Molecular Simulations of Osmosis and Reverse Osmosis in Aqueous Electrolyte Solutions

F. Paritosh and S. Murad
Chemical Engineering Dept., University of Illinois at Chicago, Chicago, IL 60607

Osmosis and reverse osmosis are phenomena of considerable importance in both life and physical sciences. Reverse osmosis is an energy-efficient technology useful for separating a wide range of solutions, including those encountered in water purification (desalination), waste treatment, and food processing (Eisenberg and Middlebrooks, 1985; Lacey, 1972; Sourirajan, 1970). In this note we report molecular computer simulation studies, using a method developed by us recently (Murad et al., 1996, 1993) to study osmosis and reverse osmosis in aqueous electrolyte solution using a semi-permeable membrane.

It has been previously thought that the reason why water permeates the semipermeable membrane, while ions do not (resulting in osmosis or reverse osmosis), is either because (i) strong hydrogen bonding interactions between water and the membrane essentially close the thin dense membrane layer to the salt ions, while water can still diffuse through, or (ii) physicochemical interactions between the ions and the membrane repel the ions away from the membrane surface, thus allowing only water to permeate. Our simulations have shown that osmosis and reverse osmosis in aqueous electrolyte solutions can take place, even in the absence of forces of types mentioned in (i) and (ii) above. Although all the ions studied by us (Li^+, Na^+, Cl^-) have smaller molecular diameters than water (see Table 1), we find that the separation is still primarily due to molecular size differences. Our results show that water molecules strongly cluster around the ions, thus effectively increasing their molecular size considerably, and preventing them from permeating the membranes, while water molecules can still permeate the membrane.

Theory and Method

In our simulation of osmosis/reverse osmosis of aqueous electrolyte solutions, we have used a method recently developed by us (Murad et al., 1993) (based on the molecular dynamics technique) to study such phenomena. The simulation cube (of size L) consists of 256 particles, initially with all the particles in a face centered cube (FCC) configuration. All molecules on the plane $x = L/4$, and $3L/4$ are tethered to their initial FCC position by a simple harmonic potential $\phi_T = 0.5K\delta^2$ where δ is the scalar distance between the tethered molecules and the tethered sites, while K is a spring constant in tethering potential. This setup is shown in Figure 1, and leads to 64 molecules constituting the two semi-permeable walls. The resulting pores in the membrane have a diameter of about 4.0–4.5 Å. This compares well with the pores of 3 to 5 Å (Goldsmith et al., 1972) in actual membranes used for reverse osmosis of aqueous solutions. The solution compartment initially contains $[96\text{-}N_B]$ (N_B refers to number of ions) solvent particles, while the solvent compartment initially contains N_S solvent molecules, which vary be-

Table 1. Parameters for Potential Models Used in Simulations

Type	$10^7\ \epsilon$(J)	σ (Å)	B/k_B (K)	C/k_B (Å^6·K)	ρ_{ij} (Å)
Na^+-O^-	252.116	2.44	—	—	—
Li^+-O^-	496.50	1.9933	—	—	—
Cl^--O^-	68.158	3.73234	—	—	—
O^--O^-	77.9774	3.1535779	—	—	—
Na^+-Cl^-	—	—	1.46×10^7	8.11×10^4	0.317
Li^+-Cl^-	—	—	3.76×10^6	1.416×10^4	0.342
Cl^--Cl^-	—	—	4.04×10^7	8.47×10^5	0.317
Li^+-Li^+	—	—	5.78×10^5	467.47	0.342
Na^+-Na^+	—	—	4.92×10^6	1.22×10^4	0.317
Wall-wall	295	2.4597	—	—	—
Wall-Na^+	132.83	2.59	—	—	—
Wall-Li^+	85.63	2.41	—	—	—
Wall-Cl^-	90.95	3.66	—	—	—

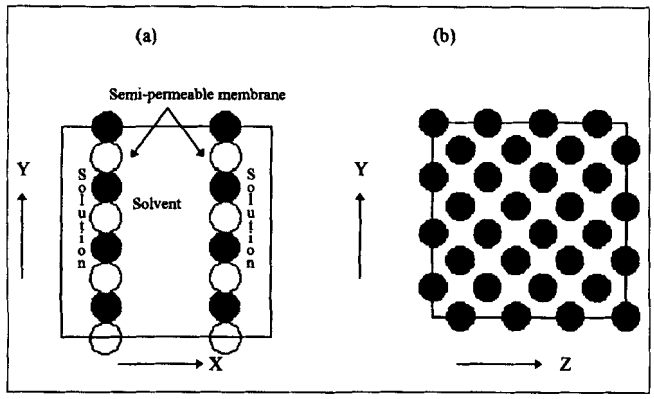

Figure 1. XY and ZY projections of simulation system.

