Molecular design of polymer membranes using molecular simulation technique

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ABSTRACT

Diffusion processes of methane, water, and ethanol in poly(dimethylsiloxane) (PDMS) and polyethylene (PE) were investigated by molecular dynamics simulation. Pure liquid water and ethanol were also simulated. Simulations of 5 nanoseconds were performed for PDMS and PE with penetrant species, methane. The diffusion of methane in the polymer matrices exhibits anomalous (non-Einstein) behavior for time scales of 1 nanosecond. The excess chemical potentials of the penetrants in PDMS and the pure liquids were calculated by the Widom method. The excluded volume map sampling (EVMS) method and the continuum configurational bias (CCB) method were used to increase efficiency of sampling. Permeation rates, which were calculated from diffusion coefficients and solubilities, were in reasonable agreement with experiments.

INTRODUCTION

Poly(dimethylsiloxane) (PDMS) is the well-known membrane which separates ethanol from the aqueous solution by the pervaporation. The pervaporation is a separating method of the liquid mixtures by membranes (Huang, 1991). The components of liquid mixtures supplied on the feed side of the membrane diffuse to the permeate side of the membrane where pressure is

diminished, and the vapor with different compositions leaves the membrane. The separation process is accounted for by the sorption–diffusion model.

The sorption–diffusion model describes permeation of small molecules through a nonporous polymer membrane. Sorption of small molecules on the surface of a membrane causes a concentration gradient in the membrane, and the gradient causes diffusion of the molecules. The permeation rate P of small penetrants depends on solubility and diffusivity, and is expressed by

$$P = DS \tag{1}$$

where D is the diffusion coefficient and S is the solubility of penetrants. When considering the separation of the mixture of two components, the separation factor is expressed by the ratio of the permeation rates.

It is useful to predict solubility and diffusion coefficient for design of functional separation membranes using molecular simulation technique. Diffusion coefficients of small penetrant molecules in an amorphous polymer matrix can be calculated by molecular dynamics (MD) simulation. Solubilities can be calculated by the Widom test particle insertion method (Widom, 1963).

The diffusion coefficients of small penetrant molecules in amorphous polymer matrices have been calculated from MD simulations. All these calculations were performed for nonpolar small molecules; helium, methane, and oxygen etc. In the early works the calculated diffusion coefficients of small penetrants in polyethylene (PE), polyisobutylene (PIB), and atactic polypropylene (a-PP) were 10 to 100 times higher than experimental values (Takeuchi and Okazaki, 1990; Boyd and Pant, 1991; Müller-Plathe, 1992). Some authors attributed those deviations to the united atom approximation (Müller-Plathe et al. 1992a; Pant and Boyd 1992, 1993). On the other hand, the diffusion coefficient of methane in PDMS was close to the experiment, in spite of the use of the united atom approximation (Sok et al. 1992).

For a simple liquid, the diffusion coefficient can be calculated by relatively short time runs of MD simulation. For a small molecule in a polymer matrix, however, very long time runs of MD simulation are required. Müller-Plathe et al. (1992b) performed several nanoseconds of MD simulation for He and O_2 in PIB. The diffusion of He and O_2 through the polymer matrix exhibits anomalous (non-Einstein) behavior for time scales of at least 0.1 and 6 nanoseconds for He and O_2, respectively.

The Widom method, which calculates excess chemical potential, and the Gibbs ensemble method, which simulates phase equilibrium directly, have been applied to the Lennard-Jones fluids. For high density fluids or chain molecules, however, these methods could not be applied, because efficiency of sampling was highly reduced. De Pablo et al. (1992) improved these methods for chain molecules: they introduced configurational bias for the dihedral

angle sampling, and calculated the chemical potential of linear hydrocarbon of carbon number up to fifteen. Laso et al. (1992) applied this method to the Gibbs ensemble method.

In this study, we calculated the diffusion coefficients of methane, water, and ethanol in PDMS and PE by the MD simulation. For comparison, we calculated diffusion coefficients of pure water and ethanol. We also calculated the insertion probabilities $P(R)$ of hard-sphere atoms of radius R into the polymers and the liquids. Solubilities of the small molecules in PDMS were calculated from the excess chemical potentials, which were evaluated by the Widom test particle insertion method. The permeation rates of the small molecules in PDMS were calculated from the diffusion coefficients and the solubilities.

