Molecular Dynamics Study of the Calcium Ion Transfer across the Water/Nitrobenzene Interface

Daniel J. V. A. dos Santos* and José A. N. F. Gomes[a]

A study on the calcium ion transfer across the water/nitrobenzene interface is presented. The potential of mean force was calculated and a good agreement was found between the experimental and the calculated free energy of transfer. This is a monotonically increasing function of the distance to the interface, and the process was found to be non-activated. The evolution of the first and second hydration shells was analysed as a function of the distance to the interface; the first hydration shell remains intact whereas the second hydration shell suffers a severe water loss. Water finger formation was also found, with behaviour similar to that already described for other ions in different interfaces. As far as we know, a direct comparison between the calculated number of water molecules dragged with an ion into the organic phase and the experimental results is presented for the first time and a very good agreement was found.

Understanding the properties of the interface between two immiscible liquids is very important both from an experimental and from a theoretical point of view.[1] Ion transfer across this type of interfaces is also a very important phenomenon in various fields, ranging from chemistry to biology and pharmacology. It plays a crucial role in electrochemistry, phase transfer catalysis, drug delivery and liquid chromatography.[2–4]

Since the interface between two immiscible liquids is a narrow region with very different properties from the liquid bulk behaviour, most of the common experimental techniques cannot be used. However, the gap between the amount of information gathered by computer simulation and laboratory experiments at the molecular level has narrowed in the last few years due to the use of new surface-specific experimental techniques, like surface infrared sum frequency generation, second harmonic generation[5] or X-ray reflectivity techniques.[6] With this recent experimental information, the wealth of results that can be obtained by computer simulation can now be validated.

The transfer process across immiscible liquid/liquid interfaces has been studied by computer simulation for charged particles,[7–12] for uncharged particles[13] and for assisted ion transfer.[14] The use of molecular dynamics and Monte Carlo techniques has contributed enormously to the understanding of the surface properties and dynamics.

The study of ion transfer across immiscible interfaces is a relatively new area of electrochemistry,[15] and despite the recent advances a full understanding of the ion transfer process is still lacking.[16, 17] The construction of a unified theory of ion transfer is a challenge not yet accomplished. Due to the lack of detailed experimental results, very few direct comparisons could be done with previous computer simulations of ion transfers across liquid/liquid interfaces. Until recently, only the free energy for the ion transfer was usually compared with electrochemical experimental data.

In this paper we investigate the structural and energetic features of the transfer of a calcium ion across the water/nitrobenzene interface using constrained molecular dynamics. As one of the most studied interfaces by the electrochemical community, detailed experimental results[18, 19] make it a beautiful candidate for a theoretical study. The potential of mean force, radial distribution functions and coordination numbers are calculated and the results discussed. The calculation of the potential of mean force is very important, since it is inaccessible by classical laboratory experiments and the Gibbs free energy governs the ion transfer.

Simulation Details

For the water potential we used the simple point charge (SPC) model.[20] For the intramolecular nitrobenzene potential we used the CHARMM22[21] force field and for the intermolecular potential we used the parameters of Michael and Benjamin.[22]

The water angle and all bond lengths were constrained using the SHAKE[23] algorithm. For the calcium potential we used the parameters of Åqvist.[24]

To obtain the Lennard-Jones parameters between sites of unlike atoms for the nitrobenzene molecules the Lorentz–Berthelot[22] mixing rule was used. For the Lennard-Jones interaction between all other unlike atoms, the geometric[24] rule was applied.

[a] Dr. D. J. V. A. dos Santos, Prof. J. A. N. F. Gomes
    CEQUP
    Departamento de Química da Faculdade de Ciências
    Universidade do Porto
    R. Campo Alegre 687, 4069-007 Porto (Portugal)
    E-mail: dasantos@fc.up.pt

All simulations were performed with a modified version of the DL POLY[25] molecular dynamics package in the *NpT* ensemble ($p = 1$ bar and $T = 300$ K) using a Nosé–Hoover[26, 27] thermostat and barostat in the Melchionna et al.[28] implementation. An isotropic average pressure was used for the coupling with the desired external pressure as it is common in other studies of systems with interfaces.[29, 30]

Periodic boundary conditions were applied in all three directions and the velocity Verlet algorithm was used for the integration of the equations of motion with a time step of 1 fs. Ewald summations[31–34] were applied to calculate the long range electrostatic forces. A 10 Å cutoff was used for the short-range interactions and a 13.5 Å for the long-range interactions. A multiple time step was also used for interactions greater than 11.2 Å with an update frequency of 8 time steps. A system check in the microcanonical ensemble was performed to verify the validity of the parameters and a good energy conservation was found.

