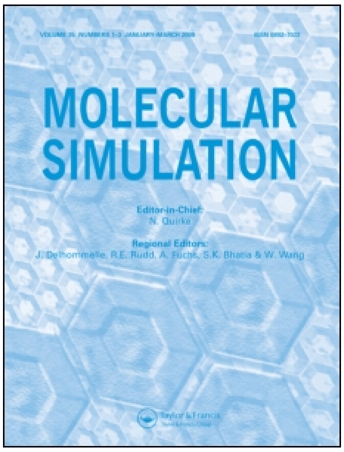

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Molecular Simulations of Membrane Based Separations of Supercritical Electrolyte Solutions

K. Oder[a]; S. Murad[a]
[a] Chemical Engineering Department, University of Illinois at Chicago, Chicago, IL, USA

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MOLECULAR SIMULATIONS OF MEMBRANE BASED SEPARATIONS OF SUPERCRITICAL ELECTROLYTE SOLUTIONS

K. ODER and S. MURAD*

Chemical Engineering Department, University of Illinois at Chicago,
Chicago IL 60607, USA

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Computer simulations of solutions of electrolytes (NaCl and KCl) in supercritical water undergoing membrane based separations have been carried out. These studies used a technique developed recently, in which the system is maintained at steady state by periodically recycling the solvent molecules that permeated the membrane. Our results showed that ionic clusters, formed as a result of water molecules surrounding the ions, play a significant role in these separations. The effect of the main osmotic driving forces, such as pressure, temperature, concentration, and electric fields on the rate of permeation across the membrane was studied. In addition, we also looked at the effect of changes in the pore size and the attractive force between the membrane and solvent/solute. Finally, we examined the stability of the ionic clusters in these simulations.

Keywords: Reverse-osmosis; molecular simulations; electrolytes; supercritical solutions

INTRODUCTION

The use of membranes in the chemical industry for separation processes is growing as a result of improvements in their selectivity and robustness. The main objective of this study is to obtain a better understanding of the molecular forces that significantly affect such separations. This information can be helpful in designing more efficient membranes. The studies reported in this paper use a method developed by us recently to model semipermeable membranes using an extension of the NVT molecular dynamics

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*Corresponding author. e-mail: murad@uic.edu method [1]. One of the most important features of this method is that by varying the molecular parameters of the membrane, one can easily control its geometry and permeability [2]. In addition, the molecules that constitute the membrane are allowed to vibrate or wobble as has been found to be important for realistic simulations of zeolite membranes, for example [3]. This paper reports an extension of this technique that allows processes involving realistic fluids under steady state conditions to be investigated. The method could previously be only used to follow the time evolution of a system to its final equilibrium condition, from an initial non-equilibrium state [2].

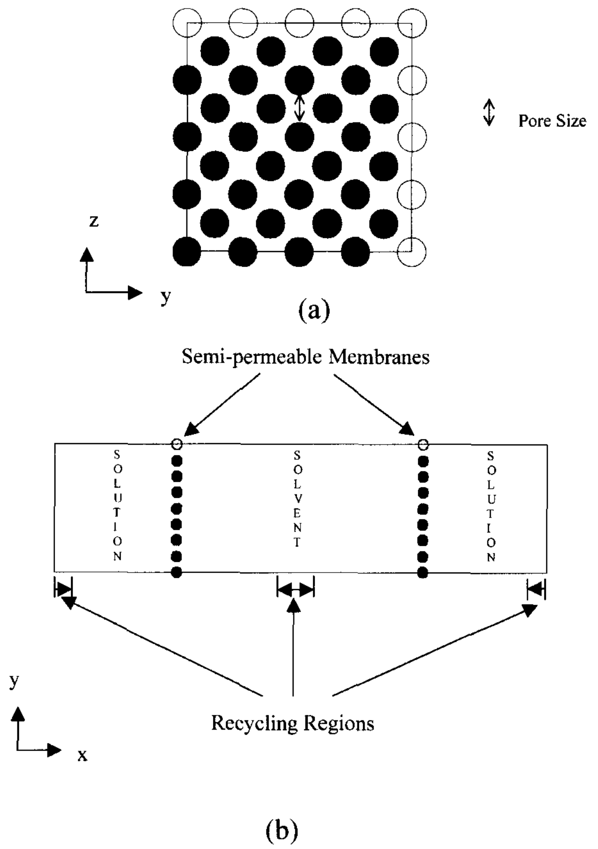
We will demonstrate the usefulness and validity of this new technique, by using it to study the effect of changes in state conditions, and membrane morphology on the mass transfer rate across the membrane. These results, apart from being of intrinsic fundamental interest by themselves, can also be used to test the accuracy of various micro-continuum theories for reverse osmosis as well [4–6].

