The effect of thickness, pore size and structure of a nanomembrane on the flux and selectivity in reverse osmosis separations: a molecular dynamics study

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Received 30 July 2004; in final form 25 August 2004
Available online 11 September 2004

Abstract

Molecular dynamics simulations examine the effect of pore size, structure and membrane thickness on flux and selectivity in reverse osmosis. Membranes are modeled using layers of barrier molecules tethered harmonically to periodic lattice sites. Permeation occurs within a Knudsen like regime where close confinement in nanopores precludes water–water interactions, leaving water–pore interactions to determine hydraulic resistance. Results show the solvent flux to be rather insensitive to an appropriately defined tortuosity. Ion selectivity seems to correlate primarily with overall hydraulic resistance, irrespective of the number of membrane layers.
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1. Introduction

The processing of brine (aqueous NaCl) solutions to potable water is one of the major challenges of science, in view of the projected world wide shortage of water in most regions of the world. Considering the vast reserves of sea water available, any improvement in the efficiency of currently used technologies, can have a tremendous impact on the quality of human life in many regions of the world [1]. The most successful and energy efficient current technology for processing sea water into drinking water is reverse osmosis. Although successful commercial plants are currently in operation in many parts of the world, one problem with the current technology is that it requires high pressures (over 1 MPa) to obtain the required flux and selectivity necessary for commercially viable operations. This makes desalination rather energy intensive, resulting in the current high retail price of water [2]. There is therefore an urgent need to understand, at the molecular level, the various forces responsible for the separation of ions from water, and to use this knowledge to make reverse osmosis membranes more efficient. With the recent developments in nanotechnology, nanomembranes will become an important component of new processes. It is therefore important that such membranes are better understood. Experimental studies with such nanomembranes are currently difficult. Molecular modeling methods such as molecular dynamics, therefore provide a useful tool to carry out preliminary screening studies of these processes [3].

In this Letter, we have conducted a molecular simulation study to examine the role of pore structure, size and membrane thickness on the flux and selectivity of water permeating a nanomembrane. The improved understanding of reverse osmosis obtained from such studies can then possibly be used to develop more efficient membranes for such separations in the future.

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2. Method and models

Osmosis and reverse osmosis were simulated using a technique developed by us, which has been described in detail [4,5]; only a brief summary is therefore given here. All molecules were initially located at positions that correspond to an FCC structure. The molecules at $x = L_x/4$ and $3L_x/4$ constitute the basic membrane layer, and were tethered to their FCC sites using a simple harmonic potential, as explained in detail in [6], and also shown in Fig. 1. Two types of membranes are then built around this basic structure. For example a three molecular layer membrane would be generated as follows: for a 'straight' pore membrane, two identical layers, one on either side would be added to form the final membrane. Here, these were added at a distance of $L_x/32$ from the basic layer, although these could be added at any desired distance. In the 'tortuous' case, the other two layers would be displaced, so as to have a molecule in the adjacent layers centered at the largest pore of the basic membrane layer (similar to adjacent FCC layers). This would require a molecule entering the membrane via the largest pore to move up/down or left/right to continue to permeate the membrane. The system setup and the membrane structures are shown in Fig. 1a–c. The diameter of the molecules that constitute the membrane can be varied to adjust the permeability of the membrane. In our studies, the diameter was adjusted such that the size of the resulting pores were 0.3–0.5 nm. The simulation system was a parallelepiped with $L_x = 4L_y = 4L_z$. L_x

was made larger than L_y and L_z, to increase the distance between the two semi-permeable membranes. This arrangement, along with periodic boundary conditions, makes the retentate and permeate compartments infinite in the y and z directions.

The simulations consisted of upto 1024 molecules. The dimensions of the simulation system were fixed to correspond to the density of the initial retentate solution. The number of molecules in the permeate compartment was then fixed to correspond to the correct solvent density. While the permeate compartment always had an initial pressure of approximately 1 bar, the initial pressure on the retentate side varied between 1000 and 5000 bars.

