence that small ions remain hydrated on the transfer from the water to the organic phase. Can we obtain direct molecular information about the possibility that an ion drags with itself a substantial part of its old solvation shell?

Many of the experimental studies of ion transport across the liquid-liquid interface have used the water–1,2-dichloroethane (DCE) system. I describe here a molecular dynamics computer simulation study of ion transport in this system, showing that the common picture of a sharp interface separating two dielectric media has serious deficiencies as a basis for understanding the mechanism of ion transport. Surface roughness and capillary distortions play important roles in the transfer process, and the dynamics of ion transfer is governed by a barrier in the free energy profile across the interface. I present two approximate theoretical models for this quantity and assess their accuracy by comparison with the exact trajectory calculations.

The molecular model for the interface between water and DCE has been described (*7*). The system constitutes a liquid slab of 343 water molecules and a liquid slab of 108 DCE molecules at 300 K. These liquid slabs are brought into contact to form an elongated box of cross section 21.7 Å by 21.7 Å. The individual liquid's potential energy functions used in the integration of the equations of motion include a standard choice of intermolecular and intramolecular interactions that have been shown to give the separate liquids reasonable properties. The interaction energy between molecules belonging to different liquids is calculated using the standard combination rule for mixtures (*8*). This choice of potential energies leads to a system of two immiscible liquids that form an interface that is flat on average and is perpendicular to the long axis of the box (denoted by Z, so that, on average, water occupies the region $Z < 0$ and DCE occupies the region $Z > 0$). No specific potential terms or external constraints have been used to guarantee the immiscibility, and the observed immiscibility in the simulation arises from the properties of the individual liquids, in particular, the hydrogen bonding within the water.

Although my calculations have shown that the water-DCE interface is molecularly sharp, thermal fluctuations superimpose capillaries as long as 8 Å on the sharp interface and generate quite a rough surface. These capillaries are constantly moving "fingers" of water (and, to a lesser degree, of DCE) that protrude into the other liquid on the time scale of tens of picoseconds. However, the long time average (hundreds of picoseconds) of the surface results in a relatively smooth density profile that gives rise to a surface thickness of about 1 nm (Fig. 1A).

To study the dynamics of ion transfer across the interface, we start with an ion that is equilibrated in the center of the DCE slab, far away from the interface (such that the ion-water interaction energy is near zero). The potential energy functions for the ion-liquid interactions include a sum of Coulomb and Lennard-Jones terms between each liquid atom and the ion. I obtained the required parameters from the Lorentz-Berthelot combining rules (*8*), using the Lennard-Jones parameters for the liquid atoms published previously (*7*), and the ion's parameters (see below). The dynamics are then followed for 50 ps for each of 20 trajectories with independent initial conditions selected from a Boltzmann distribution at $T = 300$ K. This is repeated for five different ions: Na^+, K^+, Cl^-, F^-, and $(CH_3)_4N^+$. In this report I present the results for only the Cl^- ion, whose Lennard-Jones parameters are taken to be $\sigma = 3.93$ Å and $\varepsilon = 0.832$ kcal/mol. The results for the other ions support the major conclusions of this report, and the details of these calculations will be presented elsewhere (*9*). In order to simulate the potential drop across an electrified interface, I have repeated the whole procedure described above utilizing an external electric field with two different intensities. I have also obtained trajectories for the reverse process, starting from an ion in the water phase and using an external potential drop across the interface to drive the ion to the DCE phase.

The fundamental property of the system that governs the dynamics and thermodynamics of the ion transfer is the free energy,