MODEL AND SIMULATION DETAILS

The PDMS sample is modeled as CH_3–[–$Si(CH_3)_2$–O–]$_{30}$–$Si(CH_3)_3$ and the PE sample is modeled as CH_3–[–CH_2–]$_{120}$–CH_3. There are no cross-links and branches. The potential function AMBER/OPLS (Jorgensen and Tirado-Rives, 1988) is used except for PDMS and water. The GROMOS force field (Sok et al., 1992) is used for PDMS, and the SPC/E (Berendsen et al., 1987) for water. All CH_4, CH_3– and –CH_2– groups are treated as united atoms.

Simulations were carried out for the systems containing five polymer chains in cubic periodic boxes. The simulations for pure liquid water and ethanol were also carried out for the systems containing 216 and 128 molecules, respectively, in cubic periodic boxes. Initial structures were generated by the modified self-avoiding random walk (Clarke and Brown, 1989). After eliminating the excess overlaps of atoms by the steepest-descent energy minimization, MD simulation was performed. The experimental densities at 300K were used, i.e. 0.95, 0.855, 0.9965, and 0.7851 g/cm^3 for PDMS, PE, water, and ethanol, respectively (Sok et al., 1992; Pant and Boyd, 1992; Eisenberg and Kauzmann, 1969; Jorgensen, 1986). The equations of motion were solved using the Verlet algorithm. The Lennard-Jones terms of the potential were cut off at 10 Å except for liquid water (9 Å). Long range Coulomb interactions were handled by the Ewald sum method. The bond lengths were constrained to the equilibrium bond lengths by the SHAKE algorithm.

For pure polymer systems, the equations of motion were solved with a time step of 5 fs under the constant NVE condition. Temperature scalings were imposed every 5 ps to prevent creep of temperature in long time simulation. MD simulation was performed for 625 ps at 300 K and 150 ps at 1000 K to relax the structure, and then for 625 ps at 300 K to analyze the amorphous

structure: the last 500 ps was used. For the simulations of pure liquid water and ethanol, the equations of motion were solved with a time step of 0.5 fs under the constant NVT condition. The NVT method by Nosé (1984) was utilized. After 150 ps of MD runs to equilibrate the systems, a trajectory of 50 ps was sampled for water, and of 100 ps for ethanol. Detailed description for calculation method is elsewhere (Tamai et al., 1994).

One or five penetrant molecules were inserted into the polymer structures using the modified self-avoiding random walk. For the system which contains five penetrant molecules, the initial positions of five penetrants were determined so that an arbitrarily chosen penetrant was separated from any other penetrants by at least 10 Å to disperse the penetrant molecules in the unit cell. Sampling time was 2000 or 5000 ps. A time step of 5 fs was used for the methane/polymer systems, and a time step of 2 fs was used for the water/polymer and ethanol/polymer systems. Diffusion coefficients were calculated from the least-square fits of the mean-square displacements of centers of mass of the penetrant molecules averaged over all possible time origins,

$$D = \lim_{t\to\infty} \frac{1}{6t} \langle [\boldsymbol{R}(t) - \boldsymbol{R}(0)]^2 \rangle \tag{2}$$

where $\boldsymbol{R}(t)$ is a position of center of mass of a penetrant at time t and $\langle \ldots \rangle$ means the ensemble average.

The excess chemical potentials of methane, water and ethanol in PDMS and of water and ethanol in the pure liquids were calculated by the Widom test particle insertion method. To increase the efficiency of sampling, the EVMS (Excluded Volume Map Sampling) method (Deitrick et al., 1989) was used. In the insertion of ethanol, the CCB (Continuum Configurational Bias) method (de Pablo et al., 1992) was used in combination with the EVMS to increase the efficiency of dihedral angle sampling. Insertion trials of 10000 times were performed on 1000 coordinates for each system. The excess chemical potentials were calculated from the averages of the Boltzmann factors of test molecules

$$\mu_r = -kT \ln \langle \exp(-U/kT) \rangle_N, \tag{3}$$

where U is the interaction energy of a test molecule to the host atoms, k is the Boltzmann constant, and T is the temperature. Solubilities in the ideal gas phase were calculated by

$$S_g = \exp(-\mu_r/kT), \tag{4}$$

and solubilities in the liquid phase were calculated by

$$S_l = \exp(-\Delta\mu_r/kT) \tag{5}$$

where $\Delta\mu_r = \mu_r^p - \mu_r^l$, and μ_r^p and μ_r^l are excess chemical potentials in a polymer and in a liquid, respectively.