METHOD

The method for simulating solutions undergoing osmosis/reverse osmosis with semi-permeable membranes has been described in detail in previous papers and will only be briefly explained here [7–9]. The simulations nominally consisted of 1024 particles initially in a faced center cubic (FCC) configuration in a system with $L_x = 4L_y = 4L_z$ (see Fig. 1). All particles with $x = L_x/4$ and $3L_x/4$ in the initial FCC configuration were designated as the membrane molecules (64 molecules). The molecules constituting the membrane were modeled as Lennard-Jones (LJ) particles, and tethered to their FCC positions using a simple harmonic potential,

$$\phi = \frac{1}{2} \cdot \mathrm{k} \cdot \delta^2 \tag{1}$$

In Eq. (1), k is the simple harmonic constant, and δ is the displacement of the particle from its initial FCC position. The diameter of the membrane pore was fixed at 2.75 Å for most of the simulations except for one case where it was changed to study the effect of the pore size on the permeation rate. The solution compartment consisted of 480 particles. The number of particles designated as solute or solvent molecules depends upon the concentration of the solution being studied, while the density of the solution compartment fixes the system size. The number of particles in the solvent



(a)

(b)

FIGURE 1 A schematic diagram of: (a) the membrane; (b) the simulation system. Periodic boundary conditions lead to a system infinite in the y and z directions with alternating solution and solvent compartments in the x direction separated by semi-permeable membranes.

compartment is determined by the desired density of the solvent compartment, and in our studies was generally less than 480.

The translational equations of motion were solved using a fifth order Gear predictor–corrector algorithm and while a fourth order method was used for the rotational motion. The quaternion method was used for the rotational motion. Temperature was kept constant using the Gaussian constraint method [1]. Supercritical steam was modeled using the SPC model for water [10] and for the ions we used the primitive model [11] described by,

$$u_{ij} = 4\varepsilon_{ij}\left[\left(\frac{r}{\sigma}\right)^{-12} - \left(\frac{r}{\sigma}\right)^{-6}\right] + \frac{q_i q_j}{r}. \qquad (2)$$

where r is the distance between the center of mass of ions, and ε and σ are the Lennard-Jones (LJ) interaction parameters, and q the ionic charge. The parameters for the intermolecular models used are given in Table I. Long range interactions were accounted for by the reaction field method [12, 13]. Periodic boundary conditions were employed resulting in the simulation system being infinite in the y and z directions, and consisting of alternating solution and solvent compartments of equal size (see Fig. 1) in the x-direction. All results reported (unless stated otherwise) are reduced using chloride LJ parameters.

The method was adapted to study steady state processes based on a technique suggested recently [16], and similar in spirit to two recent methods developed for steady state simulations [17, 18], and involves recycling solvent molecules (that permeate the membrane) periodically. If done often enough this would result in a system approaching steady state. The molecules to be recycled were chosen randomly, one molecule at a time from a designated section of the solvent or solution compartment (as dictated by the direction in which solvent molecules permeate the membrane). This section was initially 2 units thick, and in the middle of the compartment (as far away from the membranes as possible as shown in Fig. 1b). They were then replaced (again one molecule at a time) at a random location in a similar section of the other compartment (solution or solvent as required), but only if it passed the usual Metropolis particle displacement requirement [19, 20] widely used in Monte-Carlo. This ensured that the recycling process, even though it was being carried out rather far away from the membrane (usually 10–20 solvent molecule layers away) did not produce any unusual disturbance in the system to affect the solvent permeation rate across the membrane. In some cases the width of these sections had to be increased to enable the particle recycling to be carried out successfully within a reasonable number of trials, but it was never in a region where it could

TABLE I Molecular interaction parameters for Eq. (2) [10, 14, 15]