The system was prepared by first equilibrating the two liquids in two independent boxes of similar cross section, one containing 762 water molecules and the other containing 216 nitrobenzene molecules, for 150 ps in the *NpT* ensemble. After this equilibration, the box with a smaller cross section was scaled to match the other and a new box was constructed joining the two boxes along the *z*-axis with a gap between the liquids of 4 Å. Another equilibration of 100 ps was performed. The calcium ion was inserted at a fixed position, 10 Å from the interface, and the particles' positions were manipulated to construct a simulation box with the nitrobenzene molecules in the middle. A new equilibration of 300 ps in the *NpT* ensemble followed.

The final simulation box has a cross section of 27.4×27.4 Å², where the long axis of the box is the *z*-axis with a length of 80.5 Å. The separation between the interfaces was 30.5 Å along the water phase and 50 Å along the organic phase. In agreement with previous simulations in other interfaces, this large separation seems to be enough to assure that no interfacial correlation exists between the interfaces.

The potential of mean force (pmf) calculation started with the ion at 10 Å from the interface in the water side and the reaction coordinate (distance to the interface) was divided in slabs of thickness 0.05 Å. For each slab, the calcium ion position was fixed and the *z*-force component acting on the ion was collected for 3 ps. After this time, the ion was moved 0.05 Å in the reaction coordinate and another 3 ps of simulation was performed. When the ion reached the organic phase, 6 ps were used to collect the forces, due to the slower dynamics of the nitrobenzene molecules. For equilibration purposes, one third of each slab run was not used on the calculations of the energetic and structural properties.

When the ion reached the organic bulk phase, about 12.5 Å from the interface, a reverse ion transfer was performed in a similar way, beginning with the last configuration of the direct transfer. A total simulation time of 4.2 ns was performed.

The free energy of transfer is obtained by integrating over the *z*-component of the force acting on the fixed ion,[35] Equation (1).

$$\Delta G = G_{z_f} - G_{z_i} = -\int_{z_i}^{z_f} \langle ||\vec{F}_z|| \rangle_z \, dz \tag{1}$$

The term z_i is the reference state and corresponds to the ion in bulk water. The ensemble average of the force is performed with the ion fixed at a *z*-position. The *z*-position of the ion is fixed by the use of constraints that correspond to the application of a force of the same magnitude but opposite direction to the one felt by the ion on an unconstrained system.

The free energy of transfer is the average between the forward and backward ion transfer process. The error associated with the pmf was obtained by a block analysis. The pmf data was divided into ten blocks and the error corresponds to the rms deviations of the results of the blocks.[31] All Figures presented involving the ion transfer are averages, unless explicitly stated otherwise, over the forward (from water to nitrobenzene) and backward (from nitrobenzene to water) transfer process.

Results

The system simulated is represented in Figure 1 by a density profile. The starting and ending positions of the calcium ion transfer process are also represented by two crosses. Both liquid bulk densities were found to compare well with experimental values (water 0.997 and nitrobenzene 1.204 g cm⁻³).[36]
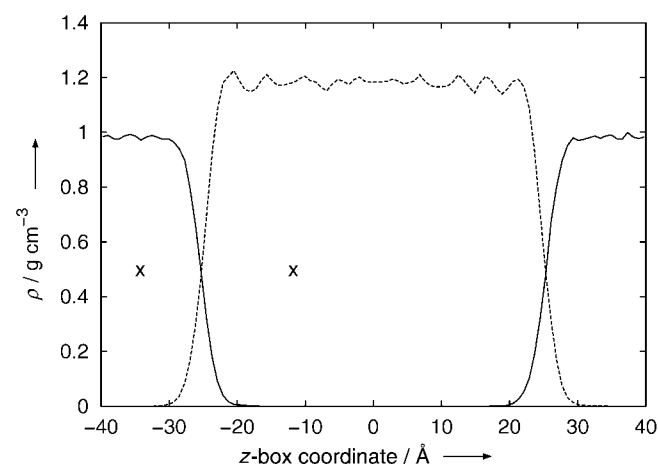

