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Probing the internal structure of reverse osmosis membranes by positron annihilation spectroscopy: gaining more insight into the transport of water and small solutes

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Abstract

Reverse osmosis (RO) has been employed as a key separation process in many industrial applications. In recent years, the use of positron annihilation spectroscopy (PAS) including positron annihilation lifetime spectroscopy (PALS) and Doppler broadening of annihilation radiation to characterise the internal structure of the skin layer of thin film composite membranes has renewed research interest for further development and optimisation of the RO process. In this paper, we highlight the need for better understanding of the skin layer internal structure. We review relevant PAS techniques that could provide an unprecedented level of insight to our understanding of the internal structure of the active skin layer of RO membranes. PALS data reported in previous studies revealed that commercially available RO membranes have a mean free-volume hole-radius of 0.20-0.29 nm in the active skin layer. Data corroborated from the literature show a good correlation between the mean free-volume hole-radius of RO membranes and the rejection of boric acid which can be considered as a model small and neutral solute. The data also highlight the need for a comprehensive inter-laboratory study to standardise free-volume hole-radius measurement using PALS. In addition to free-volume hole-radius, free-volume fraction and thickness of the active skin layer appear to be important membrane properties governing neutral solute rejection. A roadmap is suggested to enhance the understanding of the transport of small and neutral solutes in RO. This includes integrating PAS with other techniques (e.g. molecular dynamics simulation) to describe the internal structure of RO membranes.

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Probing the internal structure of reverse osmosis membranes by positron annihilation spectroscopy: Gaining more insight into the transport of water and small solutes

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Abstract

Reverse osmosis (RO) has been employed as a key separation process in many industrial applications. In recent years, the use of positron annihilation spectroscopy (PAS) including positron annihilation lifetime spectroscopy (PALS) and Doppler broadening of annihilation radiation to characterise the internal structure of the skin layer of thin film composite membranes has renewed research interest for further development and optimisation of the RO process. In this article, we highlight the need for better understanding of the skin layer internal structure. We review relevant PAS techniques that could provide an unprecedented level of insight to our understanding of the internal structure of the active skin layer of RO membranes. PALS data reported in previous studies revealed that commercially available RO membranes have a mean free-volume hole-radius of 0.20-0.29 nm in the active skin layer. Data corroborated from the literature show a good correlation between the mean free-volume hole-radius of RO membranes and the rejection of boric acid which can be considered as a model small and neutral solute. The data also highlight the need for a comprehensive inter-laboratory study to standardise free-volume hole-radius measurement using PALS. In addition to free-volume hole-radius, free-volume fraction and thickness of the active skin layer appear to be important membrane properties governing neutral solute rejection. A roadmap is suggested to enhance the understanding of the transport of small and neutral solutes in RO. This includes integrating PAS with other techniques (e.g. molecular dynamics simulation) to describe the internal structure of RO membranes.

Keywords: boron; free-volume hole; N-nitrosodimethylamine (NDMA); positron annihilation spectroscopy (PAS); and reverse osmosis (RO).

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1. Introduction

Reverse osmosis (RO) is an important separation process for seawater desalination, potable water reuse, and many other applications. RO membranes can reject a range of inorganic salts and soluble organic substances. RO technology has progressively evolved over the last half-century since Loeb and Sourirajan [1] synthesized the first *asymmetric* cellulose acetate RO membrane capable of removing dissolved salts for desalination purposes *in the early 1960s*. Another important milestone was the development of *the interfacial polymerisation technique for producing thin-film composite (TFC) membranes with high salt rejection and water permeability by Cadotte and Rozelle in the early 1970s* [2]. Subsequent development in membrane materials and manufacturing processes has resulted in significant improvements in salt rejection and membrane permeability, making RO efficient and economical for a range of applications [3]. As a notable example, modern seawater reverse osmosis (SWRO) membranes can readily achieve salt rejection of greater than 99.5% [3]. Other successful applications include brackish water treatment, potable and industrial water reuse, biotechnology, and beverage and dairy production [4-8].