All the molecular dynamics simulations were carried out using a fifth order Gear's predictor–corrector algorithm for translational motion and a fourth order predictor–corrector algorithm for rotational motion using the quaternion method [7]. Water was modeled using the SPC model [8], while for the ions, we used the so-called primitive model described by Eq. (1) [9]:

$$u_{ij} = 4\varepsilon_{ij}\left[\left(\frac{r}{\sigma}\right)^{-12} - \left(\frac{r}{\sigma}\right)^{-6}\right] + \frac{q_i q_j}{r}. \tag{1}$$

Here, r is the distance between the center of mass of ions, and ϵ and σ are the Lennard–Jones (LJ) interaction parameters. Lorentz–Berthelot mixing rules were used for cross interactions and the reaction field method was used to model long range interactions [10,11]. The parameters for the models used are given in Table 1
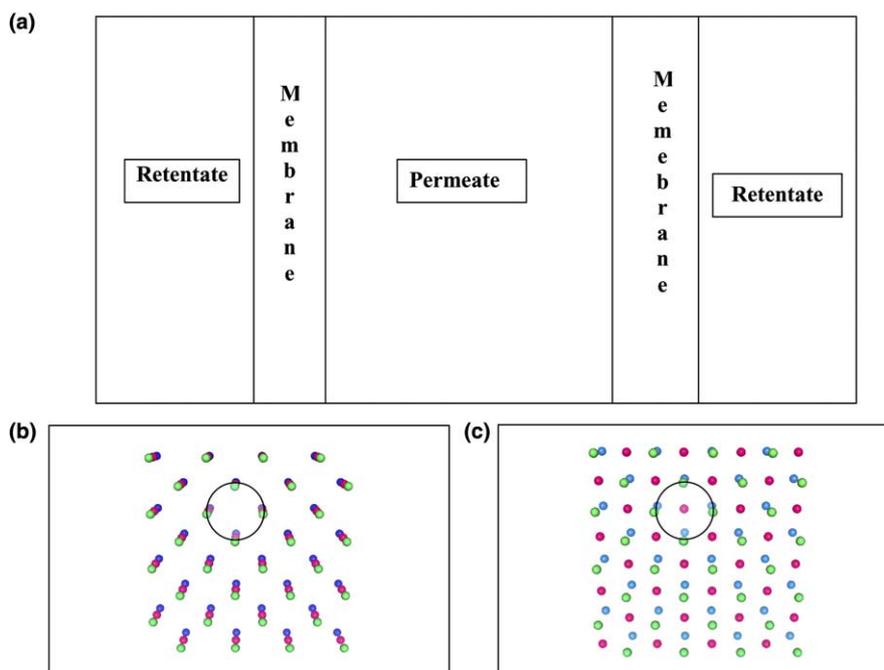

Fig. 1. A schematic of the simulation system and the two membrane structures for a three layer membrane. (a) In one unit cell of the infinite periodic array, two membranes separate the retentate and the permeate solutions. Note that in (b) the three layers are lined up behind each other, while in (c) one layer has a molecule at the center of the pore of the other two layers. The inscribed circle shown defines the pore diameter.

Table 1
Interaction parameters for potential models used

	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

[8,9]. All results reported here are reduced by Na$^+$ parameters. The membrane molecules were modeled as uncharged LJ particles; therefore, they only interacted via LJ interactions with both the solutes and the solvent. The energy parameter (ϵ) of the membrane molecules was fixed at 2.0 kJ/mole [4–6], while the diameter of the membrane molecules was adjusted to correspond to the desired pore size. The harmonic spring constant for the membrane was fixed at 200.

The permeate crossing the membrane consists of solvent (water), and also some solute (salt), depending on how well the membrane structure rejects the tightly bound solvation clusters around sodium ions. The flux of permeate diminishes as the simulation evolves, and the system relaxes towards its final equilibrium state. The simulations consisted of 600 000 time steps. Each time step was 2–3 × 10^{-16} s. The results reported correspond to the initial fluxes of the solvent (usually averaged over the initial 10 000–20 000 steps).