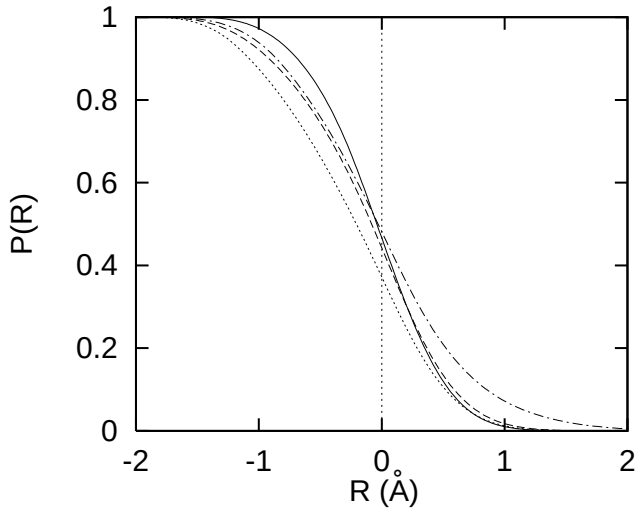

Fig. 1 Insertion probabilities $P(R)$ at 300 K. Dash-dotted line: PDMS, dotted line: PE, solid line: water, and dashed line: ethanol.

RESULTS AND DISCUSSION

We calculated the insertion probability $P(R)$, which is defined as the probability that a hard-sphere solute of radius R could be located at an arbitrary point in the matrix without overlap with the van der Waals volume of any matrix molecule (Pohorille and Pratt, 1990; Pratt and Pohorille, 1992). The method to calculate $P(R)$ is described in elsewhere (Tamai et al., 1994). $P(R)$ is related to the free volume fraction and its distribution. Time averages of $P(R)$ were calculated over the 250–1000 coordinates of trajectories. Fig. 1 shows $P(R)$ for PDMS, PE, liquid water, and liquid ethanol at 300 K. The negative values of R are allowed in the scaled particle theory (Pohorille and Pratt, 1990; Pratt and Pohorille, 1992). The point to which the hard-sphere atom of a negative radius could be inserted is included in the van der Waals volume of the matrix atoms. The free volume fractions, $P(0)$, of PDMS, PE, water, and ethanol were 0.4817, 0.3721, 0.4665, and 0.4425, respectively. The free volume fraction of PDMS is larger than any other polymer and liquids. PDMS shows broader distribution of $P(R)$. The reason for this is that PDMS has large methyl groups attached to a main chain, which keep neighbor chains apart. The broader free volume distribution will lead to larger diffusion coefficient and larger solubility of a small penetrant in PDMS.

We calculated the mean-square displacements from the 5000 ps of trajectories of five methane molecules in PDMS. The concentrations of methane in PDMS and PE are 0.69 and 0.94 g of solvent/100 g of polymer, respectively. Neither appreciable aggregation nor phase separation was observed in both systems. Fig. 2 shows the mean-square displacements as a doubly logarithmic