Despite their high salt rejection, the separation efficiency of RO membranes for small and neutral or low molecular weight (MW) molecules is still highly variable. Typical examples of these small and neutral molecules include N-nitrosodimethylamine (NDMA) (MW = 74 g/mol) and boric acid (MW = 62 g/mol). These are contaminants of significant public health or environmental concern. NDMA, a probable human carcinogen [9], is present in raw wastewater and can also be readily formed during chloramination disinfection performed prior to RO filtration. In some cases, low NDMA rejection by RO membranes (e.g., 4-75%) necessitates subsequent treatment (e.g., advanced oxidation process) or blending and dilution with other clean water to meet its target value (i.e., 10 ng/L) [10, 11]. Similarly, seawater desalination plants typically deploy a two pass RO system where the RO permeate from the first pass is treated by the second pass to reduce the boron concentration in the product water to below 0.5 mg/L [12]. It is noteworthy that commercial SWRO membranes can only achieve a moderate boron rejection (below 90%) at environmental pH values (e.g., pH 6-8) where boron exists primarily in the form of boric acid [12]. Difficulties associated with the separation of small compounds present a major challenge to economically operate these water treatment systems. Any improvement on rejection capacity can reduce part or all of the post

treatment, but requires a comprehensive understanding of solute transport in RO filtration [8, 13].

Solute permeation through RO membranes has been traditionally described by the solution-diffusion model where RO membranes are assumed to have no visible pores [14]. In the solution-diffusion model, the permeate partitions into the membrane material and diffuses through the RO membrane. Due to difficulties to analyse the internal structure of RO membranes, the solute rejection mechanism has been inferred mostly from the physicochemical properties of the solute [15, 16]. A recent development in positron annihilation lifetime spectroscopy (PALS) which employs a slow positron beam has allowed for the measurement of the mean size of subnanometre-scale holes (i.e., free-volume hole-size) within polymer chains in thin film samples. PALS is an analytical technique using positron annihilation spectroscopy (PAS). It is noteworthy that the free-volume holes cannot be determined by surface characterisation techniques such as transmission electron microscopy (TEM) and scanning electron microscopy (SEM). Other pore size analytical methods such as differential scanning calorimeter and gas adsorption-desorption methods are not suitable or do not have adequate sensitivity to quantify sub-nanometre-scale hole-size [17, 18]. As a result, PAS is the only viable technique to characterise of the internal structure of RO membranes. The number of PALS studies for RO membrane characterisation has increased significantly over the last few years [19-25]. However, contribution of free-volume holes to solute permeation has not yet been fully understood. It is also noteworthy that other properties of the free-volume hole including shape and free-volume fraction cannot be measured by PALS. Thus, further development of supplementary tools (such as molecular dynamics simulation [13]) to characterise these properties (that may influence the diffusion of neutral solutes through TFC RO membranes) is also crucial to better understand their transport behaviour.

Given the need to clarify the potential of PAS/PALS for elucidating solute separation mechanisms, this review aims to provide a comprehensive understanding of solute-membrane interactions in RO filtration, particularly focusing on free-volume hole-size analysed by PALS. The specific objectives are to evaluate the relationship between free-volume hole-size and the rejection of small and neutral solutes; and discuss the potential of the current PAS techniques for characterising RO membranes.

2. RO membranes

2.1. Active skin layer

Most commercial RO membranes are polyamide or polyamide derivative thin-film composites. Indeed, since the development of interfacial polymerisation techniques for membrane production in the 1970s [2, 26], TFC RO membranes have become the industry standard. A typical TFC membrane comprises an active polyamide (or polyamide derivative) skin layer on top of a polysulfone microporous supporting layer, which is further supported by a polyether non-woven fabric backing layer (Figure 1). The thicknesses of these three layers are approximately 0.05-0.2, 50, and 100 μm , respectively [27-30]. The active skin exclusively determines the water permeability and solute separation efficiency of the membrane. The polyether backing and polysulfone support layers do not contribute to the separation process and their role is solely to provide mechanical support to the active skin layer.

The active skin layer is formed by interfacial polymerisation where an aqueous solution containing a polyfunctional amine placed on the support layer reacts with another solvent solution containing polyfunctional acid chloride at their interface [31]. The polymerisation is usually incomplete and there can be a number of unreacted amine and carboxylic functional groups [32]. Interfacial polymerisation conditions (e.g., monomer concentration, solvent properties, reaction time and temperature) influence the characteristics of the active skin layer and determine the separation performance and water permeability of the RO membrane [33-35]. It is widely accepted that free-volume holes are present between cross-linked polymer chains of the active skin layer into which water molecules and small solutes can partition (Figure 1) [23, 36, 37].

Figure 1: Layers of typical thin composite flat sheet membrane and free-volume holes in the proposed chemical structure of cross-linked polyamide active skin layer.

