

Adsorption and Solvation of Ethanol at the Water Liquid–Vapor Interface: A Molecular Dynamics Study

Michael A. Wilson^{*,†,‡} and Andrew Pohorille^{†,‡}

Exobiology Branch, NASA–Ames Research Center, MS 239-4, Moffett Field, California 94035-1000, and Department of Pharmaceutical Chemistry, University of California–San Francisco, San Francisco, California 94143

Received: August 30, 1996; In Final Form: January 28, 1997[®]

The free energy profiles of methanol and ethanol at the water liquid–vapor interface at 310 K were calculated using molecular dynamics computer simulations. Both alcohols exhibit a pronounced free energy minimum at the interface and, therefore, have positive adsorption at this interface. The surface excess was computed from the Gibbs adsorption isotherm and was found to be in good agreement with experimental results. Neither compound exhibits a free energy barrier between the bulk and the surface adsorbed state. Scattering calculations of ethanol molecules from a gas phase thermal distribution indicate that the mass accommodation coefficient is 0.98, and the molecules become thermalized within 10 ps of striking the interface. It was determined that the formation of the solvation structure around the ethanol molecule at the interface is not the rate-determining step in its uptake into water droplets. The motion of an ethanol molecule in a water lamella was followed for 30 ns. The time evolution of the probability distribution of finding an ethanol molecule that was initially located at the interface is very well described by the diffusion equation on the free energy surface.

Introduction

The interaction of alcohols with aqueous interfaces plays an important role in a variety of physical and biophysical processes. The binding of ethanol to water–membrane¹ and protein² interfaces is of great pharmacological interest, although it remains uncertain if it acts directly on protein receptors or on lipids.^{3,4} The adsorption of small solutes at the water liquid–vapor interface is an important step in the uptake of atmospheric pollutants by water droplets,^{5–9} and the uptake kinetics of a large number of gas phase solutes by water droplets have recently been investigated in an extensive series of experiments.^{5–8} The results of these experiments were interpreted as indicating a large free energy barrier between the surface adsorbed state and the interior of the water droplet. This barrier has further been modeled as the process of “nucleating” the solvation structure around a molecule before it can diffuse into the bulk interior of the droplet.¹⁰

Fundamental to all these processes is the underlying free energy profile for transferring molecules through the interfacial region between two bulk phases. Here, we report the free energy profiles for the adsorption of methanol and ethanol at the water liquid–vapor interface obtained from molecular dynamics (MD) computer simulation. The interaction potentials used in the computer simulation are critically tested by comparing the calculated and experimental results on adsorption. In addition to classical measurements of the Gibbs adsorption isotherm,^{11,12} recent neutron and X-ray scattering¹³ and nonlinear optics¹⁴ experiments, which provide a more direct probe of adsorption, are exploited. Once the reliability of the potentials is established, we make a detailed study of the adsorption kinetics of ethanol at the water liquid–vapor interface. The results of the equilibrium and kinetic simulations are used to determine the molecular mechanism of the uptake of the alcohols by the water surface.

Methods

NVE molecular dynamics calculations were carried out on a single molecule of methanol or ethanol interacting with a water lamella containing 488 water molecules. Periodic boundary conditions were applied in all three directions. The *x*-, *y*-, and *z*-dimensions of the simulation cell were 24 Å × 24 Å × 100 Å and the *z*-axis was perpendicular to the interface. The equations of motion were solved using the Verlet algorithm with a time step of 0.002 ps. The temperature of the system was maintained at 310 K by occasionally rescaling the velocities of the atoms. This temperature was used because the present calculations are to provide benchmark results for studying adsorption of alcohols at water–oil and water–membrane interfaces at physiological temperatures.

The TIP4P potentials were used to represent the water–water interactions.¹⁵ An all-atom intermolecular potential was used to describe the alcohol molecules. The alcohol–water intermolecular potentials included van der Waals terms and Coulomb interactions between partial charges. The van der Waals terms for the alcohol alkyl carbon and hydrogen atoms were obtained from calculations which optimized the solubilities of methane and partially fluorinated methane derivatives.¹⁶ The OPLS value of the van der Waals term for the alcohol oxygen were used.¹⁷ The partial charges on the atoms of methanol were taken from the ESP model.¹⁸ The partial charges on the atoms of ethanol were obtained by fitting electrostatic potentials generated by these charges in several different conformations to the quantum mechanical potentials derived at the 6-31G** level. This was accomplished using the Grid program.¹⁹ All bond lengths were constrained to their equilibrium values using SHAKE.^{20,21} The remaining intramolecular terms were taken from the AMBER force field.^{22,23} The water–water interactions and the water–solute interactions were smoothly truncated between 7.5 and 8.0 Å. The cutoff was applied to small, charge neutral groups. These potentials and their derivation are described in more detail elsewhere.²⁴

The free energy profiles were obtained from a series of calculations in which the solute was restricted in a window along

[†] Exobiology Branch.