Figure 1. *Average density profile for the water–nitrobenzene system. The crosses represents the starting and ending position of the calcium ion transfer process. Solid line: water; dashed line: nitrobenzene.*

In Figure 2 the forward, backward and average pmf profiles for the transfer of the calcium ion are displayed. The ion transfer occurs in the region from −35 to −12.5 Å in Figure 1. The pmf is a monotonic increasing function of the distance to the interface—hence no energy barriers were found. The transfer process is nonactivated, as found for the transfer of other ions in other interfaces.[9, 11] Most of the increase in the free energy occurs while the ion is in the organic phase moving away from the interface. We obtained a good agreement between the calculated free energy and the experimental value (calcd: 64 ± 5; expt: 67 kJ mol⁻¹[19]). This is the average value for the transfer in both directions, with an hysteresis value of 10 kJ mol⁻¹.

Figures 3a–3d represents four snapshots of the calcium ion transfer process. In Figure 3a we can see the ion near the
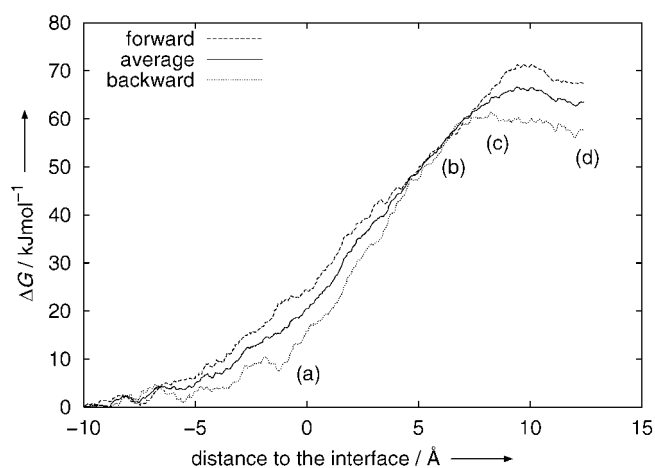
Figure 2. Potential of mean force for the forward and backward calcium ion transfer across the water/nitrobenzene interface. Negative values of the reaction path correspond to the water phase. The labels mark, for the forward process, the position of the ion when the snapshots of Figure 3 were taken.

interface, in Figure 3 b we see a well-formed water cone, and in Figure 3 c its destruction. Finally, in Figure 3 d an hydrated ion is in the bulk nitrobenzene phase. We can associate these successive steps with the evolution of the free energy of transfer by referring to Figure 2. It is solely after the water cone breaks and the nitrobenzene reorganises around the ion that the free energy of transfer stops rising and reaches a plateau. A few Ångströms further in the transfer process the ion can be considered in the bulk organic phase and the free energy does not change any further.

The coextraction of water molecules into an oil phase with alkali and other metal salts is well-known experimentally.[37] In the present study, we observe 13 water molecules being coextracted by the calcium ion, this being in good agreement with available experimental results: Iwashido et al.[38] have found 13 extracted water molecules if the extraction was made in the presence of 2,2',4,4',6,6'-hexanitrodiphenylamine or 1,3,7,9-tetranitrophenothiazine and 13.8 if the extraction was in the presence of N-(2,4,6-trinitrophenyl)-2,4-dinitro-1-naphthylamine. More recently Osakai et al.[19] have found 15 water molecules if the calcium ion was extracted in the presence of sodium tetraphenylborate and 12 if the extraction was made in the presence of sodium dipicrylaminate.

