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Positron annihilation lifetime spectroscopy as a tool for further insights into the transport of water and solutes during reverse osmosis

逆浸透における溶質と水分子の輸送機構解析ツールとしての陽電子消滅寿命分光

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Abstract: Reverse osmosis (RO) filtration is an important separation process for water treatment and many industrial applications. Despite many decades of research and development efforts, solute transport through an RO membrane is still not fully understood. This article provides an insight into transport of small and uncharged solutes in RO membranes, with a particular focus on free-volume hole-size of the membrane active skin layer determined by positron annihilation lifetime spectroscopy (PALS). Free-volume hole-size is one of the most important membrane properties governing solute rejection. In fact, the rejection of boric acid (which is a small and uncharged solute) by RO membranes decreases with increasing free-volume hole-radius. In addition to free-volume hole-size, other properties of the active skin layer may also influence the rejection of uncharged small solutes. Thus, future development of PALS or other analytical techniques to characterise the free-volume hole-shape, hole-size distribution, and free-volume fraction of the active skin layer can provide an unprecedented level of insight into the separation of small and uncharged solutes by RO membranes.

Keywords: boron, free-volume hole, positron annihilation lifetime spectroscopy, reverse osmosis

1. Introduction

Reverse osmosis (RO) filtration is a key separation technology in many water treatment applications. Modern seawater desalination plants are primarily based on seawater reverse osmosis (SWRO) membranes which can offer more than 99.5 % rejection of inorganic salts.[1] Low pressure reverse osmosis (LPRO) membranes have been widely employed in potable water recycling applications for the removal of soluble organic substances and partial removal of inorganic salts.[2] RO applications for specific industrial applications in food processing, biotechnology, and hydrometallurgy have also significantly increased recently.

Central to the application of RO membranes for desalination, water recycling, and many other industries is their ability to reject small and dissolved solutes. However, there remains scope for further improvement in rejection properties, particularly with respect to small and uncharged solutes. Boron and *N*-nitrosodimethylamine (NDMA) are two of the most notable examples of such solutes.

Most commercial RO membranes can only achieve up to 90 % rejection of boron at lower than pH 8.[3] As a result, most seawater desalination plants have to employ a two pass RO system (seawater is filtered twice by RO membranes) to comply with the boron limit for potable water supply.[3] NDMA has been classified as a probable human carcinogen[4] and its concentration in recycled water for potable reuse has been regulated in Australia and several other countries at 10 ng L^{-1} or below.[2] NDMA rejection by RO membranes can be as low as 10 %;[5] thus, a subsequent advanced oxidation process or a dilution with other clean water sources is often required to meet the NDMA level.

Any improvement on the rejection of these small and uncharged solutes by RO membranes can lead to a reduction in capital and operational costs. In fact, some membrane manufacturers have been developing new RO membranes designed for high boron removal (e.g. ESPAB and SWC4B membranes supplied by Hydranautics/Nitto), however the specific details behind the high boron rejection capacity of these high rejection membranes are proprietary information of the respective manufacturers.

To further optimize the rejection of small and neutral solutes by RO membranes, an understanding of the solute-membrane interaction is of paramount importance. Solute transport through an RO membrane can be described by the irreversible thermodynamic model,[6] in which the membrane is considered as a black box and the transport of solute

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is driven by the partition of the solute into the membrane followed by diffusive and convective movement across the membrane. Based on the irreversible thermodynamic model, the solution-diffusion model has been developed to describe the transport of solutes through RO membrane.[7] Another approach that has been widely used for nanofiltration membranes is the pore-flow model. The pore-flow model describes the RO membrane as a thin separation layer with cylindrical pores where solutes and water pass through by pressure-driven convective and diffusive flow.[8] It is noteworthy that the pore-flow model was first introduced by Loeb and Sourirajan[9] in the early 1960s to describe the transport of water and solutes in the cellulose acetate membranes that they have invented.

