Ions at the Liquid/Vapor Interface of Methanol

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We studied ions at the liquid/vapor interface of methanol using classical molecular dynamics techniques. Polarizable potential models were used to describe interactions among species. We characterized the transport mechanism of an iodide anion across the methanol interface. The computed potential of mean force showed a relatively small minimum well depth (i.e., −0.60 kcal/mol) located inside the Gibbs dividing surface. During the constrained mean force simulations, we found the iodide anion carrying some methanol molecules with it as it crossed the dividing interface. The computed density profiles of the salt NaI methanol interface indicated that the iodide anions were found nearer to the interface than the sodium cations, and no well-defined maxima were found for neither ion near the interface. By comparing this result with the corresponding result obtained from a simulation of the NaI saltwater interface, we can conclude that the probability of finding iodide anions at the liquid/vapor of water interface is significantly greater than at the methanol interface.

I. Introduction

Recently, we developed a set of polarizable potential models that describe the structure and thermodynamics of liquid methanol as well as the properties of its vapor/liquid interface.[1] In this paper, we examine the ions at the methanol liquid/vapor interface. It has been established that the adsorption and distribution of ions at liquid interfaces is a fundamental process encountered in a wide range of biological and chemical systems.[2−4] In particular, the manner in which solvent molecules solvate ions is relevant to chemical and physical processes such as chemical reactions at the interface. The presence of ions at the interface can be an important factor in atmospheric processes such as molecular uptake of pollutant molecules (i.e., ozone and hydroxyl) at the air/liquid interface.[5] Much of our understanding of ions at liquid interfaces is based on studies of the ion−water system, including the work of Benjamin, Wilson, and Pohorille on transferring monovalent ions (Cl^-, F^-, and Na^+) across a water liquid/vapor interface.[6,7] Jungwirth and Tobias used classical molecular dynamics techniques and polarizable potential models to examine the equilibrium properties such as density profiles and surface tensions of ions at the air/liquid interface of water. They were able to reproduce the experimental surface tensions as a function of the alkali halide ion pair, and they also proposed a molecular model of the distribution of the ions at the air/liquid interface.[8]

We have made significant contributions to this important area by examining the role of many-body effects on the transport mechanism of ions across the water vapor/liquid interface. We have demonstrated that, depending on the type of anion involved, these ions behave differently at the interface. The larger I^- and Br^- anions were found to bind more strongly to the liquid water interface than the smaller Cl^- ion. We have also compared the potential of mean forces (PMFs) of anions and cations and found that anions are more abundant at the liquid/vapor interface of water than cations.[9−10]

The liquid/vapor interface of methanol has been studied experimentally, and it has been established that the methanol surface molecules oriented so that their methyl groups point away from the bulk liquid.[11] This result is quite different from the liquid/vapor interface of water where a significant amount of dangling OH bonds (∼25%) are present at its interface.[12] As part of ongoing research on ions at liquid/vapor interfaces, we present in this paper a detailed study of the solvation properties of sodium iodide salt at the liquid/vapor interfaces of methanol and water and a description of the transport mechanism of an iodide anion across the liquid/vapor interface. There have been some studies of ion solvation in liquid methanol, and it has been established that, although the hydration structure of an ion in methanol is very similar to that of an ion in water, the dynamical property (i.e., residence time as characterized by velocity correlation functions) is quite slow compared to ion solvation in the liquid water.[13] In addition, the density of liquid methanol ($0.8\ g/cm^3$) is about 20% lower than the density of liquid water ($1.0\ g/cm^3$) at room temperature and there is a difference in the ion solubility, which could play a significant role in the solvation of ions at their liquid/vapor interfaces.

The significance of this paper can be summarized as follows: (1) The solvation properties, including the transport mechanism at the methanol liquid/vapor interface are studied using polarizable potential models, and (2) by comparing those properties to the corresponding properties of ions at the water vapor/liquid interface, we can illustrate the role solvent effects play on the ions at the liquid interfaces. The paper is organized as follows: the computational methods, results and discussions are summarized in sections II and III, and our conclusions and discussion of future research directions are given in section IV.