3. Results and discussion

We have carried out simulations in which the thickness of the nanomembranes has been varied between approximately 0.5 nm (two layers of molecules) and 1.0 nm (4 layer membrane). The pore sizes have been varied between 0.3 and 0.5 nm. As described in the previous section, two types of membrane structures have been studied. The straight structure in which the various layers of molecules are completely aligned (mirror images), and consequently the molecules can permeate the membrane in a straight path (to be referred to as the straight membrane) and the tortuous structure in which the multiple layers are aligned in an FCC structure. In such an arrangement any molecules permeating the membrane must follow a circuitous path to cross the membrane. We will refer to such membranes as tortuous membranes. In our studies we have examined the flux of solvent across the nanomembrane as a function of the pore diameter, membrane structure, and thickness. In addition we have also examined the selectivity of a membrane, defined as follows in terms of the salt mole fraction X [12,13]:

$$S = \left(\frac{X_{\text{retentate}} - X_{\text{permeate}}}{X_{\text{retentate}}} \right) 100. \tag{2}$$

Thus if all the salt is prevented from permeating the membrane the selectivity will be 100 and if none is prevented from permeating (i.e. the concentrations of the solution and permeate are equal) the selectivity will be 0. In addition, in selected cases we have also examined the effect of temperature on both the flux and selectivity, keeping other operating parameters constant. As described in the introduction, the goal of this study was to better understand the membrane characteristics that will allow higher fluxes and selectivity to be maintained. In this study we have used a rather simplified and idealized membrane structure, but we believe the behavior reported here will be indicative of that in membranes with more complex structures as well.

Results for the flux across a three layer membrane are shown in Fig. 2a. Results for other thicknesses were similar. Several conclusions can be drawn from the results shown. First, for the nanomembranes studied here, the results do not depend on the nature of the pore structure. Thus as can be seen quite clearly, the flux rate for both the straight and tortuous pores are essentially identical. This is significant, because for microscopic and macroscopic membranes this is not known to be the case [14].
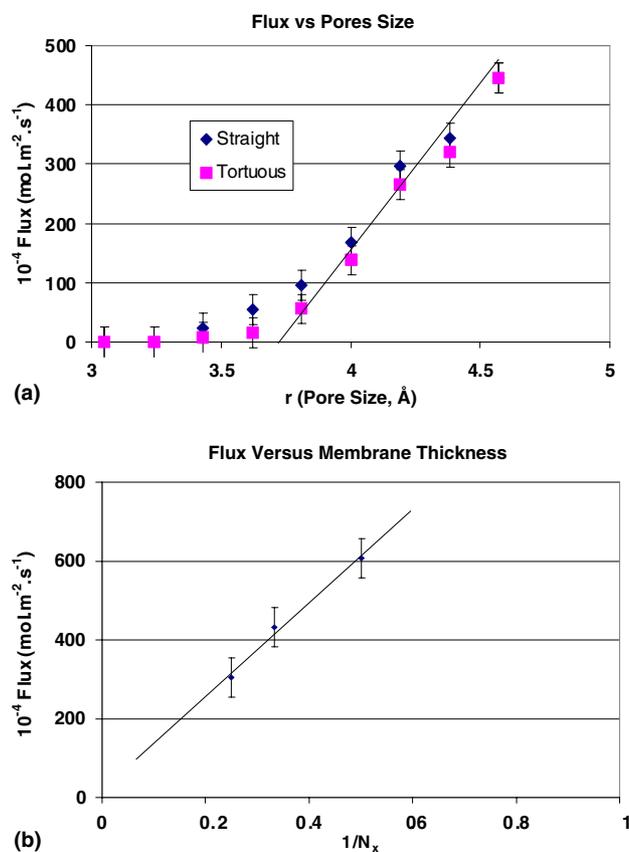

Fig. 2. (a) The flux as a function of pore size. (b) Effect of membrane thickness (number of layers N_x) on the flux at a fixed pore diameter.

In nanosystems, it appears that the actual path of flow between layers does not affect the flux. Although there must be some hydraulic resistance associated with entering and leaving the membrane (this includes breaking and reforming solvation clusters), this does not seem to pose a major hindrance to flow. In addition, in all the cases excluding the initial portions of the flux-pore size plot, the flux is almost linear w.r.t. the pore radius. In classical hydrodynamics this type of flow is observed in the Knudsen regime [15,16]. The Knudsen regime is generally applied to gas flow inside pores, and refers to flow in which the dominant phenomenon is the interaction between the gas molecules and the membrane surface, and not gas molecules interacting with other gas molecules. In the system we are studying here too, the diameter of the water molecules (about 0.32 nm) is comparable to the pore diameter, so this type of interaction can be expected to dominate the flow. The smaller pore diameter where permeation just begins is also interesting. This is the region, we believe, where flow is primarily due to the openings created in the membranes, because of the vibrations in the pore structure. Since these openings depend on the frequency with which the membrane framework is vibrating, the flow pattern here does not follow the pattern observed with the larger pore diameters. In Fig. 2b we show the flux for a fixed pore radius as a function of the inverse of the thickness of the membrane. The results show linear behavior, which agrees with the normal hydrodynamic observation in all types of flows [15]: hydraulic resistances add in series.