[‡] Department of Pharmaceutical Chemistry.

[®] Abstract published in *Advance ACS Abstracts*, March 15, 1997.

the z -axis by a harmonic restraining potential $k(z_{\min} - z)^2$ for $z < z_{\min}$ and $k(z - z_{\max})^2$ for $z > z_{\max}$, where z_{\min} and z_{\max} are the lower and upper bounds of the window. For each solute, five windows 7 Å wide and consecutively overlapping by approximately 2 Å were generated. In the first window, the solute was located in the gas phase sufficiently far from the interface that its interactions with the water lamella were very weak. In the last window, the solute was in the bulk aqueous environment in the middle of the water lamella. In each window, a trajectory 2.5 ns long was used to generate the probability density $P(z)$ of finding the center of mass of the solute at different positions along the z -axis. This $P(z)$ was then used to obtain the free energy profile $\Delta A(z)$ from the relationship

$$\Delta A(z) = -k_B T \ln P(z) + A_{\text{shift}} \quad (1)$$

where k_B is the Boltzmann constant, T is the temperature of the system, and A_{shift} is a shift that must be applied to the free energy profile in the current window so that it matches the profile of the previous window. The shift was calculated using a least-squares fit in the 2 Å region where the two free energy curves overlap.^{25,26} We use the convention that $\Delta A(z) = 0$ in the gas phase.

To investigate the adsorption kinetics of ethanol, a number of scattering trajectories were constructed using a method described previously.^{27,28} A total of 100 configurations were obtained from a 1 ns MD trajectory for the water lamella by saving a configuration every 10 ps. Each configuration was used to generate 10 initial configurations for scattering trajectories by placing an ethanol molecule in the gas phase at random points in the xy -plane, 8.5 Å from the equimolar surface of the water. The initial orientations of the ethanol molecule were sampled from a uniform distribution, whereas the initial conformations were selected from the equilibrium distribution for an isolated molecule. The initial velocities were sampled from the Maxwell–Boltzmann distribution at 310 K, subject to the restriction that the normal component of velocity of the center of mass of the ethanol molecule was directed towards the water lamella. Using these initial configurations a total of 1000 scattering trajectories were generated, each 20 ps long.

Finally, a 30 ns trajectory without window restraints was obtained for a single ethanol molecule in the water lamella. The trajectory was initiated from an equilibrated configuration in which the ethanol molecule was located at the interface. During the simulations, the molecule moved several times between the two surfaces of the water lamella, resulting in a fairly symmetric density profile. This trajectory was used to compare the motion of the molecule near the interface with predictions of a simple diffusion model.^{29–32}

Results and Discussion

Free Energy Profiles. Recent work on the uptake of solute species, including methanol and ethanol, by water droplets⁷ was interpreted in terms of a substantial barrier to the transport of surface adsorbed species into the bulk water phase. In the experiments, the change in gas phase concentration of the solute was measured as a function of the surface area of water droplets exposed to the gas. The mass accommodation coefficient was obtained from these results and a substantial free energy barrier was inferred from a simple chemical kinetics model.⁷

To test this interpretation, we calculated the equilibrium free energy profiles of methanol and ethanol at the water liquid–vapor interface. These are shown in Figure 1. The solvation free energies of the alcohols which correspond to the end points

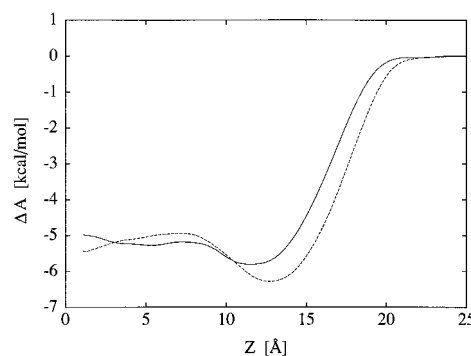


Figure 1. Free energy profiles for the transfer of methanol (solid line) and ethanol (dotted line) across the water liquid–vapor interface. The equimolar surface of water is located at 12.5 Å. The bulk water phase lies to the left of the equimolar surface, and the vapor phase lies to the right.

of the curves in the interior of the water lamella are in good agreement with experimental results. The calculated free energies of hydration at 310 K are -5.1 ± 0.2 and -5.2 ± 0.2 kcal mol⁻¹ for methanol and ethanol, respectively, whereas the corresponding experimental values are -4.94 and -4.96 kcal mol⁻¹.³³ The variation in the free energies in the interior of the lamella ($z < 5$ Å) is within the statistical uncertainties in the calculation. The free energy of hydration was calculated from the average of the free energy profile over the range $1 < z < 5$ Å.