In recent years, significant progress in deploying the positron annihilation lifetime spectroscopy (PALS) technique has been made to explore the internal structure of the membrane active skin layer at near atomic-scale. PALS allows for an accurate measurement of free-volume hole-size within the active skin layer of an RO membrane and can potentially offer a new horizon in our understanding of the transport of water and solutes in the RO process.[10,11] Despite the significant increase in the number of studies using PALS to characterise RO membranes, the significance of free-volume holes on the rejection of small and uncharged solutes has not been fully elucidated. Thus, this article aims to identify the relationship between free-volume hole-size of RO membranes and their rejection capacity for small and uncharged solutes. Directions for further developments to better understand the transport of water and solutes in RO membranes will also be delineated.

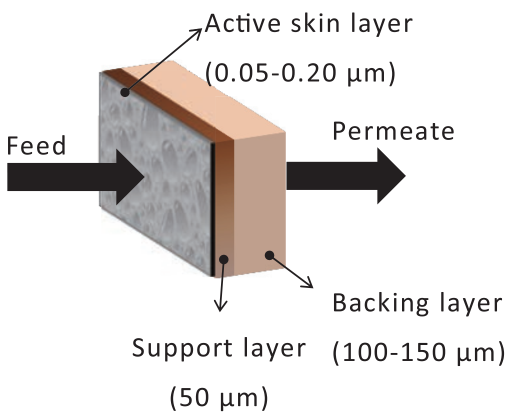


Fig. 1　Layers and thickness of a typical thin composite flat sheet membrane.

2. Thin film composite membranes

Most commercial RO membranes are thin-film composites (TFC) and comprise an active polyamide or polyamide derivative skin layer on top of a polysulfone porous support layer and a polyether non-woven fabric backing layer[12] (Fig. 1). The polyamide active skin layer is so densely packed and cross-linked that it contains subnanometer-scale free-volume holes. The active skin layer plays an important role in the permeation of water and solutes through membranes.[11] In contrast, the polysulfone porous support layer and the polyether non-woven backing layer have no significant resistance to water permeation. Their roles are solely to provide mechanical strength to the membrane. Thus, separation performance of RO membranes is governed exclusively by the physicochemical properties of the active skin layer.

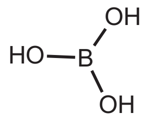
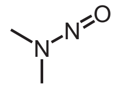
The separation performance of RO membranes is generally

Table 1　Separation properties of commercial membranes.

Model	Type	Manufacturer	NaCl rejection[a] [%]	Boron rejection[b] [%]
SWC5	SWRO	Hydranautics/Nitto	99.8	81[c]
ESPAB	LPRO	Hydranautics/Nitto	99.3	59[c]
TFC-HR	LPRO	KMS	99.6	58[d]
BW30	LPRO	Dow/Filmtec	99.5	39[d]
ESPA2	LPRO	Hydranautics/Nitto	99.6	36[c]
ESPA1	LPRO	Hydranautics/Nitto	99.3	12[d]

[a]Manufacturer's data.
[b]Determined using a laboratory-scale RO system with overall permeate flux = 20 L m^{-2} h^{-1}; feed solution contains 20 mM NaCl; 1 mM $NaHCO_3$; and 1 mM $CaCl_2$; cross flow velocity 40.2 cm s^{-1}; feedtemperature = 20.0 °C; feed pH 8.
[c]Ref. 13), [d]Ref. 14).

Table 2 Properties of boric acid and NDMA.

Membrane type	Boric Acid	NDMA
Structure		
Molecular weight [$g\,mol^{-1}$]	61.8	74.1
Log$D$ [a]	−0.62	−0.50
Molecular volume[b] [nm^3 $molecule^{-1}$]	0.071	0.124
$pK_a/(pK_b)$[c]	8.70	(3.52)

[a] ACD/PhysChem Suite software (Advanced Chemistry Development, Inc., Ontario, Canada).
[b] The molecular volume of each molecule (V_m) was estimated with the equation (V_m = Molecular volume [$nm^3\,mol^{-1}$]/N_A) where Avogadro constant (N_A) is 6.022×10^{23} mol^{-1}. The molecular volume of each molar was obtained from the ACD/PhysChem Suite software.
[c] Chemaxon (http://www.chemicalize.org/).