	Interacting sites	σ ($10^{-10}m$)	ε (*kJ/mole*)	$q(e)$
Water				
	O	3.17	0.65	−0.82
	H	0.0	0.0	0.41
Ions				
	Cl	4.42	0.49	−1.0
	Na	1.9	6.69	1.0
	K	3.36	1.12	1.0
Membrane		12.42	2.01	0.0

affect the permeation of the solvent molecules across the membranes. This procedure is a simplification of the more rigorous schemes suggested in MacElroy, and Heffelfinger and Van Swol [17, 18]. We were able to successfully use such a simplified scheme because we explicitly recycle the correct number of solvent molecules. This is done at a sufficient distance from the membranes, so that the slight inconsistency introduced in our hybrid scheme does not affect the solvent permeation rate being calculated in our studies, while allowing us to use a much simpler algorithm. We carried out tests that showed that this did result in a system in steady state, or very close to it, since normal statistical fluctuations make it impossible to make an exact determination.

Most simulations were consisted of 160,000 time steps and a few consisted of 560,000 time steps. Each time step consisted of 1.8×10^{-16} seconds (the unit of time was 3.76×10^{-12} seconds). The initial density of the solution compartment was 0.099 (reduced by the Chloride parameters). The mole fraction of the electrolyte salt in the solutions studied varied between 0.01 and 0.02. The temperature of the system was varied between 650 K and 750 K. The solution and solvent densities were fixed so that the estimated pressure of the solution compartment was between 16,400 – 22,000 kPa, while the pressure of the solvent compartment was between 4700 and 13,800 kPa.

RESULTS AND DISCUSSION

Molecular simulations are a useful tool for understanding, at a molecular level, membrane based separation processes. Our simulations show the significant role ionic clusters formed in such a system play in preventing the solute particles from permeating the membrane. Since only LJ forces accounted for the interactions between the membrane and the solute and solvent particles, no unusual coulombic forces could be responsible for these separations, and the separations would have to be primarily steric in nature. As stated in the method, the pore size for most of the simulations was 2.75 Å, and this is significantly larger than the LJ diameter of the Na^+ ion (see Tab. I). Despite the large osmotic driving force in our system, no ions were able to permeate the membrane. This was caused by water surrounding these ions and forming stable clusters that increase the effective size of the ions, which were then unable to permeate the membrane. These clusters were found to be less stable than those observed previously in aqueous ionic solutions and appeared to be smaller in size as well [21]. A typical cluster

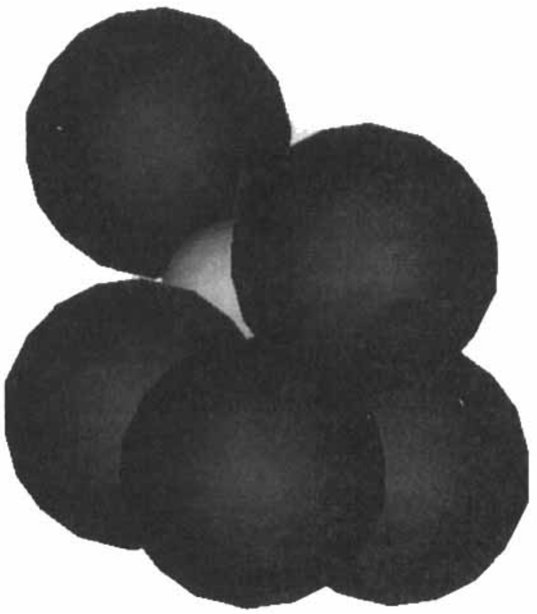


FIGURE 2 An example of the solvent–solute clusters found in our simulations, Na^+ (yellow) and water (blue). (See Color Plate II).

formed is shown in Figure 2, where Na^+ ions are shown surrounded by water molecules. These clusters form as a result of electrostatic interactions between the polar water molecule and the charge on the solute.

