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Vacancy profile in reverse osmosis membranes studied by positron annihilation lifetime measurements and molecular dynamics simulations

A. Shimazu¹, H. Goto², T. Shintani¹, M. Hirose¹, R. Suzuki³ and Y. Kobayashi³

¹Nitto Denko Corporation, 1-1-2, Shimohozumi, Ibaraki, Osaka 567-8680, Japan
E-mail: akira_shimazu@gg.nitto.co.jp

²Toyohashi University of Technology, Toyohashi, Aichi 441-8580, Japan

³National Institute of Advanced Industrial Science and Technology, Tukuba-shi, Ibaraki 305-8568 and 8565, Japan

Abstract. The positron annihilation technique using a slow positron beam can be used for the study of the vacancy profiles in typical reverse osmosis (RO) membranes. In this study, the vacancy profile in the polyamide membrane that exhibits a high permselectivity between ions and water was studied using the positron annihilation technique and molecular dynamics simulations. Ortho-positronium (o-Ps) lifetimes in the surface region of the membranes were evaluated by using a slow positron beam. The diffusion behavior of Na⁺ and water in the polyamides was simulated by molecular dynamics (MD) methods using the TSUBAME2 supercomputer at the Tokyo Institute of Technology and discussed with the vacancy profile probed by the o-Ps. The results suggested that the large hydration size of Na⁺ compared to the vacancy size in the polyamides contributes to the increased diffusivity selectivity of water/Na⁺ that is related to the NaCl desalination performance of the membrane. Both the hydration size of the ions and the vacancy size appeared to be significant parameters to discuss the diffusivity selectivity of water/ions in typical polyamide membranes.

1. Introduction

The positron annihilation lifetime (PAL) is a unique probe of molecular size vacancies in certain polymers. The ortho-positronium (o-Ps) lifetime τ_3 for various polymers appears to represent the size of the interstitial space among the molecular chains which are called vacancies in this article. PAL has successfully been applied to glassy polymers for membrane-based separation technology such as a gas separation process [1] and RO process [2]. In addition, MD simulations can be used for the characterization of the vacancy profile in some glassy polymers [3]. However, there have been few studies on the solute diffusion behavior on a molecular level through a typical polyamide as RO membrane. The aim of this study is to discuss the diffusivity selectivity of water/Na⁺ in a typical polyamide for an RO membrane using o-Ps and MD simulations. The effect of the hydration size of Na⁺ on the diffusivity selectivity is discussed.

2. Experimental

Polyamide composite membranes were synthesized from trimesoyl-chloride (TMC) and 1,3-phenylenediamine (MPD) on a porous polysulfone substrate by an interfacial polycondensation method. Variable-energy PAL measurements were carried out for the polyamide composite membranes using the system at the National Institute of Advanced Industrial Science and Technology (AIST). Details of the system and application have been previously described [4, 5]. The PAL spectra were obtained at a time resolution of 280–300 ps at the full width at half-maximum. The positron incident energy was varied from 0.7keV to 10keV at room temperature. A three-component analysis was used to determine τ_3 of the polyamides. The MD simulation of the polyamides/NaCl aqueous system was carried out using the MD program of the Materials Studio (Accelrys Inc.) using the COMPASS force field [6]. The atomic charges of the models were determined using Density Functional Theory at the B3LYP/6-31G(d) level [7]. A constant number-pressure-temperature method was used for the calculation. A typical molecular model is described in Figure 1.



3. Results and Discussion

3.1. Vacancies in polyamide thin layer probed by *o*-Ps

The typical surface structure observed by SEM of a polyamide composite membrane is shown in Figure 2. About a 400-nm-thick polyamide layer is observed on the porous polysulfone substrate. A positron beam was implanted into the surface of the composite membrane. Figure 3 shows the typical PAL spectra of the composite membrane. The mean implantation depth is determined as a function of the positron energy. For our samples, the PAL of the polyamide layer is measured at the positron energy of 0.7~1keV, corresponding to the mean depth of 17~31 nm, and the PAL of the polysulfone substrate is measured at the positron energy of 10keV, corresponding to the mean depth of approximately 1.2 μ m. The NaCl rejection of the membrane at room temperature at a pressure of 1.5 MPa with a NaCl 0.15 wt% aqueous solution feed was determined by the following equation.

$$\text{Rejection} = [1 - (C_p / C_F)] \times 100 (\%) \quad (1)$$

where C_p and C_F are the NaCl concentrations in the permeate and feed side, respectively. Figure 4 shows typical result of the relationships between τ_3 at the positron energy of 0.7keV and the NaCl rejection for the polyamide composite membranes. This result indicates that τ_3 reflects the structural property that is related to the reverse osmosis performance of typical polyamide composite membranes.