Radial distribution functions (rdfs) for the calcium ion were constructed by dividing the reaction coordinate in 20 slabs of equal size, parallel to the interface. The three-dimensional plots were obtained by constructing a mesh grid by a triangular linear interpolation technique.

Figure 4 a show the rdfs for the calcium ion and water oxygen atom, and Figure 4 b shows the rdfs for the calcium ion and the nitrobenzene oxygen atoms. The position and height of the first peak does not change in Figure 4 a but there is a decrease in the position and height of the second. The opposite occurs in Figure 4 b for the first nitrobenzene solvation shell. As the ion moves to the oil phase a nitrobenzene shell is built around the ion. In contrast with the second hydration shell, this nitro-
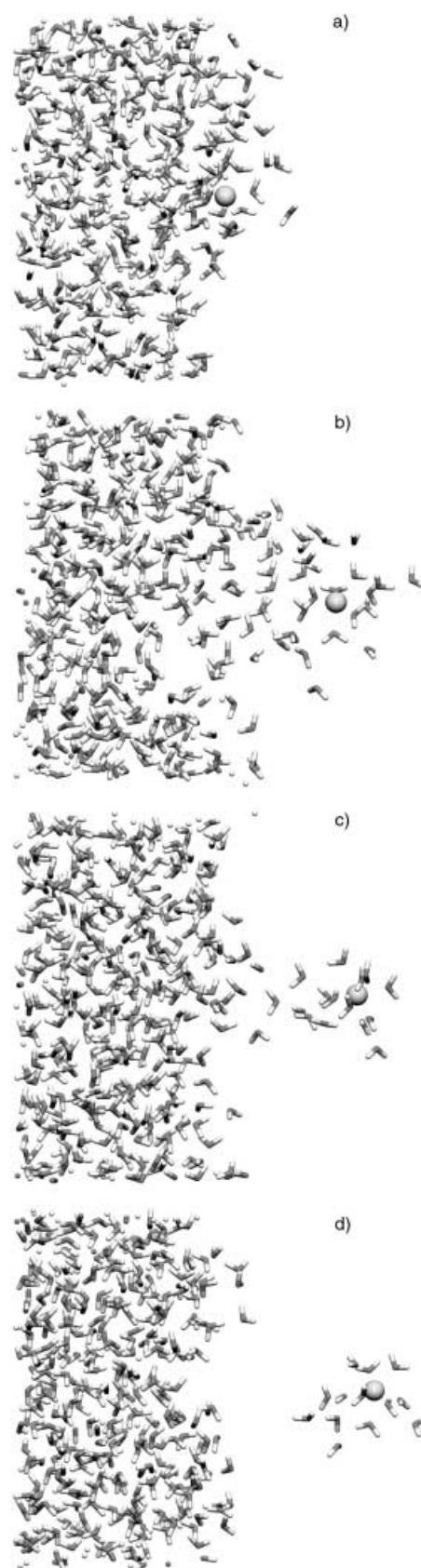