II. Computational Methods

We begin this section by briefly describing the polarizable potential models for methanol and ion−methanol used in this study.[1] The model methanol molecule has six atomic sites and is polarizable. Fixed charges and Lennard-Jones parameters were assigned to every atom, with charges selected to reproduce the experimentally determined gas-phase dipole moment. A molecular polarizability was assigned to the oxygen atom to allow the induction energies and forces to be calculated. During molecular dynamics simulations, a standard iterative self-consistent field procedure was used to evaluate the induced

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TABLE 1: Optimized Potential Parameters for Methanol, Sodium, and Iodide Used in the MD Simulation[a]

atom type	σ (Å)	ϵ (kcal/mol)	q (e)	α (Å^3)
O	3.2340	0.1825	−0.4770	2.0200
HO	0.0000	0.0000	0.3361	0.0000
CT	3.3854	0.1300	−0.0954	0.0000
HT	2.5034	0.0230	0.0787	0.0000
I^-	5.1245	0.1000	−1.0000	6.9000
Na^+	2.3787	0.1000	1.0000	0.2400

[a] σ and ϵ are the Lennard-Jones parameters, q is atomic charge, and α is the polarizability.

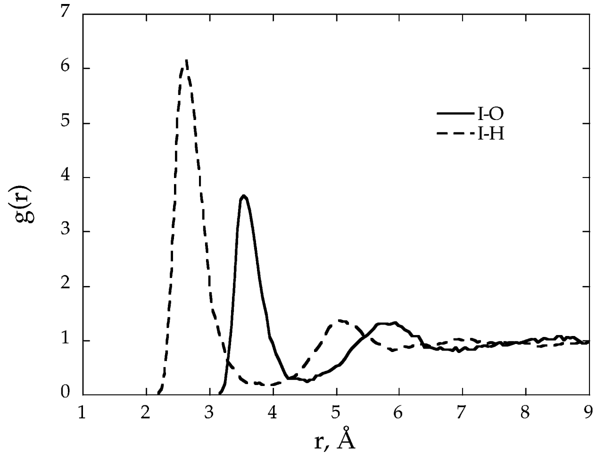

Figure 1. Computed radial distribution functions for I−O and I−H in liquid methanol near 300 K.

dipoles, which was repeated until the deviations of the induced dipoles between two sequential iterations fell below a predetermined tolerance value (0.00001 D).

Initially, we assigned the atomic polarizablities to all the atoms of the methanol molecule and, during the process of developing the potential for liquid methanol, we found the computed structure and the energetic properties were acceptable when compared to the experimental measurements; however, the induction effects are quite small (i.e., the computed average dipole moment of methanol is about 2.2 D, which is significantly lower than the corresponding experimental value of 2.87 D and ab initio simulation value of ~2.5 D). We have also assigned the molecular polarizability to the carbon atom and repeated the process of optimization, we obtained an RDF for the carbon−carbon pair that significantly deviated from the experimental RDF. We finally assigned the experimental polarizabilty to the oxygen atom and carried out further optimization processes with the final optimized parameters presented in Table 1. A more detailed description of how the polarizability was obtained and assigned to the oxygen atom can be found in ref 1.

The ion−methanol (I^- and Na^+) potential parameters were taken from our earlier work on ion−water systems.[9,10] These potential parameters were evaluated to determine how they describe the experimental data such as solvation enthalpies and hydration numbers of the sodium and iodide ions in liquid methanol. In Figure 1, we present the computed pair distributions for the iodide−oxygen and iodide−hydrogen in liquid methanol. It is worthwhile to note here that the characteristics of these distributions are very similar to that of the iodide−water system.[9,10] The peak positions in the ion−methanol system are farther out, probably because of the influence of the methyl group. The hydration energy (−64. kcal/mol) of the solvated iodide anion in liquid methanol is in fairly good agreement with the experimental measurement (−67. kcal/mol).[14] The I^- , Na^+, and methanol potential parameters are listed in Table 1.