The semipermeable walls are in the zy plane. Periodic boundary conditions automatically generate a pair of walls infinite in the zy (transverse) directions with alternating solution and solvent cells.

tween 0 and 96. By varying N_S, the pressure difference between the solution and the solvent compartment can be varied. Depending upon the osmotic pressure of the solution, and the value of N_S, either osmosis and reverse osmosis will take place in the system. The simulation consisted of 300,000 to 600,000 time steps of size 0.415 fs. The small time step was needed because of the small moment of inertia of water molecule and the vibrating membrane molecules.

In our simulation the TIP4P potential for water was used. This potential model (Chandrashekhar et al., 1984) has been found to reproduce both the structural and thermodynamic properties of water. In this model, water is represented by 4 sites, 3 of which are on the nuclei of the H and O atoms, and the fourth is on the bisector of the HOH angle 0.15 Å away from the oxygen atom towards the hydrogen atoms. The oxygen site is the only active L-J site on the water molecule; the charges (q_i) on each H atom are 0.52e and on the fourth site -1.04e. This leads to the following interaction models for water-water and water-ion interactions (r is the scalar distance between the active sites), with the parameters (B_{ij}, C_{ij}, ρ_{ij}, ϵ_{ij}, σ_{ij}) shown in Table 1.

$$U = 4\epsilon_{oo}\sigma_{oo}^{12}/r^{12} - 4\epsilon_{oo}\sigma_{oo}^{6}/r^{6} + \sum_i \sum_j q_i q_j/r \qquad (1)$$

$$U = 4\epsilon_{io}\sigma_{io}^{12}/r^{12} - 4\epsilon_{io}\sigma_{io}^{6}/r^{6} + \sum_i \sum_j q_i q_j/r \qquad (2)$$

The ion-ion interactions were modeled (Pettitt and Rossky, 1986) using

$$U = B_{ij}e^{-r/\rho_{ij}} - C_{ij}/r^{6} + q_j q_j/r \qquad (3)$$

Interactions between the atoms that constitute the membrane wall were modeled using the L-J potential with parameters given in Table 1. The tethering constant was fixed at 200 (in reduced units based on O-O parameters). Finally, the membrane-water/ion interactions were also modeled using the L-J potential, with the cross parameters obtained using the Lorentz-Berthelot mixing rules.

Results and Discussion

We have carried out simulations at 298 K, in which the solution compartment consists of aqueous NaCl or LiCl, and the solvent compartment pure H_2O (see Figure 1). In all our simulations, we started with an initial density in the solvent compartment (pure H_2O) of 1,000 kg/m^3. The solution compartment in the case of LiCl had an initial molar density of 61.98 kmol/m^3, while the concentration of LiCl varied from 1.21 molal to 6.41 molal. In the case of NaCl, the initial molar density in the solution compartment was 70.65 kmol/m^3, while the concentration varied between 1.21 molal and 6.41 molal. In all the cases studied, the pressure in the solution compartment was thus significantly higher than that in the solvent compartment (between 20–40 MPa). In our simulations, we measured a wide range of properties. In this note, however, we will report results for only the (net) number of water molecules and ions that cross the semi-permeable membrane, and the density profiles in the solution and solvent compartments. Results obtained for the (net) number of H_2O molecules that cross the semi-permeable membrane in 300,000 steps are shown in Figure 2. In our sign, convention positive values correspond to osmosis and negative values correspond to reverse osmosis. Our results show that at low concentrations reverse osmosis is observed. This is because the initial (hydrostatic) pressure difference between the solution and solvent compartment is considerably larger than the solution osmotic pressure. At higher solution concentrations, the osmotic pressure becomes quite large, and thus comparable to the initial (hydrostatic) pressure difference between the solution and solvent compartments. In the case of LiCl, we thus observe weak osmosis, while in case of NaCl, weak reverse osmosis.