According to a simple model, the vacancy is approximated by an infinite height potential well and the electrons available for the pick-off annihilation are assumed to exist as an electron layer on the surface of the well with the thickness ΔR . The *o*-Ps lifetime τ_3 is then related to the radius R of the vacancies [8].

$$\tau_3 = 0.5 \{ 1 - R / (R + \Delta R) + \sin[2\pi R / (R + \Delta R)] / 2\pi \}^{-1} \text{ ns} \quad (2)$$

where $\Delta R = 0.166 \text{ nm}$ is known to have an excellent agreement with the experimental data. Using equation (2), radius of vacancy is estimated to be 0.24~0.27nm. Each membrane in Figure 4 exhibits a high NaCl Rejection, therefore, this vacancy size is suggested to contribute to increasing the water/NaCl selectivity.

3.2. The effect of the vacancy size on the diffusivity selectivity of water/ Na^+ in the polyamide.

In order to consider the effect of the vacancy size on the diffusivity selectivity of water/ Na^+ in the polyamide, the diffusion behavior of water and Na^+ was studied using MD simulations. According to the Einstein equation, the particle diffusion coefficient D is determined by equation (3).

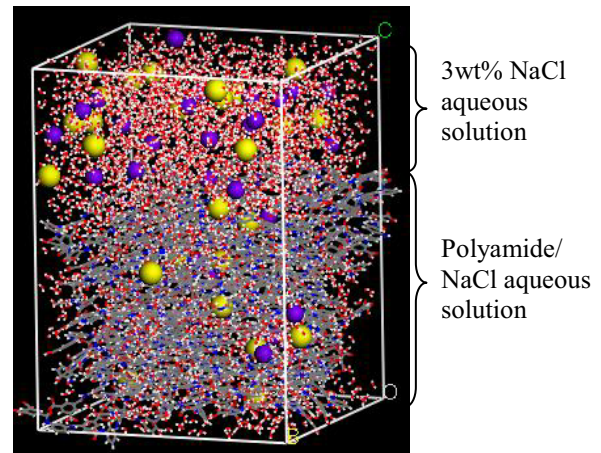


Figure 1. Schematics of typical molecular model used for MD simulations. Yellow sphere: Na^+ , Blue sphere: Cl^- , Small molecule consisting of red and white lines: Water.

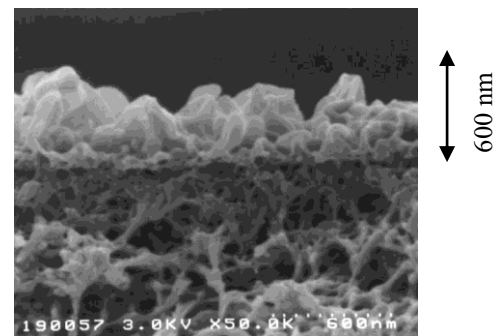


Figure. 2. Surface structure of polyamide composite membrane.

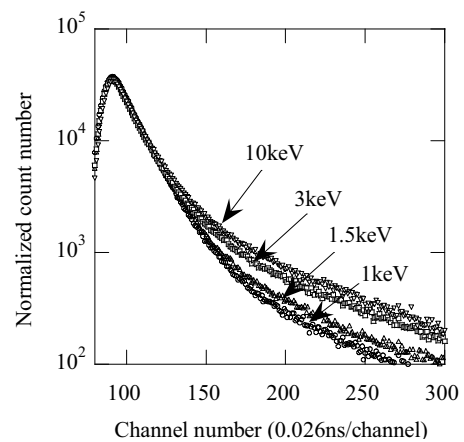


Figure. 3. Typical PAL spectra of polyamide composite membrane.