The free energy profiles exhibit several interesting features. First, there is no free energy barrier between the surface-adsorbed state and the interior of the lamella to within the statistical errors of the calculations. Second, $\Delta A(z)$ of both alcohols goes through a minimum near the interface and, therefore, these species are interfacially active. Third, the depth of the minima, relative to the free energies of solvation in bulk water, appears to increase somewhat with increasing length of the alkyl chain, from -0.7 kcal/mol for methanol to -1.2 kcal/mol for ethanol.

The free energy profile can be used to determine the density profiles of the alcohols at densities sufficiently low that alcohol–alcohol correlations can be neglected. Under this assumption, the surface excess Γ_s of solute can be calculated from the Gibbs adsorption isotherm:¹²

$$\Gamma_s = \int_{z_{\min}}^{z_{\text{Gibbs}}} [c(z) - c_g] dz + \int_{z_{\text{Gibbs}}}^{z_{\max}} [c(z) - c_l] dz \quad (2)$$

where c_g and c_l are the concentrations of solute in the vapor and bulk liquid phases, respectively, z_{\min} and z_{\max} are located at the center of the water lamella and in the vapor far from the interface, respectively, and z_{Gibbs} is the position of the equimolar surface of the water, at which the surface excess of water vanishes. The concentration profile $c(z)$ was calculated from the free energy surfaces shown in Figure 1 assuming an ideal solution,

$$c(z) = c_g e^{-\beta \Delta A(z)} = c_l e^{-\beta \Delta A_{\text{sol}}} e^{-\beta \Delta A(z)} \quad (3)$$

where $\beta = 1/k_B T$. The second equality makes use of the relation between the equilibrium vapor and liquid concentrations of the solute, $c_g/c_l = e^{-\beta \Delta A_{\text{sol}}}$, where ΔA_{sol} is the solvation free energy. This second form of the equation is more convenient because most of the experimental results were given as a function of the bulk aqueous concentration of alcohol. Since this formula is valid at low solute concentrations, the surface excess was computed for the lowest concentration for which

experimental data was reported. Its value is 3×10^{-10} mol cm $^{-2}$ when the bulk concentration of ethanol is 0.0012 mol cm $^{-3}$. For comparison, recent neutron-scattering experiments yield a surface excess of $(3-5) \times 10^{-10}$ mol cm $^{-2}$ at the same concentration.¹³ The computed surface excess of methanol is 1×10^{-10} mol cm $^{-2}$ at a bulk concentration of 0.0012 mol cm $^{-3}$. This is in fair agreement with the experimental value of 2.5×10^{-10} mol cm $^{-2}$ at this concentration.¹¹ In both cases, the concentrations appear to be sufficiently low because the surface excess is a linear function of the bulk concentration of solute. The results of recent computer simulations on the surfaces of water-methanol³⁴ and water-ethanol³⁵ mixtures were in comparable agreement with experimental results.

Because our calculations involved a single solute molecule and our analysis is based on the assumption that the solution is ideal, it is interesting to make a more detailed comparison of our results with the simulations of mixtures.^{34,35}

The density profile from simulations of the water-methanol mixture shows some evidence of enhanced density of methanol at the interface, especially at a mole fraction of 0.1.³⁴ However, the trajectories were only 50–100 ps long and it has been argued that the system was not fully equilibrated.³⁵ At lower mole fractions of methanol, a well-defined depletion layer beneath the surface cannot be ascertained from the simulation data.³⁴

The simulation of the water-ethanol system was carried out at two different system sizes (at a mole fraction of ethanol of 0.1) and for substantially longer simulation times.³⁵ The density profile of ethanol in this simulation clearly exhibits a maximum at the interface and a minimum between the bulk and the interface. Simultaneously, the density of water is enhanced in the region of ethanol depletion.³⁵ This is due to the tendency of interfacial water molecules to hydrogen bond between themselves, thereby expelling ethanol molecules. However, this effect is fairly small; the ratio of the ethanol density at its interfacial minimum value to its bulk value is about 0.5. This corresponds to a free energy barrier of only about 0.4 kcal mol $^{-1}$ between the bulk and the surface-adsorbed state.

The density profiles obtained from our free energy profiles using eq 3 show a large excess in the interfacial region which decays to the density in the bulk. In particular, these density profiles do not exhibit depletion layers between the bulk and surface (see *vide infra* Figure 4 for a density profile calculated from a long MD run, described later in the paper.) This lack of a free energy barrier is most likely due to the absence of ethanol-ethanol correlation effects in the interfacial region. Other possibilities include differences in the potential models and in handling long-range effects. However, we emphasize that both sets of calculations yield qualitatively similar results, and the computer simulations consistently predict that there is at most a small free energy barrier between the surface-adsorbed state and the bulk aqueous phase. This contradicts the interpretation of the experimental results which imply a barrier of several kcal mol $^{-1}$ between the surface adsorbed state and bulk water.⁷