Figure 3. Four snapshots of the calcium ion transfer process, at times matching the labels in Figure 2. For clarity the nitrobenzene molecules, on the right, are removed. a) Calcium ion at the interface. b) Calcium ion with a water cone. c) Calcium ion with a breaking water cone. d) Calcium ion in bulk nitrobenzene.
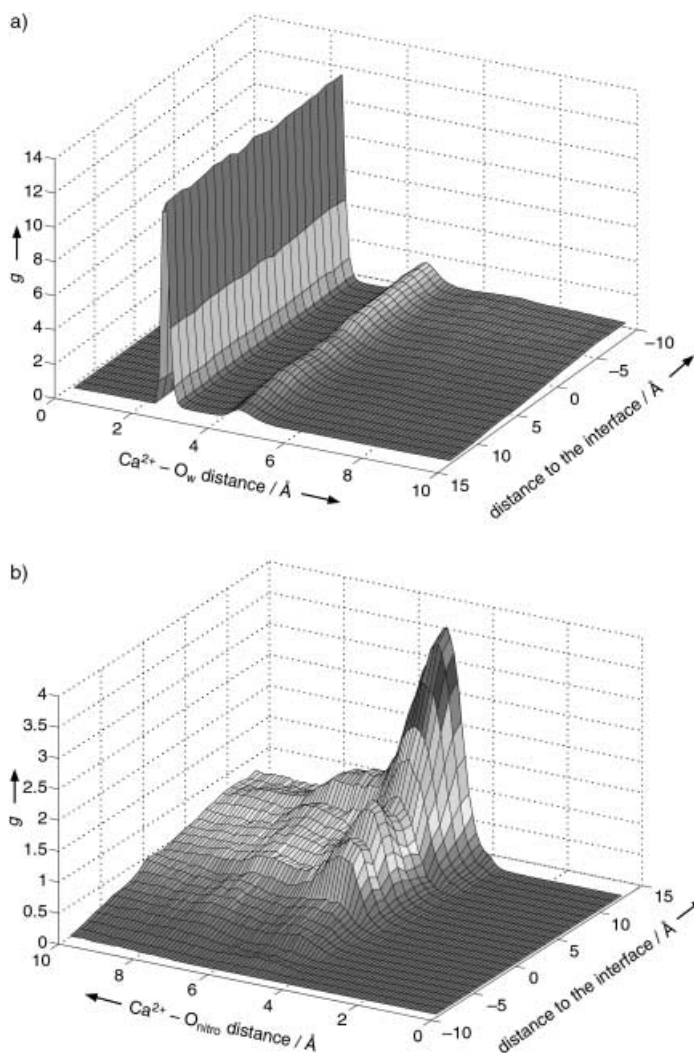
a)

b)

Figure 4. *a) Radial distribution functions for the water oxygen atom around the calcium ion as a function of the distance to the interface. b) Radial distribution functions for the nitrobenzene oxygen atoms around the calcium ion as a function of the distance to the interface. In both, negative values of the reaction path correspond to the water phase.*

Figure 5. *Radial distribution functions for the water oxygen and nitrobenzene oxygen atoms around the calcium ion in bulk nitrobenzene. Solid line: water; dashed line: nitrobenzene.*

Figure 6. *Evolution of the water coordination numbers* N_{H_2O} *for the first hydration shell, second hydration shell and the nitrobenzene solvation shell as a function of the distance to the interface. Dashed line: first hydration shell; solid line: second hydration shell; dotted line: nitrobenzene solvation shell.*

benzene shell only exists when the ion moves from the interface into the oil phase and doesn't exist in the water phase.

In Figure 5 we can see the rdfs for the calcium ion at the end of the transfer. It is interesting to note that the nitrobenzene solvation shell and the second hydration shell overlap. This is a clear indication that although the first solvation shell remains intact, the second solvation shell is being replaced by another shell of nitrobenzene molecules. A clear picture can be observed if we calculate the number of coordinated molecules by integration of the rdfs up to the first minimum or between the two minima for the second solvation shell (see Figure 6).