The most interesting observation, which also challenges previous understanding of osmosis and reverse osmosis (as discussed earlier) is that in all our simulations the ions do not

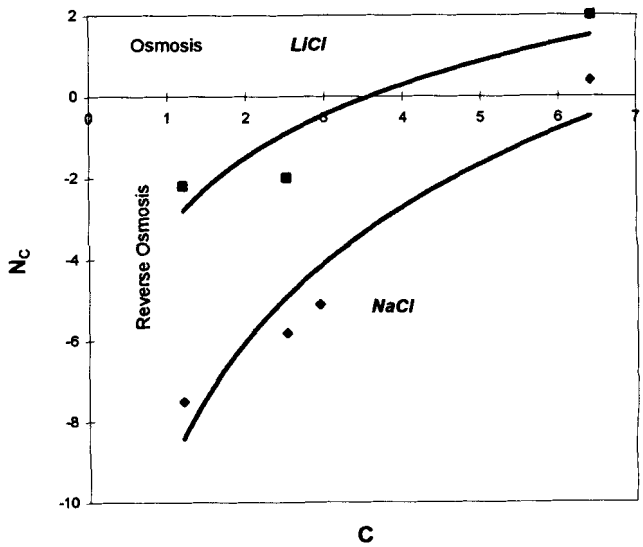

Figure 2. Effect of concentration (C) on the extent of osmosis and reverse osmosis (N_C) in LiCl and NaCl solutions.

The points represent simulation results, while the lines are least-square fits of the simulation results to show the general trends.

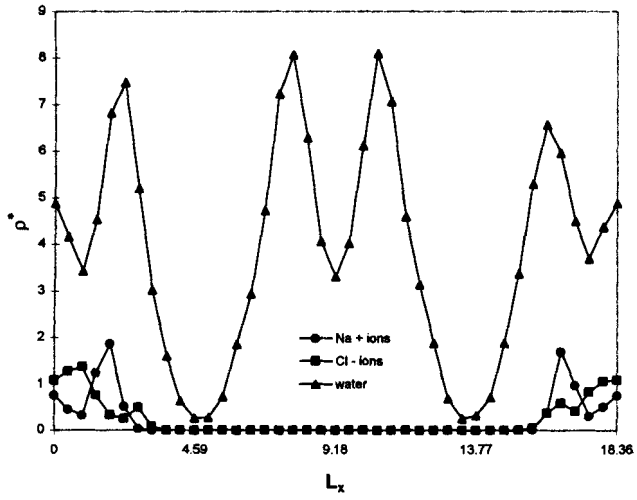

Figure 3. Density profiles of water and ions perpendicular to the membrane wall for an initial NaCl solution concentration of 6.41 molal.

The points represent simulation results, while the lines are shown to guide the eye.

permeate the membrane, even though the molecular diameter of all the ions studied is smaller than water (see Table 1). In addition, as mentioned earlier, the interaction between the membrane and water or ions is modeled as a L-J interaction. There are thus no coulombic or multipole interactions which would cause any preferential attraction or repulsion between the ions and the membrane. The primary reason why the smaller ions do not permeate the membrane is because of the formation of large, strongly bound ion-water clusters. These clusters have a large energy of desolvation, and thus desolvation rarely occurs. Consequently, the ions are prevented from crossing the membrane. This is further confirmed by Figure 3, which shows the density profiles of water and ions in the solution and solvent compartments for an initial solution molality of 6.41. Here too one observes a region near the membrane, where only water is present. This is due to H_2O molecules surrounding the ions, and thus ions are only observed after this region. After 273.9 ps, the density distribution of water is symmetrical, whereas the ionic distribution still appears to lack symmetry. This is because of the lower ionic mobility caused by the formation of hydration shells around the ions. This leads to longer equilibration times for the ions. Our simulations showed movement towards such symmetry. Our simulations were, however, long enough for the ions to diffuse uniformly throughout the system, if there was no barrier between the solution and solvent compartments. Thus, the lack of ionic permeation in our simulations cannot be attributed to the slower mobility of ions.

In conclusion, we have reported computer simulation studies for osmosis and reverse osmosis in LiCl and NaCl solutions. Our results have clearly shown that both osmosis and reverse osmosis can result in these solutions even though we have no coulombic or surface forces between the membrane and the ions. Hydration of the ions by water molecules, resulting in larger effective ionic sizes (compared to water) which have high energy of desolvation, can also explain these separations.

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Notation

c = solution concentration, molality
r = scalar distance between two sites
L = length of simulation compartment
N_C = average number of molecules permeating the membrane
B_{ij}, C_{ij} = interaction parameters in Eq. 3
ρ^* = reduced density $\rho\sigma^3$ reduced using O-O interaction parameters (Table 1)
ϵ, σ = Lennard-Jones parameters of atomic site

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