Recent microscopic characterisation of commercially available RO membranes by Yan *et al.*, [38] reveals a rather complex active skin layer structure. A high resolution scanning electron microscopic (SEM) image of the ESPA2 RO membrane (Hydranautics) obtained by Yan *et al.*, [38] is shown in **Figure 2**. The surface morphology of a typical RO membrane can be obtained from atomic force microscopy (AFM) measurements [33]. The active skin layer of an RO membrane has a surface roughness in the range of 0.05 to 0.20 μm [33, 39]. A rougher surface morphology leads to higher effective surface area. Recent TEM studies suggest that the active skin comprises a top thin layer containing cavities of 0.05-0.2 μm in size and a supporting layer directly attached to a backing layer (**Figure 3**) [8, 27, 30, 40].

Figure 2: Scanning electron microscopy cross-section image of ESPA2 membrane. (a) Cutting lines show the position of a dense layer, with an average thickness of *ca.* 20 nm. Dotted lines show passages for filtrate to go through under pressure; (b) Fractured ridge structure, a cavity can be seen on the root (Reproduced with permission from Ref. [38]. Copyright 2014 Elsevier Science).

Figure 3: Schematic cross-sectional image of the active skin layer of an RO membrane.

2.2. Solute transport through RO membranes

Solute transport across an RO membrane is generally described by the irreversible thermodynamics, pore-flow, or solution-diffusion models [14, 41-43]. The irreversible thermodynamic model [42, 43] has been widely used to describe and quantify the transport of solvent and solutes through RO membranes using a set of phenomenological equations. Nevertheless, it provides no insight into membrane properties and solute transport mechanisms. Thus, the model is not suited to describe the transport of solvent and solutes based on the membrane free-volume hole-radius. The pore-flow model is essentially based on a fixed free-volume hole network within the membrane matrix [41, 44]. This model describes the transport of solutes through these holes by pressure-driven convective flow, which can separate solutes under a size exclusion mechanism. Within this model, free-volume hole-size is an important parameter governing the diffusion and convection of solutes through the active skin layer.

In contrast to the pore-flow model where permanent free-volume holes exist in the active skin layer, the solution-diffusion model is based on the concept of a “non-porous” membrane. Salt transport through RO membranes in most studies is described with diffusion – the basis of the solution-diffusion model. In this model, the separation of solutes through a membrane occurs due to the difference in solubility and mobility of solutes that are dissolved in the membrane matrix [14, 45, 46]. The driving force producing the separation is a concentration gradient

across the membrane. Solutes diffuse the membrane through the appearing and disappearing free-volume holes between polymer chains having the thermal motion [47]. Salt and water transport in RO is facilitated by molecular diffusion involves two components - water (component i) and salt (component j). The water flux (J_i) is described by the simple equation

$$J_i = A(\Delta P - \Delta \pi) \quad (1)$$

where ΔP and $\Delta \pi$, respectively, are the pressure difference and osmotic pressure difference across the membrane, A is the water permeability constant and

$$A = \frac{D_i K_i c_{i0} V_i}{lRT} \quad (2)$$

where D_i is the water diffusion coefficient, K_i is the water sorption coefficient, c_{i0} is the concentration of water in the feed, V_i is the molar volume of water, l is the membrane thickness, R is the gas constant, and T is the water temperature. Similarly, the salt flux (J_j) across the RO membrane can be written as

$$J_j = B \Delta c_j \quad (3)$$

where Δc_j is the salt concentration difference across the membrane, B is the salt permeability constant and

$$B = \frac{D_j K_j}{l} \quad (4)$$

where D_j is the salt diffusion coefficient and K_j is the salt sorption coefficient. Unlike water flux, salt flux is independent of the difference in pressure and osmotic pressure across the membrane. A more detailed description of the solution-diffusion model can be found elsewhere [14, 47, 48]. The ability of solute separation performance of RO membranes is typically expressed with the term – apparent solute rejection (R_s)

$$R_s = \left(1 - \frac{c_{sl}}{c_{s0}} \right) \quad (5)$$

where c_{sl} and c_{so} are the concentration of solute in the permeate side and feed side, respectively.

Filtration operating conditions can be important parameters when comparing the rejection of a given solute among different TFC membranes. These conditions include permeate (or water) flux which represents permeate flow rate per unit area (e.g., L/m^2h). Permeate flux increases with applied feed pressure but solute flux remains almost unchanged [14], leading to increased dilution of solute in the permeate stream (Figure 4). As a result, solute rejection can vary depending on permeate flux. Thus, separation performance among different RO membranes needs to be evaluated under controlled filtration conditions.

Figure 4: Flux and rejection data for a model seawater solution (3.5% sodium chloride) in a good quality reverse osmosis membrane as a function of pressure (Reproduced with permission from Ref. [14]. Copyright 1995 Elsevier Science).