Steady state was maintained in these simulations, by recycling the permeated molecules every 8,000 time steps. This resulted in approximately 1 to 2 water molecules being recycled each time. Figure 3 shows that this leads to a steady state in our studies. In the figure $\langle N_c \rangle$ is defined as the average number of molecules that have permeated the membrane from the solvent side to the solution side from the beginning of the simulation. $\langle N_c \rangle$ is designated as negative for flow from the solution compartment to the solvent compartment. The value of $\langle N_c \rangle$, shown in Figure 3 (plotted against reduced time t^*), and subsequent figures is related to the mass flow across the membrane at time, by the equation,

$$J = 2 \cdot \frac{d\langle N_c \rangle}{dt} \tag{3}$$

Figure 3 also shows the effect of reducing the pressure in the solvent compartment. As expected, as the pressure is decreased in the solvent compartment, the larger pressure difference (between the solvent and

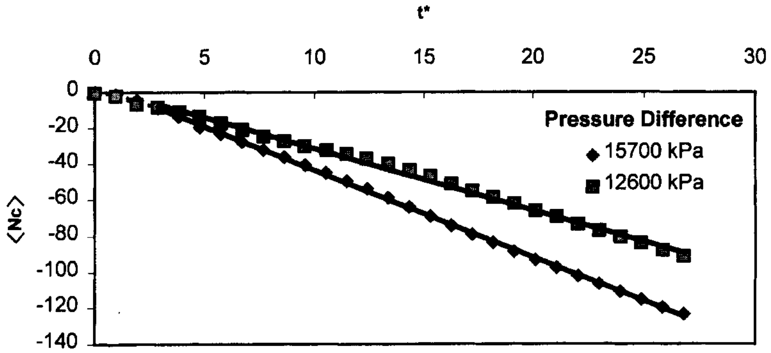


FIGURE 3 The effect of pressure on the solvent permeation rates for a 0.02 mole fraction KCl solution at 723 K. The pressure difference is the difference in the pressures of the solution compartment and the solvent compartment (similar results were observed in NaCl solutions). The initial dotted region here, and in all the subsequent figures, represents the initial equilibration time steps. Unit of time = 3.76 E − 12 seconds.

solution) causes the rate of solvent permeation to become greater, thus further validating our method. In addition, the noise to signal ratio improves for larger pressure differences.

We also investigated the effect of the other driving forces in these separations. An increase in the system temperature was found to increase the rate at which solvent molecules permeated the membrane, as shown in Figure 4. It can be seen from Table II that the permeability of the membrane, however, did not increase when the temperature was increased. For systems of the type we have studied, after a long enough time ($t \gg L^2/2D$), the diffusional motion can be represented by a tensor with two independent components, one perpendicular to the membrane (D_{per}), and the other parallel to the membrane (D_{par}). These diffusion coefficients were obtained in our simulations from the mean-squared displacements of the fluid particles. These were measured after the equilibration step, and for long enough time to satisfy the above requirements. D_{per} and D_{par} are given by [1, 2]:

$$D_{\text{par}} = \frac{\langle y^2\rangle + \langle z^2\rangle}{4t} \tag{4}$$

$$D_{\text{per}} = \frac{\langle x^2\rangle}{2t}. \tag{5}$$

The permeability of the membrane can be related to the diffusion coefficient, and has been defined as the ratio of the diffusion coefficient perpendicular to the membrane (D_{per}) and parallel to the membrane (D_{par}). If this ratio is one, then the membrane is completely permeable (*i.e.*, offers no resistance).

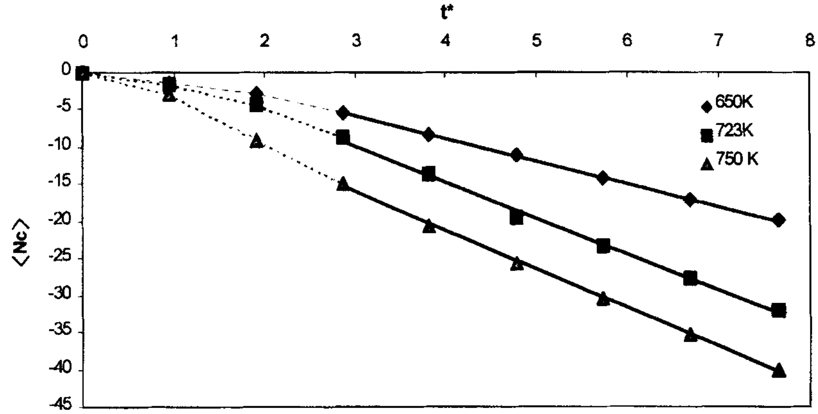


FIGURE 4 The effect of temperature on the solvent permeation rates for a 0.02 mole fraction KCl solution.