Dynamics of Surface Adsorption. Returning to the surface uptake experiments, the experimentally derived barrier for ethanol at 298 K is about 2.5 kcal mol $^{-1}$ with respect to the gas phase. This implies that there is a barrier of almost 9 kcal mol $^{-1}$ from the surface to the bulk (or a barrier of about 7 kcal mol $^{-1}$ going from the bulk to the surface). One consequence of this interpretation is that solute species that reach the interface are much more probable to desorb than become solvated by the water, yielding very small sticking probabilities. It has been argued that this free energy barrier could be due to the time

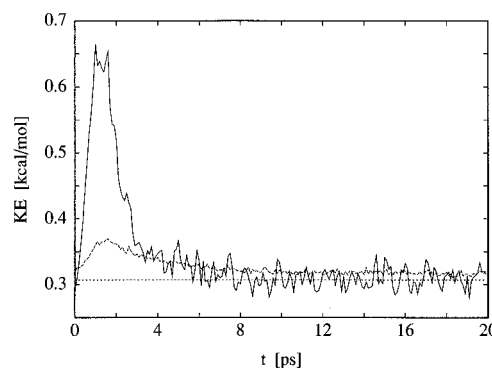


Figure 2. The average kinetic energy of the center of mass coordinate of ethanol, perpendicular to the interface (solid line) and the average total kinetic energy of the ethanol molecule per degree of freedom (dashed line) as a function of time. The dotted line represents the equilibrium value of the kinetic energy per degree of freedom at 310 K.

required to solvate the solute species before it diffuses into bulk. This was modeled as a nucleation process for a critical cluster of water molecules around the solute molecule at the interface.¹⁰

We tested these ideas for the adsorption of ethanol at the water interface using a two-step approach. First, we investigated how ethanol molecules sampled from a thermal ensemble in the gas phase become adsorbed at the interface. In particular, we wanted to determine the fraction of molecules adsorbed at the interface and the time scale over which they became thermally equilibrated. Second, we inquired into the probability that an ethanol molecule, equilibrated at the interface, remained near the surface, became solvated by the bulk water, or desorbed into the vapor. Specifically, we wanted to know if the solvation of an ethanol molecule that was initially located at the interface can be described by diffusion on the free energy surface or if there is a kinetic barrier to solvation, as suggested by the nucleation model.¹⁰

From the scattering calculations that were described in the methods section, we found that only 18 of the 1000 trajectories that were initiated with the ethanol molecule in the vapor phase described a scattering event from the water interface. This corresponds to a mass accommodation coefficient of 0.98. In most of the scattered trajectories, the ethanol molecules started with very small momenta toward the surface, and the initial interaction of this molecule with the surface was sufficiently repulsive to deflect it from the interface. This is due to the fact that the initial interaction of the ethanol dipole with the water surface is slightly repulsive for some orientations of the ethanol molecule, and does not mean that there is a free energy barrier between the vapor phase and the surface-adsorbed state.

For the sticking trajectories, the average kinetic energy along the z -direction of the center of mass motion of the ethanol molecules is shown in Figure 2. The initial rise is due to the acceleration of the ethanol molecule into the attractive potential well near the water surface. The average translational kinetic energy of the solute for the sticking trajectories decays to the equilibrium value within about 10 ps. A similar decay is observed for the average total kinetic energy. This is also shown in Figure 2. Although the molecules are slightly "hot" after 20 ps, this excess kinetic energy is smaller than $k_B T$. At the end of this time, almost all of the excess energy of the ethanol molecules has been dissipated into the water. This means that the ethanol molecules reach thermal equilibrium with the aqueous medium within a few picoseconds of striking the water lamella and do not possess enough kinetic energy to leave the surface.

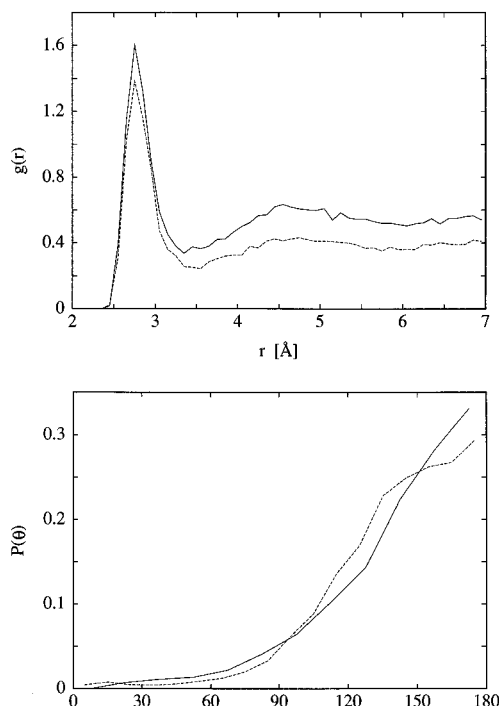


Figure 3. (a) Ethanol oxygen–water oxygen radial distribution for the ethanol molecules from the scattering trajectories averaged over the final 10 ps of each trajectory (solid line) and for the ethanol molecule located at the interface in the equilibrium free energy calculation (dashed line). (b) The distribution of the C–O bond vector (pointing from C to O) of ethanol with respect to the normal to the surface (pointing from liquid to vapor) for ethanol molecules at the end of the scattering trajectories (solid) and from the equilibrium free energy trajectory (dashed line).