2.3. Separation performance of commercial RO membranes

The rejection of sodium chloride (NaCl) is usually used to describe the separation performance of RO membranes. Typically TFC-based SWRO membranes can readily achieve

more than 99.5% NaCl rejection at a high salt concentration (e.g., 30,000 mg/L) and pressure (e.g., 5.5 MPa) [3]. Low pressure reverse osmosis (LPRO) membranes, designed for low salinity water applications (e.g., pre-treatment of ultrapure water, boiler water, brackish water and wastewater recycling), attain moderate to high salt rejection (e.g., 99.3-99.7%) (Table 1). LPRO membranes employed in water recycling applications are expected to remove some trace organic chemicals (TrOCs) in addition to salts [49, 50]. In contrast to RO membranes which reject most monovalent ions, nanofiltration (NF) membranes have a low NaCl rejection but can achieve sufficient removal of multivalent ions such as magnesium, calcium and phosphate. Although sodium ion is a very small solute (molecular mass = 23 g/mol), in an aqueous solution it exists in a hydrated form which is several times larger than the naked ion. Hydrated sodium ions can be larger in diameter than the free-volume hole of the RO active skin layer [27]. As a result, most hydrated ions will be rejected by RO membranes, resulting in a high salt rejection. Most if not all charged compounds also exhibit high rejection by RO membranes by electrostatic repulsion and size exclusion mechanisms [51].

Table 1: Separation properties of commercial NF/RO membranes.

Type	Membrane	Manufacturer	Manufacturer's data			Boron rejection ^a [%]	NDMA rejection ^a [%]
			Pressure [MPa]	NaCl rejection [%]	MgSO ₄ rejection [%]		
SWRO	SWC5	Hydranautics/Nitto	5.50	99.8	-	81 ^b	78 ^b
	ESPAB	Hydranautics/Nitto	1.05	99.3	-	59 ^b	71 ^b
	ESPA2	Hydranautics/Nitto	1.05	99.6	-	36 ^b	34 ^b
	ESPA1	Hydranautics/Nitto	1.05	99.3	-	12 ^c	23 ^c
LPRO	LFC3	Hydranautics/Nitto	1.05	99.7	-	n.a.	38 ^d
	70LW	Toray	1.55	99.7	-	n.a.	52 ^d
	TFC-HR	KMS	1.55	99.6	-	58 ^c	50 ^c
	BW30	Dow/Filmtec	1.55	99.5	-	39 ^c	48 ^c
NF	NF90	Dow/Filmtec	0.48	85-95	>97	n.a.	8 ^d
	NF270	Dow/Filmtec	0.48	-	97	n.a.	4 ^e

^a Determined using a laboratory-scale RO system with overall permeate flux = 20 L/m²h; feed solution contains 20 mM NaCl, 1 mM NaHCO₃, and 1 mM CaCl₂; cross flow velocity 40.2 cm/s; feed temperature = 20.0 ± 0.1 °C; feed pH 8.0 ± 0.1.

^b Ref. [20]

^c Ref. [52]

^d Ref. [53]

^e Unpublished

n.a.: not available

In contrast to charged solutes, the rejection of neutral solutes by RO membranes can be low and highly variable. Typical examples include boron and NDMA that are small and present in natural water in an uncharged form [52, 53] (Table 2). For example, the rejection of boric acid (MW = 62 g/mol) and NDMA (MW = 74 g/mol) by RO membranes in the literature is 12-81% and 23-78%, respectively (Table 1). It is noteworthy that the specifications of commercial RO membranes do not always include information regarding the removal of small and neutral solutes of significant health and ecological concern (e.g., NDMA and boron). Unlike charged solutes, these small and neutral solutes are primarily rejected through size exclusion whereby solutes larger than the free-volume holes of membrane are effectively rejected while allowing smaller ones to permeate through [51, 54]. In fact, the rejection of neutral solutes by RO membranes generally increase with molecular size (e.g., molecular volume) [20, 22].

Table 2: Properties of boric acid and NDMA.

Membrane type	Boric Acid	NDMA
Structure
Molecular weight [g/mol]	61.8	74.1
Molecular volume ^a [cm ³ /mol]	43	75
Molecular width ^b [Å]	0.85	1.73
Minimum projection area (MPA) ^c [Å ²]	19.5	16.3
LogD at pH8 ^c	-0.61	0.04
pK _a /(pK _b) ^c	8.70	(3.52)
Distribution of charged species at pH 8 ^c [%]	16.7	0
Dipole moment ^d [Debye]	1.11	3.71

^a ACD/PhysChem Suite software (Advanced Chemistry Development, Inc., Ontario, Canada).

^b [52]

^c Chemaxon (<http://www.chemicalize.org/>).