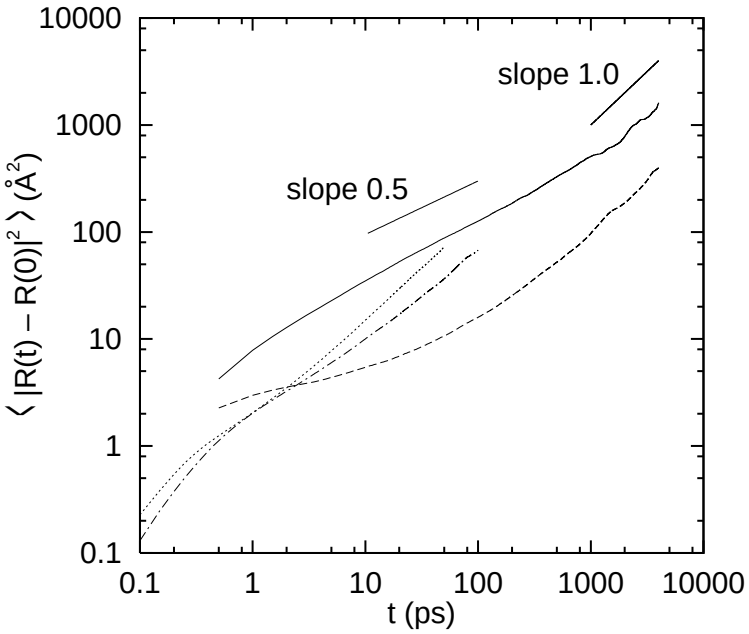

Fig. 2 Mean-square displacements of methane in PDMS and PE, water and ethanol in the pure liquids at 300 K as a doubly logarithmic plot. Solid line: methane in PDMS, dashed line: methane in PE, dotted line: liquid water, dash-dotted line: liquid ethanol.

plot. The results of pure liquid water and ethanol are also plotted. In short time regions, the mean-square displacements follow a power law of t^2. In long time regions, the mean-square displacements are linear in time, where Einstein's equation (2) is applicable. At intermediate regions, anomalous diffusion is observed and the mean-square displacements look like obeying a power law of $t^{0.5}$. The normal diffusion regions of methane in polymers begin at rather long time regions ($\sim$1000 ps for PDMS and $\sim$300 ps for PE) compared with pure liquid water ($\sim$5 ps) and ethanol ($\sim$40 ps), and the anomalous diffusion regions are also longer. Müller-Plathe et al. (1992b) showed a similar plot for diffusion of helium in polyisobutylene (PIB), where the normal diffusion region begins about 100 ps. This is the same order as our system of methane in PE. The system of methane in PDMS requires a longer time simulation to obtain the normal diffusion region. If a diffusion coefficient is calculated from a short time scale simulation for a polymer/penetrant system, it will be over-estimated.

Diffusion coefficients were calculated from the mean-square displacements by the least-square fits within the ranges of the normal diffusion regions for each system. TABLE 1 lists the calculated and experimental diffusion coefficients at 300 K. Agreement between the experimental and calculated diffusion coefficients of pure liquid water and ethanol are fairly good. MD simulation of approximately 100 ps is sufficient to obtain the diffusion coefficients with high

TABLE 1
Calculated and Experimental Diffusion Coefficients at 300 K

penetrant	matrix	$D \times 10^5 (\mathrm{cm^2 s^{-1}})$	
		calculated	experiment
methane	PDMS	0.57	2.06[a]
water	PDMS	1.53	1.45[b]
ethanol	PDMS	0.20	0.45[b]
methane	PE	0.16	0.045[c]
water	PE	0.78	—
ethanol	PE	0.07	—
water	water	2.38	2.14[d]
ethanol	ethanol	1.11	1.01[e]

[a] From measurements on PDMS with 4.9 vol.% of a silica filler (Stern et al, 1987). [b] From the transient permeation experiments at 298 K (Okamoto et al., 1988). [c] Corrected for crystallinity(Pant and Boyd, 92). [d] At 298 K (Wang, 1951). [e] At 298 K (Rathbum and Babb, 1961).

precision for the pure liquid systems. On the other hand, the calculated diffusion coefficient of methane in PDMS is about one-fourth of the experimental value, and the diffusion coefficient of methane in PE is about four times larger than the experimental value, which was corrected for crystallinity. It is difficult to achieve completely quantitative agreement for the polymer/penetrant system even if we use very long time trajectories. This is probably due to the anomalous diffusion behavior and the slow relaxation time in polymers. The calculated values of diffusion coefficients are affected by simulation time, system size, potential functions, etc. Experimental data also incur errors which are dependent on various experimental conditions. However, at least semi-quantitative agreement was able to be obtained by the MD simulation.