This conclusion is supported by the radial distribution function (RDF) of the oxygen atoms of the water molecules around the oxygen atom of the ethanol, shown in Figure 3a, and the orientational distributions of the C–O bond vector, shown in Figure 3b. The RDF averaged over the final 10 ps of all the sticking trajectories is very similar to that obtained from the equilibrium free energy calculation for the window in which the alcohol was at the free energy minimum. The differences can be attributed to the restraints imposed on the equilibrium trajectory which forced the molecule to remain very close to the surface. Since the scattered trajectories were not subjects to restraints, the ethanol molecules were able to penetrate deeper into the interface, thereby yielding a somewhat larger number of water molecules around the solute. Similarly, the probability distribution of the orientation of the C–O bond vector with respect to the surface normal is almost the same as the distribution obtained from the equilibrium trajectory. Therefore, not only have the ethanol molecules lost most of their initial energy within 10–20 ps of reaching the interface, but their orientational distributions and solvation structure at the end of 20 ps have almost completely evolved to their equilibrium values.

To address the question of how a thermally equilibrated ethanol molecule enters the bulk phase from the surface, we obtained a 30 ns trajectory of an ethanol molecule, initiated from an equilibrium configuration at the surface. The density profile of the ethanol molecule for this trajectory is shown in Figure 4. The fact that this profile is not symmetric merely reflects that 30 ns is too short to sample completely diffusive motion on a nonuniform free energy surface over a length scale of 25 Å. However, the ethanol molecule was observed to move between the two surfaces of the water lamella a number of times

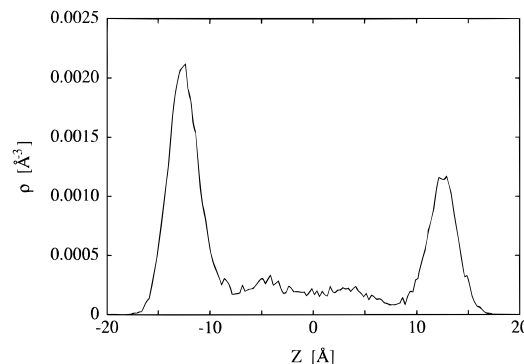


Figure 4. Density profile of the center of mass of the ethanol molecule from a 30 ns molecular dynamics trajectory at 310 K. The equimolar surfaces of the water lamella lie at ± 12.5 Å.

over the course of the simulation. During this time, it never desorbed from the lamella into the vapor phase.

To test if the motion of the ethanol molecule was diffusive, we constructed the correlation function $P(z_0; z, t)$, which is the probability of finding the molecule at position z at time t given that it was initially at z_0 . This can be compared to the solution of the one-dimensional diffusion equation in the presence of an external potential, $W(z)$,

$$\frac{\partial P(z_0; z, t)}{\partial t} = D \frac{\partial^2 P(z_0; z, t)}{\partial z^2} + \beta D \frac{\partial W(z)}{\partial z} P(z_0; z, t) \quad (4)$$

D is the diffusion coefficient of ethanol in water. The computed free energy surface was used as the external potential. The self-diffusion coefficient of ethanol in bulk water at 310 K, computed using the Einstein relation at long times, $D = \langle (r(t) - r(0))^2 \rangle / 6t$, was found to be $D = 0.2 \text{ cm}^2 \text{ s}^{-1}$.

The probability distribution of the ethanol molecule initially located between 12 and 13 Å from the center of the water lamella is compared with the solution to the diffusion equation after 20 and 60 ps, in Figures 5a and 5b, respectively. The initial distribution for the diffusion equation was equal to the equilibrium distribution between 12 and 13 Å and zero elsewhere. The agreement between the molecular dynamics results and the diffusion model is excellent. The mechanism by which an ethanol molecule becomes solvated can therefore be described as capture by the interface with almost unit probability followed by diffusion on the equilibrium free energy surface. From the solution of the diffusion equation, we find that the time scale for diffusion out of the surface adsorbed state is several nanoseconds. This can be compared with the time required to form a solvation shell around the solute, which occurs within 20 ps of the molecule sticking to the surface. Thus, contrary to the nucleation model of solvation at the interface, the formation of the solvation structure around the ethanol molecule is not the rate-limiting step in the uptake process.