determined based on the rejection of NaCl. In general, high NaCl rejection by RO membranes (> 99 %) can be readily achieved (Table 1). Although sodium and chloride ions are very small in size (molecular mass = 23 $g\,mol^{-1}$ and 35.5 $g\,mol^{-1}$, respectively), they exist in charged and hydrated form in an aqueous solution. These hydrated ions can be highly rejected due to the size exclusion mechanism in combination with electrostatic interactions. In contrast, small and uncharged solutes often exhibit low rejection by RO membranes. Typical examples include boron and NDMA that are present in natural water in an uncharged form as $B(OH_3)$ (M_W = 62 $g\,mol^{-1}$) and $C_2H_6N_2O$ (M_W = 74 $g\,mol^{-1}$), respectively (Table 2). These compounds are not hydrated and smaller in size than hydrated sodium ions.[12] The rejection of boron by RO membranes can be very low and highly variable in the range of 12 %–81 %[13,14] (Table 1). Unlike charged solutes, uncharged solutes including boric acid and NDMA are primarily rejected under the size exclusion mechanism.[15] In fact, the rejection of uncharged solutes by RO membranes generally increases in proportion to their molecular size (e.g. molecular volume)[13] (Fig. 2). Although hydrophobic interactions between these solutes and the membrane could influence the rejection of uncharged solutes by TFC membranes,[16] both boric acid and NDMA are hydrophilic (Table 2). As a result, free-volume hole-size can be one of the most important factors governing the rejection of these solutes.

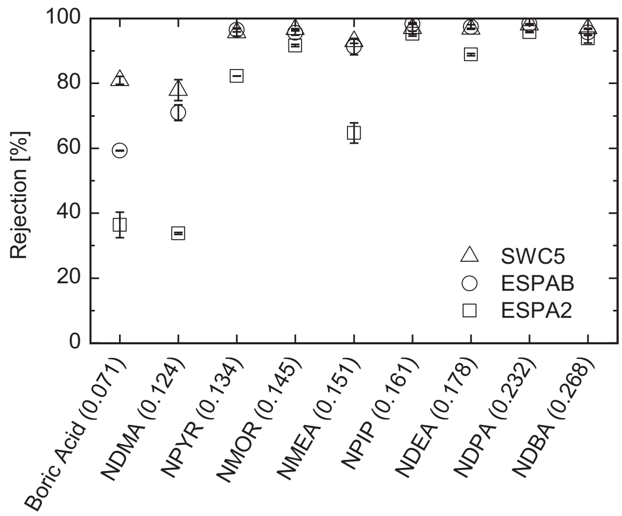


Fig. 2 Rejection of boric acid and *N*-nitrosamines (20 mM NaCl, 1 mM $NaHCO_3$, 1 mM $CaCl_2$, permeate flux 20 $L\,m^{-2}\,h^{-1}$, cross flow velocity 40.2 $cm\,s^{-1}$, feed pH 8.0 ± 0.1, feed temperature = 20.0 ± 0.1 °C).[13] The molecular volume (nm^3 $molecule^{-1}$) is shown in the parentheses. Values reported here are the average and ranges of duplicate results.

3. Membrane characterisation by PALS

PALS is currently the only available technique that can determine free-volume hole-radius within a polymeric layer including the active skin layer of RO membranes.[17] PALS using a variable energy slow positron beam can analyse free-volume hole-radius in a specified depth without the need to isolate the target active skin layer. Mean free-volume hole-radius (r [nm]) of an RO membrane can be determined from the pick-off lifetime of *ortho*-positronium ($\tau_{o\text{-Ps}}$) measured by PALS using the Tao-Eldrup model:[18]

$$\tau_{o\text{-Ps}} = 0.5\left[1 - \frac{r}{r+0.166} + \frac{1}{2\pi}\sin\left(\frac{2\pi}{r+0.166}\right)\right]^{-1}. \quad (1)$$

Table 3 Free-volume hole-radii of commercial polyamide RO membranes analysed by PALS.