^d Milsian 2.1 software.

A recent study by Fujioka et al., [55] revealed that the rejection of neutral solutes by TFC membranes was better correlated with the solute minimum projection area (MPA, the minimum 2D dimension of the solute) than either the molecular weight or molecular volume (Figure 5). Fujioka et al., [55] suggested that the size interaction between solute and membrane is important in determining neutral solute rejection. Uncharged compounds such as boric acid and NDMA are very hydrophilic (Table 2) but most commercial RO membranes are classified as hydrophobic. Thus, hydrophobic interactions (e.g., adsorption) between these

types of solutes and membranes hardly occur [56]. As a result, free-volume hole-size is expected to be the most important factor governing the rejection of a given neutral solute.

Figure 5: Rejection of 28 neutral TrOCs by the NF90 membrane as a function of their molecular weight, molecular volume and minimum projection area (20 mM NaCl, 1 mM NaHCO₃, 1 mM CaCl₂, permeate flux 20 L/m²h, feed pH 8.0 ± 0.1, feed temperature 20.0 ± 0.1 °C) (Reproduced with permission from Ref. [55]. Copyright 2014 Elsevier Science).

3. Membrane characterisation by PAS

3.1. Principle

The free-volume hole-structure of thin films including the active skin layer of RO membranes can be evaluated using PAS. The most commonly used analytical methods in PAS are: (a) PALS in which the lifetime spectrum of positrons and/or positroniums is measured; and (b) Doppler broadening of annihilation radiation (DBAR) in which the energy spectrum of the annihilation γ -rays is measured. PALS can be used to evaluate the free-volume hole-radius of the membrane active skin layer. On the other hand, DBAR can be used to examine electron momentum distributions and provides information on the positron (positronium) annihilation process and/or analysis of the chemical composition at the annihilation site within the membrane active skin layer.

3.1.1. PALS

PALS is currently the only technique capable of determining the free-volume hole-radius within the active skin layer of an RO membrane [17, 22]. The analysis is performed by injecting positrons into the membrane sample where positrons annihilate with electrons

resulting in the emission of annihilation γ -rays. Some of the positrons injected into insulating materials (e.g., polymers) combine with an electron and then form a hydrogen-like bound state of an electron – positronium ion (Ps). Ps can exist in two different states. One is a spin-antiparallel state, *para*-Ps (*p*-Ps), and the other is spin-parallel state, *ortho*-Ps (*o*-Ps). In vacuum, *p*-Ps annihilate into 2- γ rays (2- γ decay) with an intrinsic lifetime of 125 ps while *o*-Ps annihilate into 3- γ rays (3- γ decay) with an intrinsic lifetime of 142 ns. When *o*-Ps is generated in an insulating sample, they are trapped in free-volume holes and subsequently self-annihilate. Within the free-volume hole *o*-Ps can also annihilate with surface wall electrons by 2- γ decay (pick-off annihilation) with a lifetime shorter than 142 ns. With decreasing free-volume hole-size the probability of pick-off annihilation increases, and *o*-Ps life-time becomes shorter. Although the *o*-Ps annihilates with a lifetime much shorter than 142 ns in a polymer sample, it still survives far longer than the *p*-Ps (i.e., 125 ps) and free positrons (i.e., ~ 0.4 ns) which enables the lifetime of *o*-Ps decaying in a free-volume hole to be measured by PALS. The lifetime of *o*-Ps (τ_{o-Ps}) in pick-off annihilation can be expressed using the Tao-Eldrup model [57, 58]:

$$\tau_{o-Ps} = 0.5 \left[1 - \frac{r}{r + 0.166} + \frac{1}{2\pi} \sin\left(\frac{2\pi r}{r + 0.166}\right) \right]^{-1} \quad (6)$$

where r (≤ 1 nm) is the radius of the free-volume hole approximated as a spherical shape.

There are two major methods for measuring positron lifetime. One is called the “fast positron method”, using fast positrons obtained by β^+ decay of ^{22}Na radioactive isotopes (RIs) [19, 23] (Figure 6a). The other is called the “slow positron method”, in which slow positrons generated by moderation of fast positrons are used (Figure 6b).

In the fast positron method, ^{22}Na sealed by a Kapton thin film is used as a positron source. The positron beam is typically a few millimetres in diameter. This positron source is sandwiched by two pieces of sample of several millimetres in diameter and about 1 mm apart (Figure 6a). Positrons generated from the positron source have up to 540 keV in energy and can penetrate up to 0.1 mm in depth into the sample. Thus, the information obtained by this method is the average value of the bulk sample. Positron and 1.27 MeV γ -ray are both emitted from ^{22}Na almost simultaneously. Positron lifetime is defined as the time difference between the detection timing of the 1.27 MeV γ -ray (i.e., start timing signal) and the detection timing

of the annihilation γ -ray (i.e., stop timing signal). It is noteworthy that Ps is not formed in the Kapton thin film and hence *o*-Ps lifetime measured by the first positron method is the information solely originating from the sample.