As there does not appear to be a kinetic barrier to the uptake of ethanol at the water liquid–vapor interface, and since the free energy of solvation and the surface excess of ethanol are in good agreement with experimental results, we return to the calculation of the mass accommodation coefficient. Even though the incoming ethanol molecules have lost nearly all of their excess kinetic energy within a few picoseconds of striking the surface, there is still a chance that they will thermally desorb on a longer time scale. Consequently, the molecular dynamics results provide only an upper limit to the true mass accommodation coefficient. The correction p due to the probability of a molecule thermally desorbing versus becoming dissolved in water can be estimated from the free energy difference between the the surface adsorbed state and the vapor, A_{s-v} , and the free

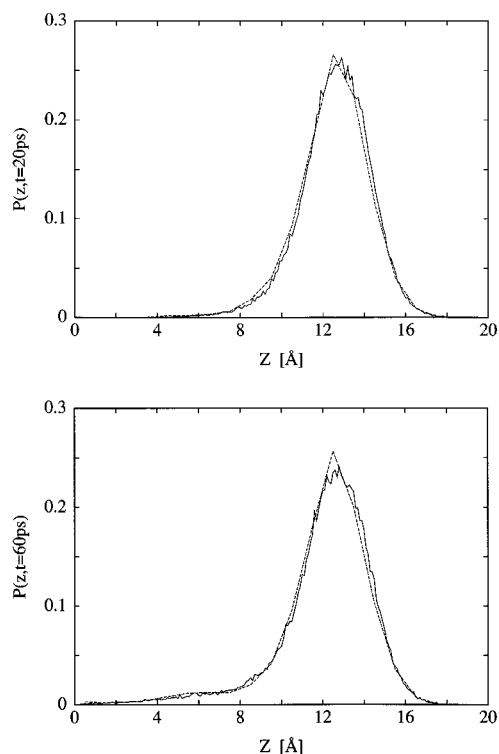


Figure 5. The probability distribution of the position of the ethanol molecule, initially located between 12 and 13 Å calculated from the diffusion model (eq 4) (solid line) and from a 30 ns molecular dynamics trajectory (dashed line): (a) after 20 ps and (b) after 60 ps.

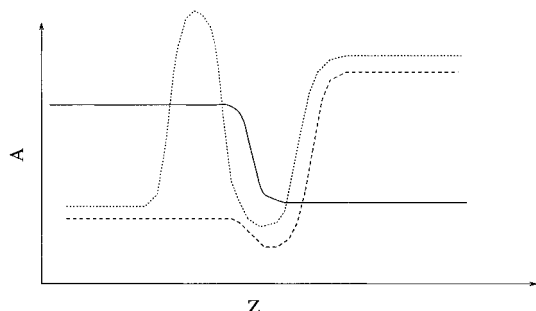


Figure 6. Schematic free energy surface implied by the existence of a barrier between the surface adsorbed state and bulk water (dotted line) and the free energy surface computed from the molecular dynamics (dashed line). The density profile of water is drawn (solid line) to show the approximate location of the surface.

energy difference between the surface-adsorbed state and the liquid, A_{s-l} , $p = e^{-\beta A_{s-l}}/e^{-\beta A_{s-v}}$. For ethanol, if $A_{s-v} = 6.3$ kcal/mol and $A_{s-l} = 1.1$ kcal/mol, then $p = 0.001$. Consequently, we expect the correction due to thermal desorption of ethanol molecules is small.

Whereas the molecular dynamics calculations indicate a mass accommodation coefficient of 0.98 at 300 K, the experimental results on the uptake of ethanol by water droplets indicate that the mass accommodation coefficient ranges from about 0.18 at 255 K to 0.04 and 295 K.⁷ The reasons for the difference between the experimental results and the molecular dynamics results are not clear. One possibility to consider is that the computed free energy surface is qualitatively incorrect, since it does not contain a substantial free energy barrier between the surface adsorbed state and bulk aqueous solution, as drawn schematically in Figure 6. This could result from a poor description of the structure of interfacial water or solute-solvent interactions. This, however, seems unlikely, given the generally good agreement between simulations and experiments on the

structural and thermal properties of the water liquid-vapor interface³⁶ and on surface excess of methanol and ethanol.

Another possibility for the discrepancy is the assumption that the total flux of molecules to the droplet surface is equal to the kinetic theory of gases result, $F = \rho c/4$, where ρ is the density of the gas and c is the thermal velocity of the gas molecules. Since this result is strictly true only for a planar surface, it may not be correct for a droplet moving through the gas at a fairly large velocity. Since the droplet train experiments are carried out under steady-state flow of gas and droplets through the reaction chamber, the concentration of gas in the path of the water droplet may be less than in the surrounding medium. This concentration will depend upon the gas phase diffusion constant, the droplet size and frequency, and possibly on turbulence due to the passage of the droplet through the gas. Consequently, the experimentally determined mass accommodation coefficients are probably a lower bound to the true mass accommodation coefficient.