We used a constrained mean force approach to evaluate the free energies associated with the transfer of an ion across liquid interfaces. The reaction coordinate for ion transfer can be considered to be the z_s position of the ion. The Helmholtz free energy difference, $\Delta F(z_s)$, between a state where the ion is located at z_s, $F(z_s)$, and a reference state whzere the ion is at z_o, is simply

$$\Delta F(z_s) = F(z_s) - F_0 = -\int_{z_0}^{z_s} \langle f_z(z'_s)\rangle \, dz'_s \qquad (1)$$

where $f_z(z'_s)$ is the z component of the total force exerted on the ion at a given z position (z'_s) averaged over the canonical ensemble. F_0 was chosen as the free energy of the system with the ion located in the bulk methanol region. During the simulation, the z coordinate of the ion was reset to the original value after each dynamical step, and the average force acting on the ion was then evaluated. The average forces were subsequently integrated to yield the free energy profile or the PMF. The Z axes for the ion and the simulation cell were constrained by removing the z component of the force and the velocity at every step during the molecular dynamics simulation. The molecular dynamics simulations were performed on a system consisting of an ion and 500 methanol molecules, in a rectangular simulation cell with linear dimensions of 32 Å × 32 Å × 82 Å. For the calculations reported in this paper, the position of the ion ranges from $z = 0$ to 34 Å, with a position increment of 1.0 Å. The total simulation time at each ion position was averaged over a 300 ps in addition to 100 ps for equilibration. The average forces for a given ion position were converged within a 100 ps simulation time.

The molecular dynamics simulation of salt NaI methanol liquid/vapor interface was carried out using a slab of 875 methanol molecules plus 62 sodium and 62 iodide ions to give a concentration of 2.2 M. The system was placed in a rectangular cell with dimensions of 32 × 32 × 135 Å, and periodic boundary conditions were applied in three dimensions. The particle mesh Ewald was used to evaluate the nonbonded interactions (i.e., Coulombic and polarization).[15] The results such as the surface tensions and density profiles were averaged over 3 ns to ensure a completed sampling of the system. In addition to the salt methanol liquid/vapor interface simulations, we have also repeated the simulations of pure liquid/vapor interface of methanol with a system size (i.e., 1000 molecules) larger than our previously study[1] and 2.2 M NaI saltwater liquid/vapor interface (i.e., 1000 water molecules plus 40 sodium and 40 iodide ions) for comparison purpose.

III. Results and Discussions

Figure 2a shows the free energy profile for transferring an iodide anion across the methanol liquid/vapor interface at 298 K as a function of its distance to the interface. The free energy profile decreased slowly as the iodide anion approached the Gibbs dividing surface. Before the iodide anion reached the dividing interface and eventually moved to the vapor phase with a significant free energy of solvation, a relatively small minimum free energy (−0.6 kcal/mol) was observed. This is an interesting result, although not unexpected, due to a fairly large polarizability (6.9 Å^3) of the iodide anion. This observation was confirmed by performing reverse simulations (from vapor to liquid phase) to compute the free energy profile of inserting an iodide anion from the vapor phase to the liquid phase. The minimum position was found to be further inside the dividing