Figure 6: Schematic diagram of PALS measurement techniques (a) fast positron method and (b) slow positron method.

In contrast to the fast positron method, the slow positron method uses a monoenergetic positron beam with an energy spread of ~ 10 eV. Slow positrons are generated by moderation of fast positrons created by intense RI sources or electron accelerators. These slow positrons can be guided as a beam through the vacuum-duct (beamline) to the measurement chamber and injected into a sample. By adjusting the injection energy (E_{in}) typically from 0.5 keV to 30 keV of a slow positron beam, the positron implantation depth can be controlled allowing depth analysis from several nm to several μ m of free-volume hole-radius in the material. The mean positron implantation depth z_m is estimated by the semi-empirical formula z_m [nm] $\approx 40E_{in}^{1.6}$ [keV] / ρ [g/cm³], where ρ is density of sample [59]. For example, a positron incident energy of 1.0 keV corresponds to a mean implantation depth of about 40 nm for polyamide membrane samples. The stopping profile $P(z, E_{in})$ of positrons in materials is approximately given by the following semi-empirical equations:

$$P(z, E_{in}) = \frac{2z}{z_0^2} \exp \left[- \left(\frac{z}{z_0} \right)^2 \right] \quad (7)$$

$$z_0 = \frac{z_m}{\Gamma(3/2)} \quad (8)$$

where z is the depth (in nm), Γ is the gamma function, and $\int_0^\infty P(z, E_{in}) dz = 1$. $P(z, E_{in})$ is defined as the stopping profile of positrons before thermal diffusion and the actual annihilation depth profile of positron and o -Ps can be broadened due to their diffusions occurring prior to annihilation. However, $P(z, E_{in})$ can be used as actual annihilation depth profile of positron/ o -Ps provided that the diffusion length of positron/ o -Ps is adequately small compared to the mean implantation depth z_m . It is important to note that typical o -Ps diffusion length is within a few nm [60]. With this approximation, the measured value of positron annihilation parameters Q can be given by $Q = \int_0^\infty P(z, E_{in}) \times Q(z) dz$. When positrons are injected into a sample with distinct multi-layers, Q is given by using the stopping probability η_i and intrinsic positron annihilation parameters Q_i in the layer number i (e.g., $i = 1$ is the top layer and $i = 2$ is the second layer located under the top layer) as follows:

$$\eta_i(E_{in}) = \int_{x_i}^{x_{i+1}} P_i(z, E_{in}) dz \quad (9)$$

$$Q = \sum_i \eta_i(E_{in}) \times Q_i \quad (10)$$

where x_i is the depth from the surface to the interface between the layer of $i - 1$ and the layer i . Calculated $P(z, E_{in})$ for $E_{in} = 1.0, 2.0$ and 3.0 keV are illustrated in **Figure 7**. The distribution profile of positron implantation depth becomes more widespread as E_{in} increases (**Figure 7**). In general samples have to be mounted under vacuum conditions during measurement in the slow positron method.

Figure 7: Typical distribution of positron implantation depth in a polyamide membrane sample with a positron incident energy of 1.0, 2.0 and 3.0 keV (Unpublished).

A typical example of a positron lifetime measurement system using a slow positron beam is described in Figure 6b. The lifetime of positron is measured as the time difference between the pulsing trigger from the beam pulsing system (start timing signal) and the detection timing of the annihilation γ -ray detected by a scintillation detector (stop timing signal) [61]. The measurement is carried out under vacuum (e.g., 10^{-5} Pa). Approximately $2-3 \times 10^6$ events of positron annihilation are collected to obtain one positron lifetime spectrum. A typical lifetime spectrum obtained using the slow positron method is shown in Figure 8. In general, lifetime spectrum is analysed with a few parameters in an exponential decaying curve $\sum_i \frac{I_i}{\tau_i} \exp\left(-\frac{t}{\tau_i}\right)$ where τ_i and I_i are the lifetime and relative intensity ($\sum_i I_i = 1$) of component i , respectively. In most cases, components longer than 1 ns can be attributed to the *o*-Ps lifetime. The positron lifetime spectra can be analysed by deriving τ_i and I_i using a non-linear least-squares fitting program in which the time resolution function of the measurement system is taken into account. Further details of PALS are described elsewhere [17, 59].