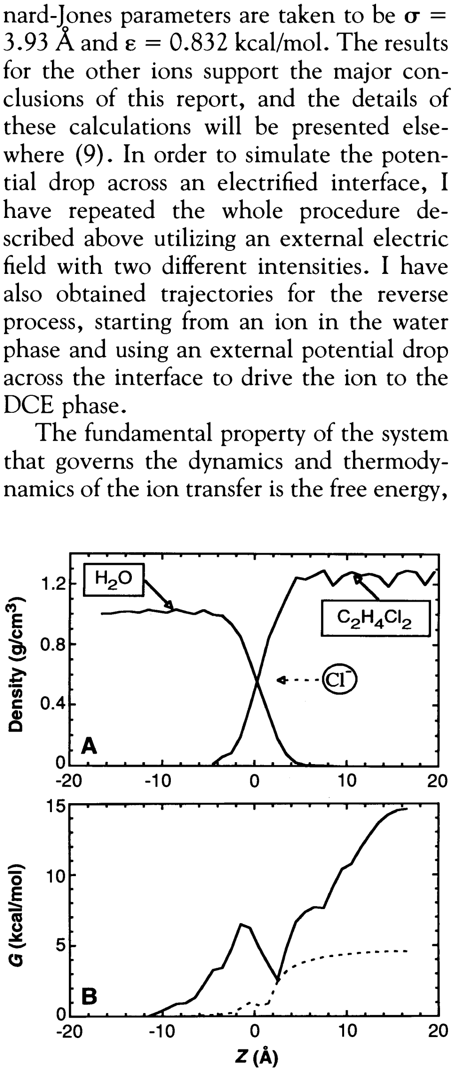

Fig. 1. Transfer of Cl^- across the interface between water and 1,2-dichloroethane. (**A**) The density profiles of the two immiscible liquids. (**B**) The free energy profile for the ion transfer process calculated on the basis of two different approximate theoretical models, as explained in the text.

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$G(Z)$, of the ion as a function of the distance Z along the interface normal. The free energy of transfer of the ion between the two phases, $\Delta G_t = G(\infty) - G(-\infty)$, can be estimated from electrochemical measurements with the help of certain "extrathermodynamical" assumptions (*10*), but it is the shape of G(Z) (in particular, whether there is a barrier) that governs the dynamics of the transfer. Heretofore, the only knowledge about this important quantity was based on simple continuum models whose parameters were chosen to reproduce the experimental rates. No theory or numerical calculations of G(Z) based on a molecular model were available.

Two model calculations of G(Z) for the transfer of Cl^- across the water-DCE interface are presented in Fig. 1B. The first model (dashed line, Fig. 1B) treats the system as two homogeneous dielectric media separated by a flat and mathematically sharp interface; the dielectric constant of each liquid is taken to be equal to its bulk value (*11*) up to the Gibbs dividing surface, which is defined such that the excess of one liquid on one side of the surface is exactly balanced by the deficit of the same liquid on the other side of the surface. In the system I used, it is the point at which the water density is approximately 0.5 g/cm^3, which is near $Z \approx 0$ Å. The free energy G(Z) is calculated from the expression

$$G(Z) = G_{\mathrm{ideal}} + G_{\mathrm{cavity}}(Z) + G_{\mathrm{elec}}(Z) \qquad (1)$$

where the cavity term is calculated by an extension of the scaled particle theory (*12*) to two "immiscible" hard sphere liquids, as will be described in detail elsewhere (9). The electrostatic contribution is calculated by solving the Poisson equation numerically for a charged sphere that is approaching the interface.

In the second model (solid line, Fig. 1B) the cavity term is the same, but the electrostatic contribution is determined differently: The electric field at a point Z from the interface, calculated from the molecular model of the system, is used to "charge up" the ion, and the free energy is calculated according to linear response theory. The main difference between these two models for G_{elec} is that in the second one the change in the liquid structure near the ion (and thus the "dielectric saturation") is approximately taken into account.

The free energy of transfer from the water to the DCE phase ΔG_t given by the purely electrostatic model is 5 kcal/mol, whereas the model that incorporates some information about the liquid structure near the ion gives ΔG_t = 15 kcal/mol. The experimental value is 12.4 kcal/mol (*10*). More relevant to the problem of ion transfer dynamics is the fact that the electrostatic model predicts no barrier for the transfer, whereas the second model does predict such a barrier.