In order to clarify the origin of the free energy change, the study of the chemical environment around the calcium ion is very important. In Figure 6, we show the evolution of the first and second water hydration shells and the nitrobenzene solvation shell around the calcium ion. The first hydration shell does not change, whereas a completely different picture appears
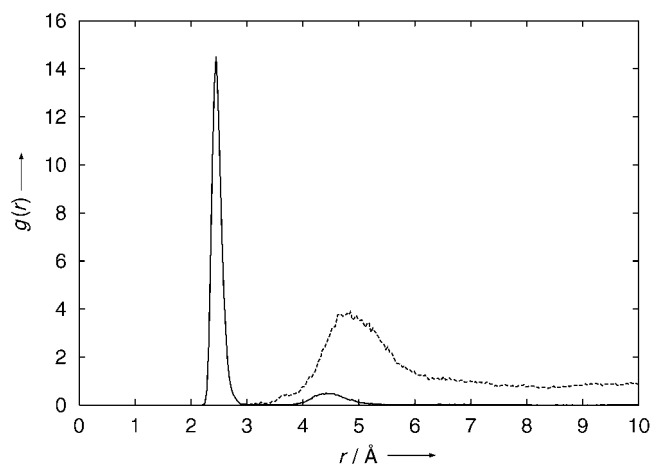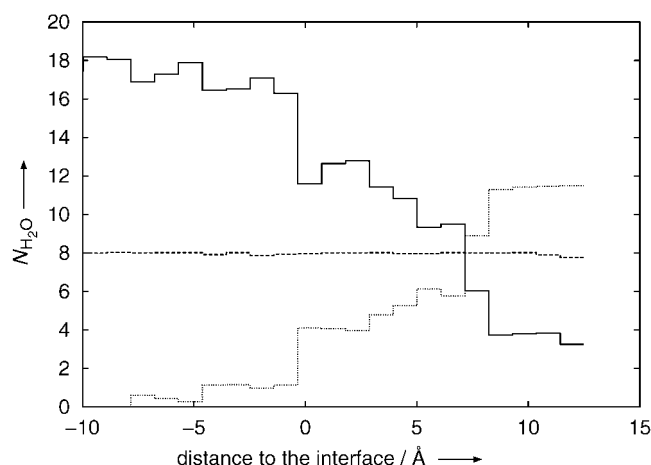
for the second shell. By referring to this Figure we can divide the evolution of the second hydration shell in three different zones:

1) The water side corresponds to a weak water loss—As the ion moves from bulk water to the interface, there are less water molecules available for solvation and two water molecules are lost.

2) When the ion moves into the oil phase there is a rapid loss of water molecules—As the ion penetrates the oil phase, about three water molecules of the second hydration shell remain in the water side. In this second zone, a water cone is formed and as the ion moves further into the oil phase and the water cone stretches, four water molecules leave the second hydration shell but remain in the cone. When the water cone starts to break, five water molecules are lost in a two-step process.

3) After the break-up of the water cone, the composition of the second hydration shell does not change any further and the ion can be considered in the bulk oil phase.

In Figure 6 we can also observe a symmetry between the evolution of the second hydration and the nitrobenzene shells. This is a clear indication that the depletion of water molecules in the second hydration shell and the build-up of the nitrobenzene shell are concerted. The loss of water molecules at the end of the first zone leads to a gain of three nitrobenzene molecules. In the second zone the nitrobenzene shell increases by two molecules and at the end of this zone a gain of another five nitrobenzene molecules is observed.

It is important to note that the sum of the first and second hydration shells for the calcium ion in the bulk nitrobenzene contains 11 water molecules (see Figure 6), and we said that the ion coextracted 13 water molecules. This means that two water molecules remain outside the second hydration shell for the duration of our simulation. This interesting feature can only happen with an ion that has a large charge and can give us an idea of the error involved in the number of transfered water molecules: 13 ± 2.

If we compare our result with the results of Fernandes and co-workers[11] for the transfer of trimethylammonium and some ions of the first and second group of the periodic table across the water/heptan-2-one interface, we can see that the most similar behavior is observed for the strontium ion. This is expected due to the $+2$ charge of both ions. Nevertheless, the transfer of the strontium ion across the water/heptan-2-one interface is done with the loss of one water molecule of the first solvation shell. If the strontium ion transfer was to occur in the water/nitrobenzene interface the water loss would be bigger due to the more hydrophilic character of the heptan-2-one in relation to the nitrobenzene. Recently, Schweighofer and Benjamin[39] have studied the transfer of tetramethylammonium ion across this same interface. They found that the tetramethylammonium ion does not coextract any water molecule. This result emphasises the markedly different nature of the ions. While the calcium ion has a clear hydrophilic character, the tetramethylammonium ion has a character that although hydrophilic is more dependent on the hydrophilicity of the oil phase: In the transfer process across a water/heptan-2-one[11] interface, four water molecules were coextracted.

In the model of Osakai[19] and co-workers for the transfer of hydrophilic ions, the ion transfer process is regarded as the transfer of the hydrated ion. The results obtained in this work also support this idea with a slight difference: In their model the solvation shells do not mix and we found that a degree of mixing does exist for the second hydration shell (for other ions with a smaller charge density this could occur in the inner shell). Their estimation of the radii of the hydrated ions is based on the crystal ionic radii, the number of coextracted water molecules and the density of the bulk water. Their estimation for the calcium ion is 4.67 Å. We have observed that this value is correct for the ion in bulk water, but it decreases to 4.5 Å when the ion is in bulk nitrobenzene.