Figure 8: Example of lifetime spectrum obtained using the slow positron method (Unpublished).

3.1.2. Doppler broadening of annihilation radiation

Unlike PALS from which information associated with the size of free-volume holes is obtained by measuring positron/Ps lifetimes, DBAR can yield other/additional information related to the structure of the sample by measuring the annihilation γ -ray energy spectrum. For example, the shape of the energy spectrum around the 2- γ annihilation peak (511 keV) is affected by the chemical composition and electron state at the site of the positron annihilation

within the sample. Therefore, DBAR can often detect changes in the nano-structure of samples even if their free-volume hole-sizes are the same.

2- γ decay probability of *o*-Ps due to the pick-off annihilation increases with decreasing free-volume hole-size and consequently 3- γ decay probability decreases. Therefore, we can obtain information on free-volume hole-size if we measure ratio of 2- γ decay to 3- γ decay. When *o*-Ps is annihilated with 2- γ decay, γ -ray energy is detected at 511 keV. On the other hand, *o*-Ps annihilated with 3- γ decay is detected at a lower energy with a broader distribution (e.g., 365–495 keV) [22]. The 3- γ /2- γ annihilation ratio is evaluated by analysis of the energy spectrum.

The γ -ray energy spectra can be collected by using a Germanium detector [62, 63]. With the slow positron method, the top surface of the sample can be analysed by DBAR. DBAR is useful to qualitatively evaluate changes in chemical composition, electron bonding state, and free-volume hole-size. Although this review focuses particularly on PALS which is directly linked to the measurement of free-volume hole-radius, it is noteworthy that DBAR can be used in conjunction with PALS to analyse the inner structure of free-volume holes.

3.2. Characterisation of RO membranes

3.2.1. Free-volume hole-radius of the active skin layer

Over the past decade PALS techniques have been progressively applied to the analysis of the internal structure of NF/RO membranes [63-71]. The free-volume hole-radius of commercial NF/RO membranes reported in literature is summarised in Table 3. The beam intensity (E_{in}) range (1.0-2.0 keV) used corresponds to a mean positron implantation depth of 40-200 nm for a material density of 1.0 g/cm³. The reported free-volume hole-radius for SWRO, LPRO and NF membranes are in the range of 0.24-0.26, 0.20-0.29, and 0.26-0.31 nm, respectively (Table 3). There is thus only a small variation in free-volume hole-radius among the three different membrane categories (i.e., SWRO, LPRO and NF), while the separation of neutral solutes (i.e., boron and NDMA) apparently increases in the order of NF, LPRO and SWRO (Table 1). The overall trend reported suggests that membrane classification (i.e., NF, LPRO and SWRO) is not necessarily based on the free-volume hole-radius. Discussions about the importance of free-volume hole-radius on solute rejection are provided in Section 4. It is important to note that free-volume hole-size is equivalent in size to monomers comprising the

active skin layer. For example, m-phenylenediamine and trimesoylchloride, which are traditionally used for the interfacial polymerisation of the active skin layer [72], are approximately both 0.35 nm in width and 0.9 and 1.5 nm in length, respectively. These small monomers allow the construction of subnanometre-scale polymer network with free-volume holes.

Table 3: Free-volume hole-radius of commercial NF/RO membranes analysed by PALS.

Type	Membrane	Manufacturer	Material ^a	E_{in} [keV]	<i>o</i> -Ps lifetime [ns]	Hole radius [nm]	Ref.
SWRO	SWC5	Hydranautics/Nitto	PA	1.0	1.75	0.259	[20]
	SW30	Dow/Filmtec	PA	-	1.56	0.240	[24]
LPRO	ESPAB	Hydranautics/Nitto	PA	1.0	2.07	0.289	[20]
	ESPA2	Hydranautics/Nitto	PA	1.0	2.07	0.289	[20]
	LF10	Nitto	PA	2.0	1.27	0.203	[22]
	FT30	Dow/Filmtec	PA	-	1.37	0.217	[23]
	ESPA2	Hydranautics/Nitto	PA	1.0	1.83	0.267	[69]
	TFC-HR	KMS	PA	1.0	1.83	0.267	[69]
	AG	GE	PA	1.0	1.48	0.231	[70]
	AK	GE	PA	1.0	1.57	0.241	[70]
NF	NTR729HF	Nitto	SPS	2.0	1.79	0.265	[22]
	NTR7250	Nitto	SPS	2.0	1.85	0.271	[22]
	ESNA-K1	Hydranautics/Nitto	PA	2.0	1.93	0.279	[64]
	ESNA-K1	Hydranautics/Nitto	PA	2.0	2.30	0.312	[65]
	DK	GE	PA	1.0	1.76	0.262	[70]

^a PA: Polyamide; SPS: Sulphonated Polyether-Sulphone; n.a.: not available.