In Fig. 3a we have reported the selectivity of the membrane as a function of pore diameter for the three layer membrane; results for the other cases were similar. First, we observe that the selectivity drops from 100 (no solutes permeating the membrane) to 0 (all solute permeating the membrane) rather suddenly within a narrow pore diameter range of generally less than 0.1 nm. This can have somewhat important implications for membrane technology [12,13]. It shows that to maintain high selectivity, manufacturers must have strict control over the pore diameter of the membrane, or the selectivity can be seriously affected. In Fig. 3b, we show the transitional selectivity pore size (defined as the pore diameter where the selectivity changes steeply from 100 to 0) as a function of membrane thickness. The trend is for each membrane layer to become less restrictive (larger pore size) as membrane layers are added. Pore radius varies almost linearly with the inverse of the membrane thickness. In fact, these opposing features compensate each other. The total hydraulic resistance in all three cases is nearly the same (within the error bars), as is evident from the equal fluxes at equivalent transmembrane pressure drops. Thus one can conclude that selectivity correlates mainly with overall hydraulic resistance of the membrane, and is substantially less sensitive to molecular scale details that determine this resistance.
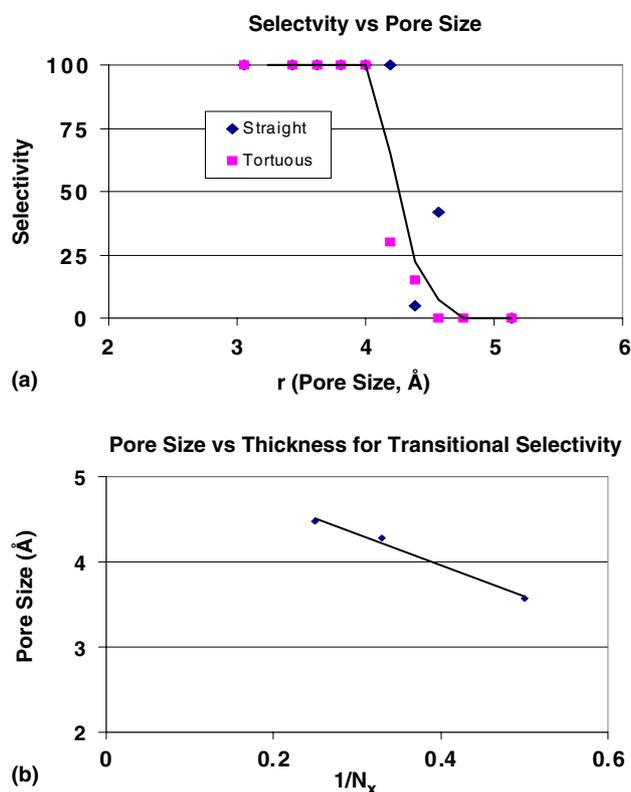

Fig. 3. (a) The selectivity of the membrane as a function of pore size. (b) Selectivity as a function of membrane thickness (N_x) for a fixed pore size.

Finally, we have also examined the effect of temperature on the flux and selectivity. Our results are in agreement with what could have been expected [12,13]. The flux is higher for a given pore diameter, and the pore diameter for transitional selectivity, as defined here, decreases with an increase in temperature. The latter result can be explained by the weaker clusters at higher temperatures, which makes it easier for water to permeate the membrane.

4. Conclusions

We have carried out a molecular dynamics study to examine the role of pore size, structure, and membrane thickness on the flux and selectivity of the membrane. The simulations suggest that membrane selectivity for dissolved ions depends mainly on overall resistance to solvent permeation. In the Knudsen regime observed here, solvent flux does not appear to depend upon tortuosity of nanomembranes. One of the goals of our study was to demonstrate the possibility of using molecular simulation methods to carry out screening studies of problems of interest in chemical processing. Our results show, that simulations can play an important role in such applications.

Acknowledgements

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