One important limitation of the present calculations is that they involved only single solute molecules interacting with the water surface. If the surface does become saturated with essentially a complete monolayer of solute, the physical nature of the surface with which the incoming ethanol molecules interact is quite different than the simple water liquid-vapor interface. At higher concentrations of ethanol, the incoming molecules interact with a surface that becomes increasingly hydrophobic, and the mass accommodation coefficient might be quite different than that calculated here. The free energy surface will also change at higher ethanol concentrations. It should, however, be noted that the free energy that can be inferred from the simulation of the surface of a water-ethanol mixture³⁵ is qualitatively similar to the single molecule free energy surfaces of the present calculations, and while ethanol molecules were observed to exchange between the surface and bulk in the mixture, no molecules were observed to evaporate.

There has also been some differences between mass accommodation coefficients obtained from different experimental techniques. Recent experiments on the uptake of HCl by water/sulfuric acid mixtures in a flow reactor yielded a mass accommodation coefficient of 0.8 ± 0.2 at a temperature of 274 K,³⁷ while uptake measured in a droplet train apparatus yielded mass accommodation coefficients of 0.18 ± 0.02 at the same temperature.⁶ It is possible that using the kinetic theory is more appropriate for the geometry of the flow reactor than for the droplet train apparatus, but these issues are difficult to resolve.

Conclusions

We have calculated the equilibrium free energy profiles for the solvation of methanol and ethanol across the water liquid-vapor interface at 310 K. The resulting hydration free energies are in good agreement with experimental results. The free energy curves of both alcohols exhibit fairly deep interfacial minima, indicating substantial positive surface excess concentrations. These concentrations, estimated from the Gibbs adsorption isotherm, are also in good agreement with experimental results. Neither free energy curve exhibited a free energy barrier between the surface adsorbed state and the interior of the water lamella. Extensive calculations of the interaction of ethanol molecules with the water lamella show that, first, ethanol molecules from the vapor are adsorbed at the surface with a mass accommodation coefficient of 0.98 and second, the motion of ethanol molecules from the surface into bulk water can be described as diffusion on the equilibrium free energy surface.

These results are not in agreement with the model used to interpret recent experiments on the uptake of solutes by water

droplets, which indicates not only that a free energy barrier exists between bulk water and the surface but that this barrier is larger than the free energy of desorption.^{7,10} This model assumes a simple chemical kinetics description of the adsorption, desorption, and solvation processes. Such an approach can be questioned because, in the absence of well-defined states corresponding to bulk water, surface, and vapor phase separated by free energy barriers, a simple rate law might not exist for this model.

From scattering calculations, we observed that ethanol molecules became equilibrated within 10–20 ps of collision with the water interface and developed both an equilibrium solvation structure and an equilibrium orientational distribution at the interface. Consequently, the initial solvation of the ethanol molecule at the surface is quite fast. As the time scale for diffusion into the bulk is much larger than the time scale for the exchange of water molecules in the solvation shell around the solute, the formation of the solvation structure around the ethanol molecule is not the rate-limiting step in the uptake process. In light of these results, we suggest that the assumption that the total flux of gas to the surface can be treated using simple kinetic theory is not necessarily correct and can provide only a lower bound to the mass accommodation coefficient. Undoubtedly, gaining a good, general understanding of uptake of different molecules by water droplets will require further, careful studies using a variety of experimental techniques as well as computer modeling.

Acknowledgment. This work was supported by NIH Grant GM47818-01 and by NASA Exobiology Grant NCC 2-772. Computer resources were provided in part by the National Cancer Institute Frederick Biomedical Supercomputer Center. M.W. thanks D. Hanson, P. Davidovits, G. Nathanson, D. Ray, and M. L. Schlossman for a number of interesting discussions.