In Fig. 2 I summarize the results of the dynamic trajectories for the transfer of Cl^- from the DCE to the water phase. Figure 2A (no external electric field) shows that, when the ion starts at ≈9 Å (line 1) or at ≈6 Å (line 2) from the Gibbs dividing surface, most of the trajectories are "nonreactive"—the ion does not cross. However, although for line 3 the ion starts (at ≈5 Å) in almost the same position as for line 2, most of the trajectories are reactive: All of the ions reach the Gibbs surface to within a molecular diameter, and many cross and are solvated by the water. Figure 2B shows the results of the trajectory calculations with two different values of the electric field. In both cases, the ion starts from the middle of the DCE slab (Z ≈15 Å). The effect of including the electric field gradient is to add a linear term to the free energy profile for the ion transfer and thus reduce the barrier to the transfer and increase the driving force. When E = 0.1 V Å^{-1}, the gradient is not strong enough to overcome the barrier, and in only 15% of the 20 trajectories is the ion able to get to within a few molecular diameters of the Gibbs surface in 25 ps. However, when E = 0.2 V Å^{-1}, in more than 75% of the trajectories the ion is able to cross the Gibbs surface in 15 ps.

It is clear from Fig. 2 that the ion transfer is an activated process. Otherwise, considering the net driving force toward the water phase (and the distance the ion travels), 50 ps would be more than enough time to complete the transfer in all cases. We also find (9) that the distance between the ion and the average position of the surface is not a very useful "reaction coordinate," at least in the transition region. Two almost identical positions of the ion from the average surface may have significantly different interactions with the water, and their fate may be quite different. An examination of the animated trajectories shows that the main difference between the successful and nonsuccessful trajectories is the existence of a water "finger" that is able to interact with the ion. Thus, although the average position of the ion in two different configurations may be the same, the reactive trajectory is the one in which a water

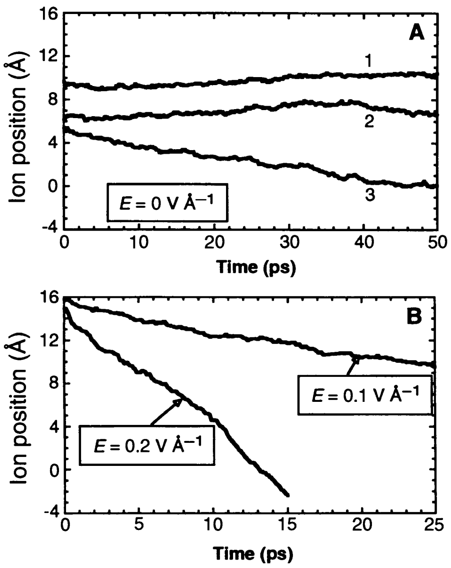

Fig. 2. Molecular dynamics of Cl^- ion transfer from the 1,2-dichloroethane to the water phase. Each line represents the average (20 trajectories) position of the ion relative to the interface. In (**A**), there is no external electric field, and lines 1 through 3 correspond to different initial positions of the ion. In (**B**), the two lines correspond to different values of the external field, as indicated. Note the different time scales in the two panels. In all cases, the integration of the equations of motion uses the velocity version of the Verlet algorithm (*13*) with a time step of 0.5 fs.

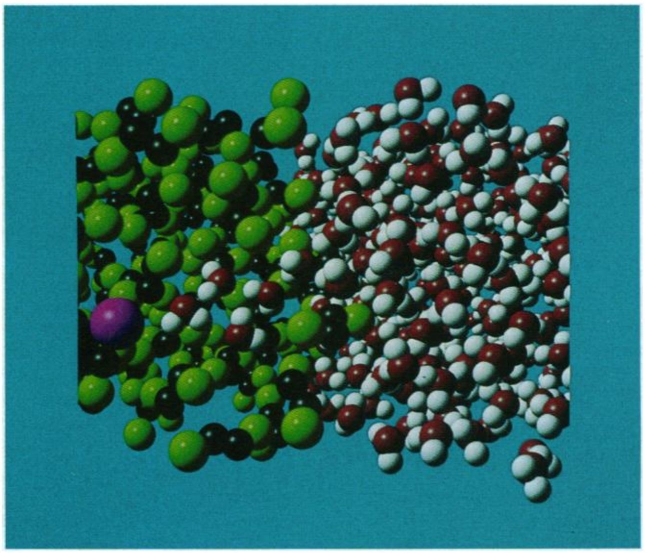

Fig. 3. A snapshot of a water "finger" interacting with the Cl^- ion located in the 1,2-dichloroethane phase. The size of the liquid atoms has been reduced in order to more clearly expose the ion.

"finger" happens to "find" the ion. The existence of these "fingers" was proved in my earlier study of the neat surface (*7*), and Fig. 3 shows an example of such a "finger" interacting with the ion.