TABLE II Diffusion coefficients perpendicular (D_{per}) and parallel (D_{par}) to the membrane and membrane permeability ($D_{\mathrm{per}}/D_{\mathrm{par}}$) for systems reported in Figure 4

Temperature (K)	D_{per} (±0.5)	D_{par} (±0.6)	*Membrane permeability*
650	4.15	5.30	0.80
723	4.50	6.29	0.73
750	5.07	6.16	0.83

It can also be seen from Table II that an increase in temperature causes all the diffusion coefficients of the solvent to increase, which is responsible for the observed increase in the permeation rate.

Simulations were also carried out to determine the effect of increasing the molecular interactions between the membrane and the solvent molecules (this is similar, for example, to increasing the hydrophilic nature of the membrane) and the size of the pore. When the LJ energy parameter of the membrane ($\varepsilon_{\mathrm{wall}}$) was increased by a factor of two, the permeation rate increased about 25 percent (see Fig. 5). This increase in the permeation rate is related to stronger adsorption of the solvent molecules on the membrane. We found that the diffusion coefficient of the solvent molecules (perpendicular to the membrane surface) and the permeability of the membrane remain unchanged within our statistical error (see Tab. III). The increase in the permeation rate is caused by the increase in the number of water molecules present near the membrane, which are then forced to permeate the membrane by the osmotic driving forces.

We also looked at the effect of an increase in pore size on the solvent permeation rate. When the pore size was increased to from 2.7 to 2.75 Å (by

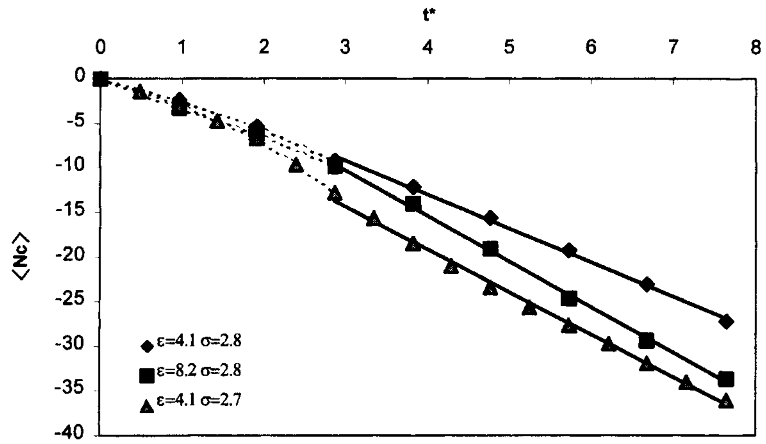


FIGURE 5 Effect of changing the molecular characteristics of the membrane on the solvent permeation rates for a 0.017 mole fraction KCl solution.

TABLE III Solvent diffusion coefficient and membrane permeability ($D_{\mathrm{per}}/D_{\mathrm{par}}$) as a function of changes in molecular characteristics of the membrane

Simulation	(D_{per}) (±0.5)	*Membrane permeability*
$\varepsilon = 4.1$ $\sigma = 2.8$	5.41	0.94
$\varepsilon = 8.2$ $\sigma = 2.8$	5.01	0.92
$\varepsilon = 4.1$ $\sigma = 2.7$	4.98	0.87

decreasing σ_{wall}), the permeation rate increased; however, the diffusion coefficient and the membrane permeability remained about the same. These results are very similar to a recently completed study with LJ fluids [22].

Finally, we were unable to see an increase in the permeation rate when an external electric field was used (electro-osmosis). This is perhaps caused by the density being rather low in our studies, compared to aqueous solutions, where such an increase was observed [21].

CONCLUSIONS

A simulation method for studying reverse osmosis at steady state has been applied to supercritical electrolyte solutions. These simulations demonstrated that relatively stable ionic clusters are present in such solutions, and they prevent the solute from penetrating the membrane. In addition, it was also shown that increasing the temperature of the supercritical water increased its permeation rate through the membrane. The molecular forces between the membrane and the solvents were also studied and we found that the more hydrophilic the membrane, the higher the permeation rate of the solvent.

Acknowledgement

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