Membrane type	Model	Manufacturer	Free-volume hole-radius [nm]	Reference
SWRO	SWC5	Hydranautics/Nitto	0.26	Fujioka et al.[13]
LPRO	LF10	Nitto	0.20	Chen et al.[20]
	ESPA2	Hydranautics/Nitto	0.29	Fujioka et al.[13]
	ESPAB	Hydranautics/Nitto	0.29	Fujioka et al.[13]
	AG	GE	0.23	Ito et al.[21]
	AK	GE	0.24	Ito et al.[21]

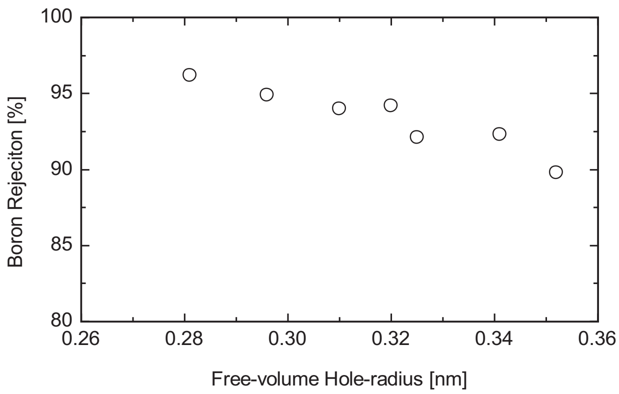


Fig. 3 Boron rejection as a function of free-volume hole-radius of SWRO membranes (TDS = 35.000 mg L^{-1}, feed pH 6.5, flow rate = 3.51 L min^{-1}, temperature = 25 °C, boron = 5 mg L^{-1}).[10]

It is noteworthy that free-volume holes are approximated as a spherical shape.

The free-volume hole-radius of RO membranes analysed by PALS using a variable slow positron beam is summarised in Table 3. The range of beam intensity (1 keV–2 keV) used in these studies corresponds to a mean positron implantation depth of 40 nm–120 nm, which was determined so that most positrons are implanted into the active skin layer of typical RO membranes. The reported mean free-volume hole-radius for LPRO membranes is in the range of 0.20 nm–0.29 nm[13, 19, 20] (Table 3). Although a notable difference in free-volume hole-radius is observed among RO membranes, these data alone do not provide any significance of the difference on solute rejection.

4. Effects of free-volume hole-radius on solute rejection

Because the free-volume hole-radius of RO membranes could be a dominant factor governing uncharged solute separation, rejection of a given solute could vary in response to changes in free-volume hole-size. In fact, a strong correlation between uncharged solute rejections and free-volume hole-size has been reported in previous studies.[10, 19, 20] For example, Henmi et al.,[10] evaluated boron rejections using similar types of SWRO membranes and reported that the rejection of boron decreased with increasing free-volume hole-radius (Fig. 3). Fujioka et al.,[13] reported that the free-volume hole-radius of a SWRO membrane (0.26 nm) was smaller than that of LPRO membranes (0.29 nm), and accordingly boron rejection by the SWRO membrane (81 %) was greater than that of the LPRO membranes (36 %–59 %) (Fig. 4).

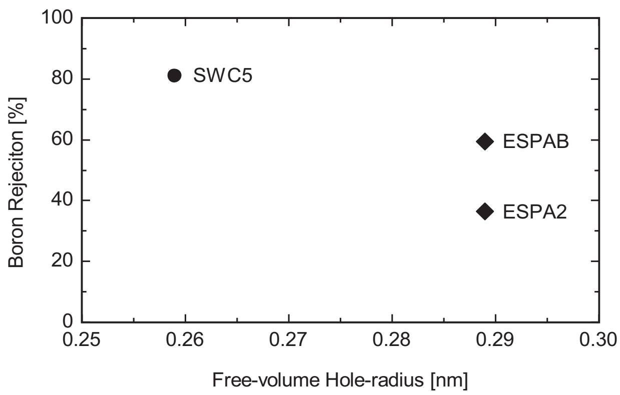


Fig. 4 Boron rejection as a function of free-volume hole-radius of a SWRO membrane (SWC5) and LPRO membranes (ESPAB and ESPA2) (20 mM NaCl, 1 mM $NaHCO_3$, 1 mM $CaCl_2$, feed pH 8.0 ± 0.1, permeate flux = 20 L m^{-2} h^{-1}, feed temperature = 20 °C, boron = 5 mg L^{-1}).[13]