Finally, I have considered (but do not show) the reverse process, namely, the ion starting in the middle of the water phase ($Z \approx -12$ Å) and the polarity of the electric field reversed so that the ion will climb the free energy "hill." The interesting feature here is that the interaction between the water and the ion is still quite appreciable even when the ion reaches the "bulk" of the DCE phase (as judged by the ion's location Z). This clearly shows that the ion carries at least part of the hydration shell. An examination of the animated trajectories shows that the structure of the interface becomes highly disordered, the effective surface region (the region where the density of each liquid is within 10 to 90% of the bulk value) is broadened, and liquid capillaries longer than the one characteristic of the neat surface are observed.

The molecular model described above has provided both a detailed molecular picture of ion transport dynamics and answers to long-standing questions. In particular, direct, molecularly based evidence for the existence of a barrier for the transfer process has been given, and the roles of surface roughness and capillary fluctuations in the ion transfer have been stressed. However, there are several other key issues that this model is capable of addressing. For example, the role of ion pairs in facilitating the transport has been suggested in the literature, and calculations on ion-pair transport similar to the one reported above would be desirable. One important step is to perform comprehensive calculations on several ions with increasing size. This will allow the investigation of the experimentally relevant case of ions whose net free energy of transfer is close to zero. The results of these calculations will be reported elsewhere (*9*).

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Cross-Shelf Sediment Transport by an Anticyclonic Eddy Off Northern California

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A combination of satellite imagery, shipboard profiles, drifter tracks, and moored current observations reveals that an anticyclonic eddy off the coast of northern California transported plumes of suspended sediments from the continental shelf into the deep ocean. The horizontal scale of the eddy was about 90 kilometers, and the eddy remained over the continental shelf and slope for about 2 months during the summer of 1988. The total mass of sediments transported by the eddy was of order 10^5 metric tons. Mesoscale eddies are recurrent features in this region and occur frequently in eastern boundary currents. These results provide direct evidence that eddies export sediments from continental shelves.

Over continental margins, the rotation of the Earth and the presence of coastal boundaries cause ocean currents to be mainly parallel to isobaths, and, as a result, heat, mass, nutrients, and particles are transported mainly along continental shelves. Cross-shelf flows are much weaker, are intermittent, and consequently are more poorly understood (*1*). However, property gradients across continental shelves are much larger than gradients parallel to continental shelves, and thus even weak cross-shelf flows can produce large fluxes. Cross-shelf transport processes link the coastal environment and the deep sea and affect the global cycling of carbon and nitrogen (*2*). The movements of bottom sediments across continental shelves and the export of sediments to the deep ocean influence the fate of primary production and the transport of waste in the coastal ocean, but specific transport mechanisms are difficult to identify (*1*). We report physical and bio-optical oceanographic observations (*3*, *4*) that show an anticyclonic mesoscale eddy moving from the deep ocean up onto the continental shelf off northern California during the summer of 1988. Layers of resuspended bottom sediments extending as high as 50 m above the sea floor were advected by the eddy across the shelf. Around the periphery of the eddy, sediment plumes extended tens of kilometers beyond the continental shelf break.

The sediment plumes occurred within a coastal upwelling system off northern California between Point Reyes and Point Arena (*5*). The distribution of sea surface temperature (SST) on 17 July 1988 [Julian day (JD) 199] shows an extensive region of cold water adjacent to the coast that resulted from wind-driven upwelling (Fig. 1A). The velocity field of the anticyclonic eddy in which the sediment plumes were observed is clearly evident as a rotary circulation pattern centered near 38°39′N, 123°54′W (labeled A in Fig. 1A) (*6*). The eddy was located inshore of a narrow, meandering current jet that coincided with a filament of cold water and extended about 300 km offshore (*7*). The anticyclonic rotation of the eddy is also evident in a satellite SST image from 11 July (JD 193), which shows a plume of cold upwelled water wrapping around the southern portion of the eddy in a clockwise sense (Fig. 1B).

Moored temperature and current time series from the continental slope show that, as the eddy moved onshore, both water temperature and equatorward (along shore) current speed at a depth of 10 m increased (Fig. 2, A and B). This general warming of surface waters by about 3.5°C occurred despite strongly upwelling-favorable winds, which normally lead to cooling of surface

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