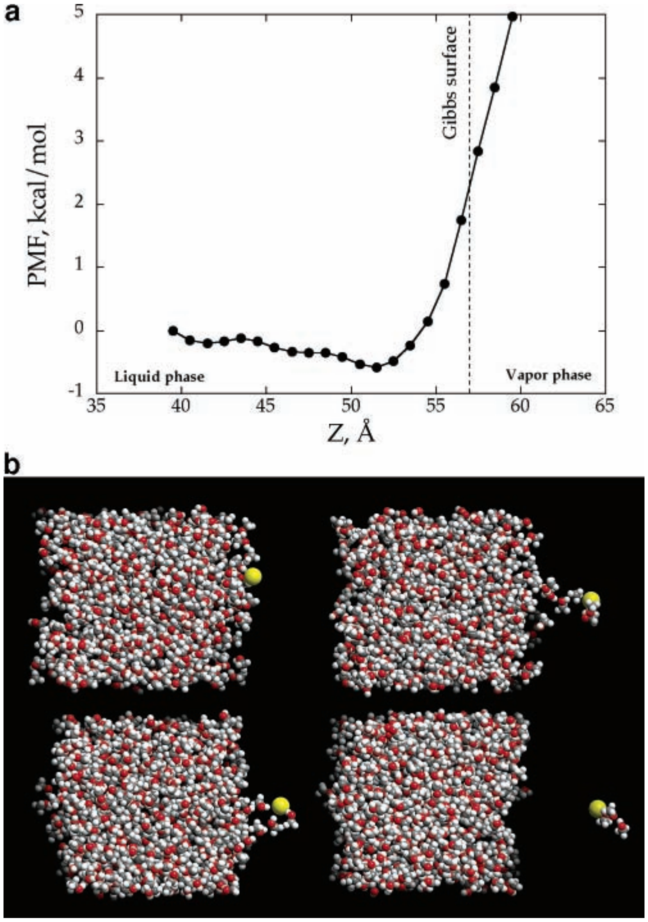

Figure 2. (a) Computed free energy profile for the iodide anion binding to the liquid/vapor interface of methanol obtained from MD simulations at 300 K. (b) Snapshots were taken from molecular dynamics simulations using mean force approaches showing the iodide anion leaving the liquid/vapor interface of methanol.

surface when compared to our previous study of an iodide anion at the liquid water interface.[9,10] To the best of our knowledge, these results can be qualitatively reasoned as follows; because the majority of hydroxyl groups were oriented toward the bulk liquid methanol, it is not necessary for the iodide anions to be at the interface. Instead, the iodide anions were present below the interface, allowing them to maximize the hydrogen-bonding network and retain the first solvation shell. The snapshots in Figure 2b, which were taken along the transfer coordinate, indicate that a number of methanol molecules accompanied the iodide anion as it crossed the interface from the liquid phase to the vapor phase. Upon close examination of these iodide anion−methanol structures, we found that they resembled the structures reported for the cluster anion−methanol gas-phase simulations; the iodide anion is exposed to the surface to maximize the hydrogen-bond interactions.