5. Findings by the authors

While the free-volume hole-size of RO membrane is indeed an important factor determining uncharged solute rejection as described above, a variation in free-volume hole-size is not necessarily correlated with a variation in uncharged solute rejection. A recent study performed by Fujioka et al.,[13] revealed a remarkable difference in boron rejection by two LPRO membranes (i.e. ESPA2 and ESPAB) with equivalent free-volume hole-radius (i.e. 0.29 nm) (Fig. 4). A similar difference in rejection between the two LPRO membranes was also observed for several other small and uncharged compounds (e.g. NDMA and *N*-nitrosomethylethylamine (NMEA)).[13)]

In addition to free-volume hole-size, there are other physicochemical properties of RO membranes that may play an important role in solute rejection. These properties include free-volume hole-shape, free-volume hole-size distribution and free-volume fraction, all of which can vary considerably depending on manufacturing method and polymer materials even if the RO membranes have an identical mean free-volume hole-radius. These properties have not yet been determined by current characterization techniques. Although further development is still needed, PALS has arguably the best potential to characterise these properties.

6. Directions for future development

While the contribution of membrane properties described above (i.e. free-volume hole-shape, hole-size distribution and free-volume fraction) toward the rejection of uncharged solutes still remains unclear, the quantification of these properties may lead to a breakthrough in understanding the solute-membrane interaction during RO filtration.

Firstly, free-volume holes analysed using PALS are assumed to be spherical and uniform size and their shapes cannot be determined by PALS. Many previous studies[15,21] have reported that the molecular width of solutes among molecular size parameters shows the best correlation with solute rejections, indicating that shape and size interactions between free-volume holes and solutes are important factors influencing solute rejection. Thus, it is necessary to reconcile the difference between the actual hole-shape and hole-size distribution and the assumption of current PALS techniques (i.e. spherical shape and uniform size). Free-volume fraction of the active skin layer is another property that can influence solute rejection according to the pore-flow model.[22] Solute and water fluxes can vary largely depending on free-volume fraction. The degree of free-volume fraction among several TFC membranes may be compared using *o*-Ps intensity (I_3) data obtained through PALS.[23] In fact, Sasaki et al.,[24] reported that boron rejection by modified SWRO membranes does not depend on the free-volume hole-radius but is dependent on $V \times I_3$, where V = free-volume hole-space ($V = 4/3\pi r^3$). Nevertheless, the *o*-Ps intensity (I_3), which is the ratio of the *o*-Ps component to the total implanted positron intensity, does not necessarily represent free-volume fraction; thus, the evaluation using $V \times I_3$ for understanding the role of hole-size and free-volume fraction on solute rejection may not be sufficiently accurate.

7. Conclusions

PALS using a slow positron beam has the potential to elucidate the subnanometer-scale inner structure of RO membranes. PALS data previously reported in the literature reveal that commercially available RO membranes have a mean free-volume hole-radius of 0.20 nm–0.29 nm. Free-volume hole-size can be an important parameter in determining the rejection of boron which is uncharged at environmental pH values. Data in the literature also indicate that in addition to the free-volume hole-size, other membrane properties may also play an important role in boron rejection. Major challenges lie in the measurement of free-volume hole-shape, free-volume hole-size distribution and free-volume fraction of the active skin layer, all of which may require further development of PALS or support from other analytical techniques.

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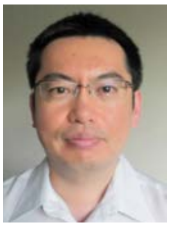
Biographies



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