Because water and ethanol tend to form hydrogen bonds in their pure liquids, they may aggregate in a polymer matrix. We performed MD simulation for the systems which contain only one penetrant molecule in the polymer matrices, in order to calculate the diffusion coefficients which are not influenced by aggregation. The concentrations of water and ethanol in PDMS are 0.16 and 0.40 g of solvent/100 g of polymer, respectively, and those in PE are 0.21 and 0.54 g of solvent/100 g of polymer, respectively. MD simulations were performed for 2000 ps. Figure 3 shows the mean-square displacements of water and ethanol in the polymers at 300 K as a linear plot. The mean-square displacements look like linear in time within the range of 50–500 ps. Diffusion coefficients were calculated from this time region. This time scale is, however,

supposed to be within the anomalous diffusion region by contrast with the diffusion of methane in polymers. The diffusion coefficients agree well with the experimental values which were determined by Okamoto et al. (1988) from the transient permeation experiments for pure components and also for 10 and 30 wt% ethanol solutions. The membrane used in the experiment is press-cured pure PDMS, whose density is 0.974 g/cm^3. The density is slightly higher than our system. The higher density and the press-cure may reduce the diffusion coefficients. Although the experimental condition is not the same as that in our calculation, we can expect that at least semi-quantitative agreement could be obtained.

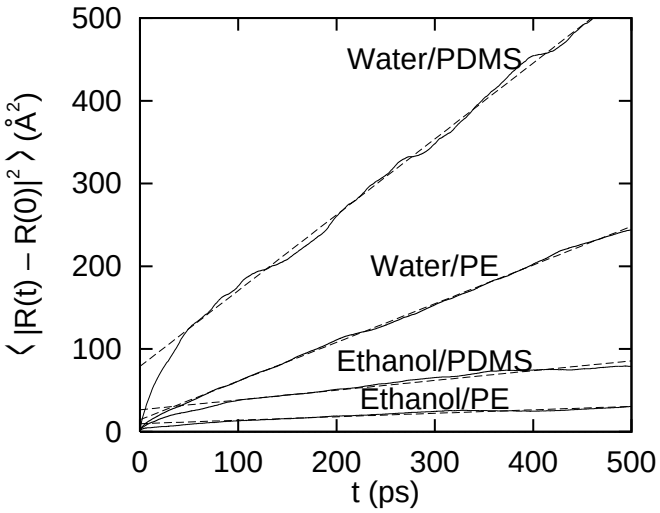

Fig. 3 Mean-square displacements of water and ethanol in the polymers at 300 K and their linear fits.

The insertion trials by the Widom method were performed for the systems: methane, water, ethanol into PDMS, water into liquid water, and ethanol into liquid ethanol. Fig. 4 shows the energy distribution functions $f(U)$ of test molecules in each system. The large $f(U)$ of penetrants into PDMS at high energy regions reflects the broader free volume distribution of PDMS. For the system of ethanol into liquid ethanol, whose insertion probability is very low, a relatively smooth energy distribution can be obtained. This shows the advantage of the use of the EVMS and the CCB method.

TABLE 2 lists the excess chemical potentials and the solubilities of methane, water, and ethanol. For the system of water into liquid water, a polarization correction energy of 5.22 kJ/mol, which was included in the SPC/E potential function, was added by assuming that induced dipole moment was the same on the average between N molecules system and $N+1$ molecules system of volume V. For the system of water in PDMS, the polarization correction energy is unknown. Because Coulombinc interaction is not dominant in this