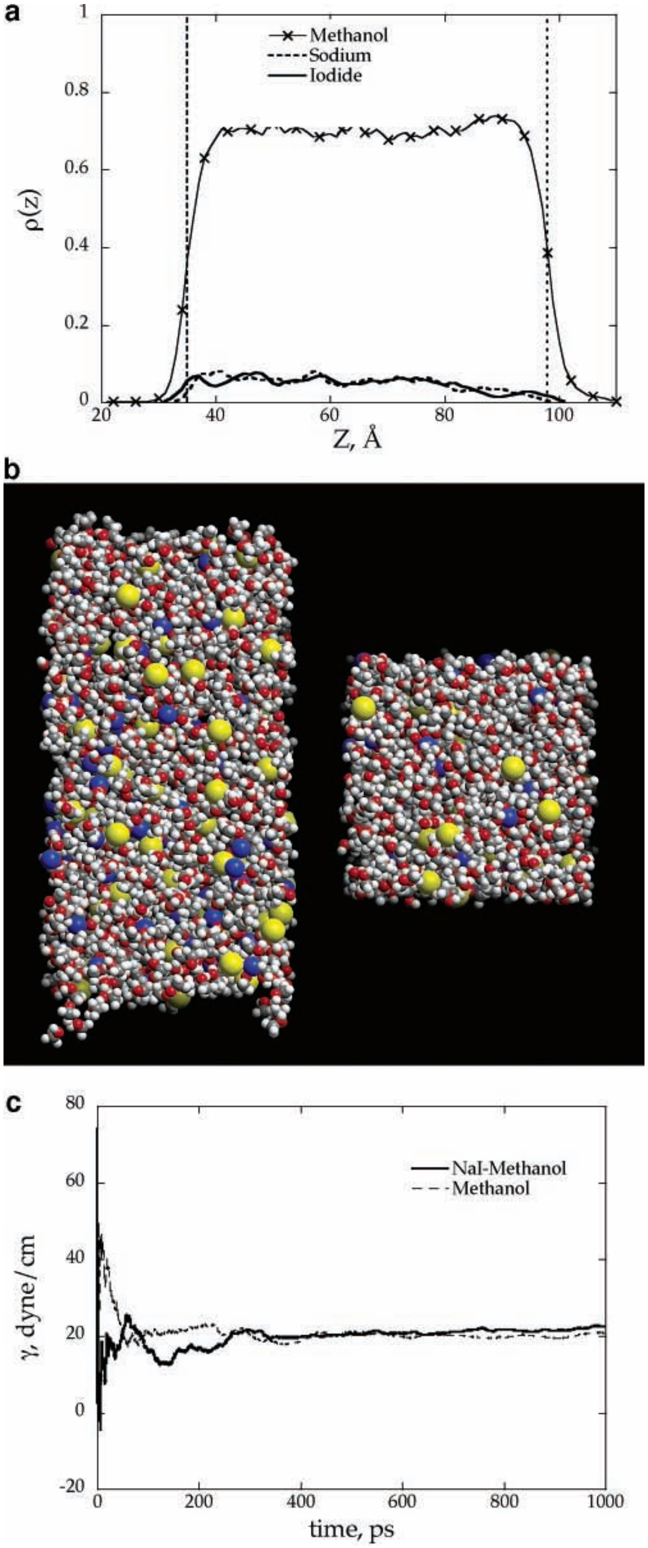

Figure 3. (a) Computed density profiles for the methanol center of mass, sodium and iodide ions of 2.2 M salt NaI methanol liquid/vapor interface. (b) Snapshots taken from molecular dynamics simulations of 2.2 M salt NaI methanol liquid/vapor interface: (left) site view and (right) top view. (c) Computed surface tensions for 2.2 M salt NaI methanol liquid/vapor interface and pure liquid/vapor interface.

As mentioned earlier, we also performed molecular dynamics simulations of a 2.2 M NaI methanol liquid/vapor interface. In Figure 3a, we present the density profiles of the methanol center-of-mass, iodide, and sodium ions obtained from averaged over 3 ns of MD simulations. Several observations are in order. (1) The characteristic of the methanol center-of-mass density profile of the salt methanol interface is very similar to the corresponding pure methanol interface, except that the density is now around 0.7 g/cm^3 instead of 0.8 g/cm^3 for pure methanol. The decrease in liquid density is likely caused by the reorganization of methanol molecules around the NaI salt. (2) The density profiles of the iodide and sodium ions are asymmetrical around $Z = 65$ Å, which is indicative of slow dynamics/equilibration processes of ions in liquid methanol as stated in the Introduction. However, we can conclude from these computed density profiles that the iodide anions were found nearer to the interface than the sodium cations. A snapshot in Figure 3b, which was taken during the molecular dynamics simulations of NaI salt at 2.2 M concentra-

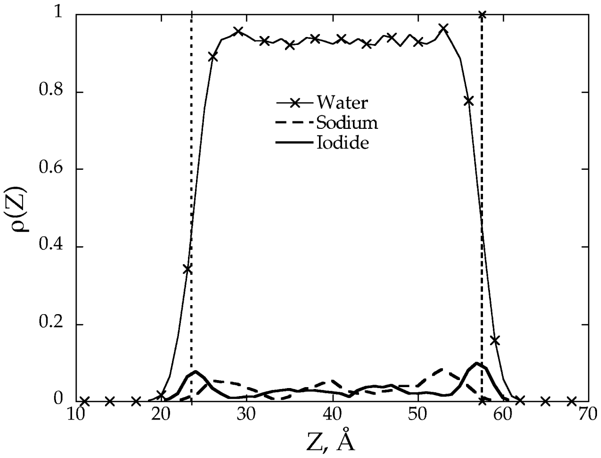

Figure 4. Computed density profiles for the water center-of-mass and sodium and iodide ions of 2.2 M salt NaI water liquid/vapor interface.

tion clearly indicates that the ions distribute randomly along the axis perpendicular to the interface and some iodide anions were found at near the interface.