Sánchez et al.[40] have proposed a new, simple model based on thermodynamic considerations for the transfer of ions between two immiscible liquids. This model is an extension of an earlier formulation by Abraham and Liszi[41] and allows the calculation of the free energy of transfer of an ion and the respective hydration shell between two immiscible liquids. In this model, for a doubly charged ion to transfer between water and nitrobenzene and for this to occur with a water layer, the radius of the ion and the water layer must be greater than 4.17 Å. For this minimum radius and a doubly charged ion, the free energy of transfer between water and nitrobenzene is 57.78 kJ mol^{-1}. Sánchez[42] also calculated the hydration number of the calcium ion in nitrobenzene and obtained 9.24 water molecules. These values are better than the values that could be obtained by the use of the Born model. Nevertheless, the error in this model when applied to the calcium ion transfer between the water/nitrobenzene interface can be due to the fact that the calcium ion has a high charge and can bind more molecules than the number predicted by the model (the model assumes that only one solvation shell is transfered with the ion).

It can be argued that the computer simulations performed by molecular dynamics until now should include counter ions or other electrolytes, since in real electrochemical systems the presence of counter ions and other electrolytes is a fact with concentrations usually around 10 mM (see for instance Cheng and Schiffrin[43]). For simulated systems with atomic detail, in order to obtain such small concentrations the systems must be very large, so large that a simulation can easily become impractical even with the use of very powerful computers. In this sense, the infinite dilution limit is commonly used and in this limit the presence of the counter ion may be avoided as in this limit the ion and the counter ion are surrounded by a large amount of liquid and they feel only weakly the presence of each other.

If we calculate the concentration of a single electrolyte ion pair in the 762 water molecules that exist in our system, we find that the final concentration is 7.3×10^{-2} M. This concentration is about one order of magnitude greater than the one usually used. On the other hand, if we calculate the average volume available to one ion at the above reference concentration we find 8.3×10^5 Å^3. This volume corresponds to a cube 94 Å in size. At these distances, the ions do not feel the presence of each other and the best approximation is to use no electrolytes in simulations with this number of particles.

Fernandes et al.[44] found that for an unpolarized and uncharged interface the ions remain preferentially in the bulk, since near the interface the amount of water is not enough for a thorough solvation. In the ion transfer, the large increase in free energy occurs after the interface crossing, hence the increase of the free energy due to the presence of the counterion should be small (the errors in the free energy are certainly larger than this contribution).

It should be recalled that, in electrochemistry experiments, the assumption is that no ion pair formation occurs. The formation of ion pairs could lead to the transfer of the uncharged species formed by the two ions with lower free energy of transfer.

Conclusions

In this work, the transfer of the calcium ion across the water/nitrobenzene interface was investigated by resorting to con-

strained molecular dynamics. This interface is one of the most studied and a vast number of experimental results exist which, unlike other interfaces, allows for a detailed comparison with simulations. The results obtained confirm that molecular dynamics simulation is a very good theoretical method for the study of the ion transfer across liquid/liquid interfaces. The predictions for the solvent coextraction appear to be very good.

The free energy for the transfer process was found to be in good agreement with experimental data; it increases monotonically with the distance to the interface and the transfer is nonactivated. The calcium ion transfer process occurs with the formation of a water cone that perturbs the interface, and the number of water molecules dragged into the nitrobenzene phase was also in good agreement with the experimental data.

As the ion crosses the interface, the first hydration shell remains intact and part of the second hydration shell is lost and a substitution of water by nitrobenzene molecules occurs. This three-stage substitution process begin as the ion approaches the interface, increases as the ion crosses the interface with the water cone formation and stops with the water cone breaking. We also found that the withdrawal of water molecules occurs with a replacement with nitrobenzene molecules and that the substitution process was concerted.

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