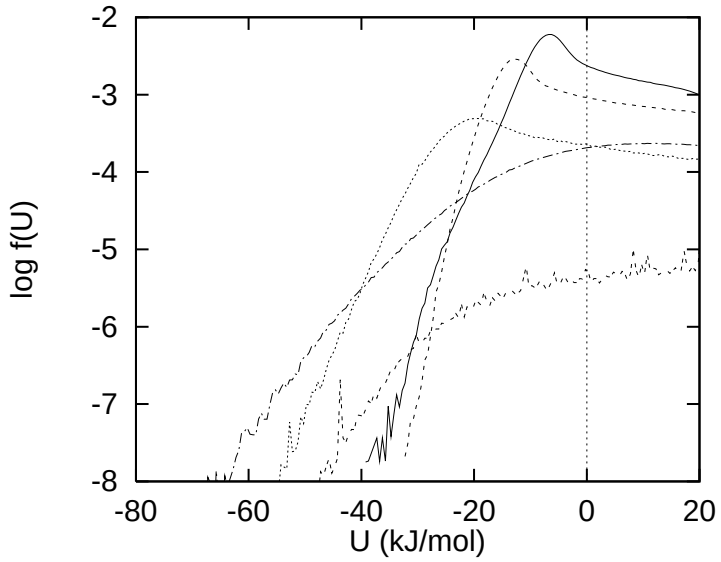

Fig. 4 Energy distribution functions $f(U)$ of small molecules in PDMS and pure liquids at 300 K calculated from the Widom method. Solid line: methane in PDMS, dashed line: water in PDMS, dotted line: ethanol in PDMS, dash-dotted line: liquid water, dash-dashed line: liquid ethanol.

TABLE 2
Excess Chemical Potentials μ_r relative to the ideal gas phase and Solubilities in ideal gas phase S_g and in liquid phase S_l at 300 K.

Solute	Solvent	μ_r(kJ/mol)	S_g	S_l
methane	PDMS	-5.84 ± 0.04	10.4	—
water	PDMS	-4.44 ± 0.13	5.93	0.97×10^{-4}
ethanol	PDMS	-15.45 ± 0.44	490	14.1
water	water	-27.48 ± 1.58	—	—
ethanol	ethanol	-8.85 ± 0.88	—	—

system, we ignored the polarization correction for this system. In the OPLS potential, no induced dipole moment effect is included in parameter fitting. Therefore, we don't take account of this effect for ethanol. In the reference state of ethanol, the free energy of the dihedral angle, -2.03 kJ/mol, was taken into consideration.

The calculated excess chemical potential of liquid water is lower than the experimental value -23.9 kJ/mol (Sarkisov et al., 1974). The solubility of methane in PDMS is close to the value 12.5, which was calculated by Sok et al. using the Widom method, but the value is higher than the experimental value 0.56 (Sok et al., 1992). Okamoto et al. (1988) determined the solubilities of aqueous solution of ethanol at various concentrations by sorption experiments. Water has a low solubility in PDMS membrane and there are

no experimental data for pure liquid water. The extrapolated value to zero concentration is smaller than 1×10^{-3}. The calculated solubility of liquid water in PDMS is very low and agrees qualitatively with the experiment. The solubility of liquid ethanol is two order higher than the experimental value, 0.0745. The method used in this simulation cannot include the effect of the relaxation of polymer chains by ethanol; the solubilities at infinite dilution are calculated by our simulation. In general, on the sorption of small molecules into rubbery polymers, solubility varies from that at infinite dilution if the penetrants have high solubility in the polymers. This fact might lead to the discrepancy between the experimental and calculated values.

The permeation rates were calculated from the diffusion coefficients and the solubilities. TABLE 3 lists those for small molecules in PDMS. The calculated values agree qualitatively with the experiments. Ethanol has a smaller diffusion coefficient than water in PDMS, but has a larger permeation rate. The reason for this is that ethanol has a larger solubility than water.

TABLE 3
Calculated and Experimental Permeation Rates of methane, water, and ethanol in PDMS at 300 K.

Penetrant	Matrix	$P(\mathrm{cm}^2/\mathrm{s})$	
		calculated	experiment
methane	PDMS	5.9×10^{-5}	1.1×10^{-5}
water	PDMS	1.5×10^{-9}	$< 1\times10^{-8}$
ethanol	PDMS	2.8×10^{-5}	4.1×10^{-7}

CONCLUSION

The larger free volume and the broader free volume distribution of PDMS result in the three times higher diffusion coefficients of methane, water, and ethanol in PDMS than in amorphous PE. Although there are some difficulties in obtaining quantitative agreement, the calculated diffusion coefficients of the penetrant molecules agree reasonably with the experiments. The solubilities of the small penetrants were calculated by the Widom method. The solubilities of methane and ethanol in PDMS were overestimated. The discrepancy between the experimental and calculated values might arise from the difference between the real solubility and that at infinite dilution for the penetrant which has a high solubility in the polymers. The permeation rates of the small molecules were calculated from the diffusion coefficients and the solubilities. The calculated values agreed semi-quantitatively with the experiments. The ethanol selectivity of the PDMS membrane was attributed to the higher solubility of ethanol than water.

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