We calculated the surface tension, γ, for both NaI salt and pure methanol liquid/vapor interface, which is defined as the difference between the pressure components in the direction parallel and perpendicular to the interface[16]

$$\gamma = \frac{1}{2}\left(\frac{p_{xx} + p_{yy}}{2} - p_{zz}\right)L_z \tag{2}$$

In the above equation, $p_{\alpha\alpha}$ ($\alpha = x, y$, or z) is the $\alpha\alpha$ element of the pressure tensor and L_z is the linear dimension of the simulation cell in the z direction. According to the virial equation, the $\alpha\beta$ element of the pressure tensor is

$$p_{\alpha\beta} = \frac{1}{V}\left(\sum_{i=1}^{N} m_i v_{i\alpha} v_{i\beta} + \frac{1}{2}\sum_{i'=1}^{N'}\sum_{j'=1}^{N'} F_{i'j'\alpha} r_{ij\beta}\right) \tag{3}$$

where N and N' are the numbers of molecules and atoms, respectively. V is the total volume of the system, m_i is the mass of molecule i, and ν_{ia} is the center-of-mass velocity of molecule i. In the above equation, $F_{i'j'a}$ is the a component of the force exerted on atom i' of molecule i due to atom j' of molecule j, and r_{ijb} is the b component of the vector connecting the center of mass of molecules i and j. From a 3 ns molecular dynamics trajectory, the calculated surface tension is 22 ± 2 dyn/cm for the salt and 21 ± 2 dyn/cm for the pure methanol interfaces. In Figure 3c, we show the running average of the accumulated surface tensions of salt and pure methanol liquid/vapor interface as a function of simulation time. We conclude that the computed surface tensions for the salt and pure methanol interfaces are nearly identical, which are in excellent agreement with the experimental measurements.[17]

In addition to the above calculations, we also carried out the simulations of 2.2 M NaI saltwater liquid/vapor interface using our own set of polarizable potential models for water and ion−water.[9,10] In Figure 4, we present the density profiles for water center-of-mass and sodium and iodide ions obtained from a 500 ps MD simulation. Upon examining these density profiles as well as the MD simulations snapshots, we can conclude that the iodide anions are exposed to the interface and not fully solvated. Furthermore, we also notice that there are two well-defined maxima at the Gibbs dividing surfaces of the iodide's density profile. This result indicates that the probability of finding an iodide anion at the interface of water is far greater than finding an iodide anion at the methanol liquid/vapor interface (see Figure 3a). We can attribute this effect to the difference between the liquid water and liquid methanol interfaces as well as the difference in the liquid densities and solubility's of the ions in these solvents. We also note here that the computed density profiles in the simulation of the water liquid/vapor interface converged quickly when compared to the corresponding methanol simulations.

IV. Conclusion

In this study, we carried out extensive molecular dynamics simulations of the solvation properties of the iodide and sodium ions at the liquid/vapor interface of methanol. We demonstrated that these ions behave differently at the interface with the iodide anions found at the interface more often than the smaller sodium ions. We also studied the mechanism for transporting an iodide ion across the methanol liquid/vapor interface. Our computed PMF for this transfer showed a well-defined minimum near the interface, as in the case of the water liquid/vapor interface, with a stabilization free energy of about −0.6 kcal/mol near the dividing surface with respect to the bulk liquid. The iodide ion was found to carry some methanol molecules as it crossed the interface.

In addition to the above finding, from the studies of 2.2 M NaI at the liquid water and liquid methanol interfaces, we can conclude that the population of iodide anions at the liquid water interface is far greater than the corresponding iodide anions at the liquid methanol interface. These fundamental results provide understanding of the behavior of ions at the interfaces of different liquids.

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