$$D = \frac{d}{dt} \frac{1}{6} \langle |r(t) - r(0)|^2 \rangle \quad (3)$$

where $\langle |r(t) - r(0)|^2 \rangle$ is the mean square displacement (MSD) of the particle over time t from the start. The MSD of water and Na^+ in the surface NaCl aqueous solution on the polyamide layer and in the polyamide layer are demonstrated in Figure 5 and Figure 6, respectively. While the water diffusivity is greater than the Na^+ diffusivity in both the surface NaCl aqueous solution and the polyamide, Na^+ diffusivity was remarkably low compared to the water diffusivity in the polyamide. The diffusion coefficients of water and Na^+ determined by the MD simulations are listed in Table 1 with the data measured by the ^1H pulsed-field gradient NMR methods [9] in which the NMR measurements were carried out for the water and Na^+ in a 3wt% NaCl aqueous solution at 298K. D_{water} and D_{Na^+} in the surface NaCl aqueous solution of the molecular model were nearly equal to those in the NaCl aqueous solution measured by ^1H pulsed-field gradient NMR methods. This suggests that the simulations reflect the real diffusion behavior of water and Na^+ . It is noted that the diffusivity selectivity of water/ Na^+ ($D_{\text{water}}/D_{\text{Na}^+}$) is remarkably high compared to that of the NaCl aqueous solution. According to solution-diffusion model [10], the high $D_{\text{water}}/D_{\text{Na}^+}$ contributes to the increased NaCl rejection of the RO membranes. Figure 7 shows the radius distribution function for Na^+ and water $g(r)_{\text{Na}^+-\text{water}}$ in the polyamide model with the vacancy radius R estimated by the Tao-Eldrup model using the o-Ps lifetimes. Some interesting remarks can be made for the $g(r)_{\text{Na}^+-\text{water}}$ versus R . $g(r)_{\text{Na}^+-\text{water}}$ represents the hydration shell size of Na^+ in the polyamide. The first peak around 0.22nm and second peak around 0.28nm correspond to the first hydration shell of Na^+ . The peaks around 0.22nm and 0.28nm are attributed to the distances between Na^+ and O of water, and Na^+ and H of water, respectively. The peak around 0.48nm corresponds to the second hydration shell of Na^+ . It is noted that the vacancy size probed by o-Ps is smaller than the first hydration shell size of Na^+ , which is about 0.35nm. This suggests that the large hydration size of the Na^+ compared to the vacancy size contributes to the increased $D_{\text{water}}/D_{\text{Na}^+}$. Figure 8 illustrates the vacancy site that can be occupied as probed by a hypothetical sphere with a radius of 0.35nm. The yellow sites in the figure represent the surfaces of the region occupied by a hypothetical spherical probe of radius 0.35nm using Voorintholt's method [11]. The calculated yellow sites are apparently few and small. This tendency was consistent with the increased $D_{\text{water}}/D_{\text{Na}^+}$ and corresponding high NaCl rejection due to the sieving effect of the hydrated Na^+ in the polyamide.

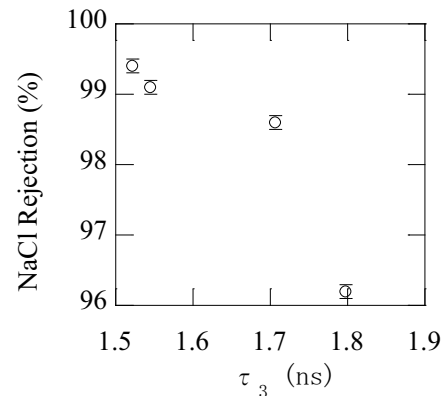


Figure 4. Relationships between τ_3 and NaCl rejection for polyamide composite membranes.