References and Notes

- (1) Dubey, A. K.; Eryomin, V. A.; Taraschi, T. F.; Janes, N. *Biophys. J.* **1996**, *70*, 2307.
- (2) Avdulov, N. A.; Chochina, S. V.; Daragan, V. A.; Schroeder, F.; Mayo, K.; Wood, W. G. *Biochemistry* **1996**, *35*, 340.
- (3) Peoples, R. W.; Li, C.; Weight, F. F. *Annu. Rev. Pharmacol. Toxicol.* **1996**, *36*, 185.
- (4) Barry, J. A.; Gawrisch, K. *Biochemistry* **1994**, *33*, 8082.
- (5) Worsnop, D.; Zahniser, M. S.; Kolb, C. E.; Gardner, J. A.; Watson, L. R.; Van Doren, J. M.; Jayne, J. T.; Davidovits, P. *J. Phys. Chem.* **1989**, *93*, 1159.
- (6) Van Doren, J. M.; Watson, L. R.; Davidovits, P.; Worsnop, D. R.; Zahniser, M. S.; Kolb, C. E. *J. Phys. Chem.* **1990**, *94*, 3265.
- (7) Jayne, J. T.; Duan, S. X.; Davidovits, P.; Worsnop, D. R.; Zahniser, M. S.; Kolb, C. E. *J. Phys. Chem.* **1991**, *95*, 6329.
- (8) Jayne, J. T.; Duan, S. X.; Davidovits, P.; Worsnop, D. R.; Zahniser, M. S.; Kolb, C. E. *J. Phys. Chem.* **1992**, *96*, 5452.
- (9) Nathanson, G. M.; Davidovits, P.; Worsnop, D. R.; Kolb, C. E. *J. Phys. Chem.* **1996**, *100*, 13007.
- (10) Davidovits, P.; Jayne, J. T.; Duan, S. X.; Worsnop, D. R.; Zahniser, M. S.; Kolb, C. E. *J. Phys. Chem.* **1991**, *95*, 6337.
- (11) Kipling, J. J. *J. Colloid Sci.* **1963**, *18*, 502.
- (12) Adamson, A. W. *Physical Chemistry of Surfaces*; John Wiley and Sons: New York, 1990.
- (13) Li, Z. X.; Lu, J. R.; Styrkas, D. A.; Thomas, R. K.; Rennie, A. R.; Penfold, J. *Mol. Phys.* **1993**, *80*, 925.
- (14) Doolen, R.; Ray, D. *Proc. Soc. Photo. Instrum. Eng.* **1995**, *2547*, 364.
- (15) Jorgensen, W. L.; Chandrasekhar, J.; Madura, J. D.; Impey, R. W.; Klein, M. L. *J. Chem. Phys.* **1983**, *79*, 926.
- (16) Pohorille, A.; Wilson, M. *J. Chem. Phys.* **1996**, *105*, 3760.
- (17) Jorgensen, W. L. *J. Phys. Chem.* **1986**, *90*, 1276.
- (18) Carlson, H. A.; Jorgensen, W. L. *J. Phys. Chem.* **1995**, *99*, 10667.
- (19) Chipot, C.; Ángyán, J. G. Grid Version 3.0: Point Multipoles Derived From Molecular Electrostatic Properties. *QCPE* **1995**, 655.
- (20) Ryckaert, J.; Cicotti, G.; Berendsen, H. J. C. *J. Comput. Phys.* **1977**, *23*, 327.
- (21) Van Gunsteren, W. F.; Berendsen, H. J. C. *Mol. Phys.* **1977**, *34*, 1311.
- (22) Weiner, S. J.; Kollman, P. A.; Nguyen, D. T.; Case, D. *J. Comput. Chem.* **1986**, *7*, 230.
- (23) Cornell, W. D.; Cieplak, P.; Bayly, C. I.; Gould, I. R.; Merz, K. M., Jr.; Ferguson, D. M.; Spellmeyer, D. C.; Fox, T.; Caldwell, J. C.; Kollman, P. A. *J. Am. Chem. Soc.* **1995**, *117*, 5179.
- (24) Pohorille, A.; Wilson, M. A.; Chipot, C. *Prog. Colloid Polym. Sci.* **1997**, *103*, in press.
- (25) Wilson, M. A.; Chipot, C.; Pohorille, A. **1996**. Submitted for publication.
- (26) Pohorille, A.; Cieplak, P.; Wilson, M. A. *Chem. Phys.* **1996**, *204*, 337.
- (27) Benjamin, I.; Wilson, M. A.; Pohorille, A. *J. Chem. Phys.* **1994**, *100*, 6500.
- (28) Benjamin, I.; Wilson, M. A.; Pohorille, A.; Nathanson, G. M. *Chem. Phys. Lett.* **1995**, *243*, 222.
- (29) Van Kampen, N. G. *Stochastic Processes in Physics and Chemistry*; North Holland: Amsterdam, 1985.
- (30) Benjamin, I. *J. Chem. Phys.* **1992**, *96*, 577.
- (31) Schweighofer, K. J.; Benjamin, I. *J. Am. Chem. Soc.* **1993**, *202*, 379.
- (32) Pohorille, A.; Wilson, M. Isomerization reactions at aqueous interfaces. In *Reaction Dynamics in Clusters and Condensed Phases*; Jortner, C., et al., Eds.; Kluwer Academic Publishers: Amsterdam, 1994.
- (33) Fang, Z.; Ionescu, P.; Chortkoff, B. S.; Kandel, L.; Sonner, J.; Laster, M.; Eiger, II. *Anesth. Anal.* submitted for publication.
- (34) Matsumoto, M.; Takaoka, Y.; Kataoka, Y. *J. Chem. Phys.* **1993**, *98*, 1464.
- (35) Tarek, M.; Klein, M. *J. Chem. Soc., Faraday Trans.* **1996**, *92*, 559.
- (36) Pohorille, A.; Wilson, M. A. *J. Mol. Struct. (THEOCHEM)* **1993**, *284*, 271.
- (37) Hanson, D. R.; Lovejoy, E. *J. Phys. Chem.* **1996**, *100*, 6397.