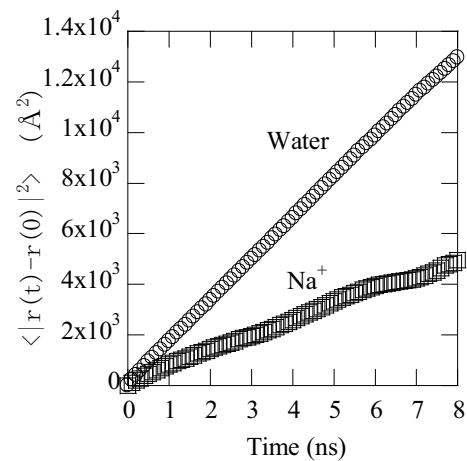


Figure 5. Mean square displacement of water and Na^+ in surface NaCl aqueous solution described in Figure 1.

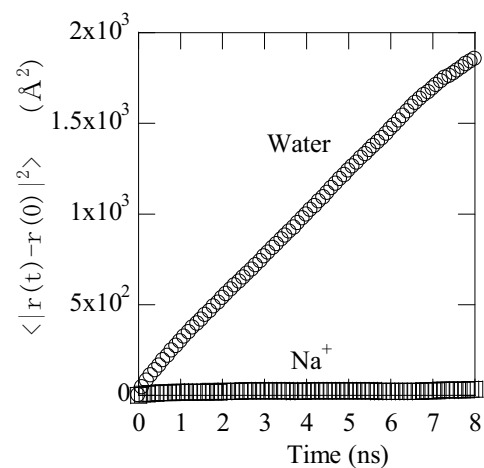


Figure 6. Mean square displacement of water and Na^+ in polyamide described in Figure 1.

4. Conclusions

The effect of the vacancy size on the diffusivity selectivity of water/ Na^+ in a typical polyamide as RO membrane was discussed using the o-Ps lifetime and MD simulations. A good correlation between the NaCl rejection and o-Ps lifetime was observed. A small vacancy compared to the hydration size of Na^+ was considered to contribute to increase the $D_{\text{water}}/D_{\text{Na}^+}$ in the typical polyamide as the RO membrane.

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5. References

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Table 1. Diffusion coefficient of water and Na^+ at 298K.

Material	D_{water}	D_{Na^+}	$D_{\text{water}}/D_{\text{Na}^+}$
¹ Surface NaCl aqueous solution	26.7	10.2	2.61
² NaCl aqueous solution _{exp}	22	13	1.7
¹ Polyamide	3.86	0.0181	213

¹Calculated by molecular dynamics simulation using model described in Figure 1.

²Measured by pulsed field gradient NMR method.

D: Diffusion coefficient ($\times 10^{10} \text{ m}^2/\text{s}$)

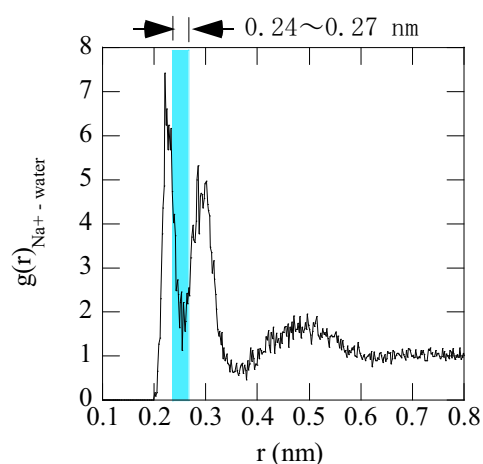


Figure 7. Radius distribution function for Na^+ and water in polyamide described in Figure 1. 0.24~0.27nm: radius of vacancy estimated using o-Ps lifetime

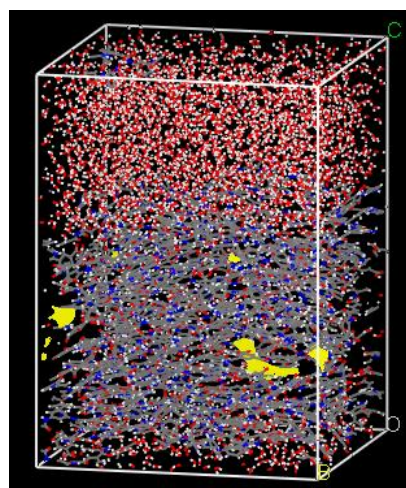


Figure 8. Vacancies that can be occupied, probed by a hypothetical sphere with a radius 0.35 nm. Yellow: vacancy site.