PALS using a slow positron beam allows the depth profile of free-volume hole-radii to be evaluated. An example using a LPRO membrane (LF10, NittoDenko) is shown in **Figure 9a** [22]. The minimum positron lifetime (i.e., 1.26 ns) – equivalent to the minimum mean free-volume hole-radius of 0.203 nm – was obtained with an incident energy (E_{in}) of 0.8-2.2 keV corresponding to an average implantation depth of about 40-150 nm (**Figure 9a**). This indicates that the active skin layer has a uniform size distribution of free-volume hole-radius across its thickness. As E_{in} further increases from 3 keV, more positrons are likely to be injected in a deeper location (e.g., >150 nm in depth) where the interface between the active skin layer and the supporting layer is found. The increased free-volume hole-size as a result of increasing E_{in} (i.e., 0.21-0.24 nm at 3.0-5.0 keV) (**Figure 9a**) may indicate the measurement of free-volume hole-radius in the matrix of the supporting layer. Overall, the results here indicate that the thickness of the active skin layer is approximately 150 nm, which is comparable to values reported from high resolution TEM analysis [29].

Figure 9: Variation in the (a) *o*-Ps lifetime and corresponding free-volume hole-radius and (b) R parameter as a function of positron incident energy for a LPRO membrane (LF10/Hydranautics) (Reproduced with permission from Ref. [22]. Copyright 2011 ACS Publications).

3.2.2. Thickness of the active skin layer

Thickness of the active skin layer and the multiple-layer structure can be estimated from changes in positron annihilation parameters (e.g., positron/*o*-Ps lifetime and their intensities), and/or the $3\gamma/2\gamma$ ratio (also called the R parameter). The R parameter, which can be determined as a function of E_{in} , represents the relative amount of 3γ annihilation that occurs in large (submicron-scale) pores or voids. The R parameter generally increases with the population of the large holes [62]. Typically, high R values can be identified at the surface and supporting layers of TFC membranes [73]. For example, R can be high at the membrane surface (0.7 keV) where more *o*-Ps can escape from shallow free-volume holes via interconnected holes and self-annihilate by 3γ decay (Figure 9b). With positrons penetrating deeper in the sample by increasing E_{in} between 0.7-1 keV, more *o*-Ps undergo 2γ pick-off annihilation resulting in a decrease in R. In the lowest R region at 1-2.2 keV, 2γ pick-off annihilation predominantly occurred across the membrane, indicating that free-volume holes with a diameter of <1 nm are most identified in the 40-150 nm top layer (Figure 9b). The top layer (<150 nm in depth) can be recognised as the active skin layer. Thereafter (e.g., 2.2-5 keV), the R parameter increased (Figure 9b). This indicates that the layer is intermediate between the dense active skin layer and porous supporting layer, which may be called the transition layer. The high R parameter in the 5-10 keV E_{in} range can be interpreted as relatively large pores existing in the supporting layer and considerable fraction of *o*-Ps

annihilated there. The results suggest that R parameter can be a useful indicator to estimate the change of phases (i.e., active skin layer and supporting layer), thus enabling estimating of the thickness of the active skin layer.

4. Effect of membrane properties on solute rejection

4.1. Free-volume hole-radius

The free-volume hole-size of RO membranes can be the single most important factor governing the separation of small and neutral solutes including boric acid. Thus, rejection of a given solute is expected to vary in response to changes in free-volume hole-size. Indeed, Fujioka et al., [20] showed that the free-volume hole-radius of a SWRO membrane (0.26 nm) was smaller than that of LPRO membranes (0.29 nm). Correspondingly, boron rejection by SWRO membranes (81%) was higher than that by LPRO membranes (36-59%). Henmi et al., [21] evaluated boron rejection using similar types of SWRO membranes and reported that the rejection of boron decreased with increasing free-volume hole-radius (Figure 10). Several other studies have also revealed a strong correlation between free-volume hole-size and rejection of several other neutral solutes [22, 70]. For example, Chen et al., [22] reported that the rejection of four neutral solutes (urea, ethylene, 1-propanol, and 2-propanol) correlated well with the molecular volume of solutes (V_m) and the volume of sphere-shaped free-volume holes (V_f) in the membrane (Figure 11). The results indicate that free-volume holes play an important role in determining the degree of rejection of neutral solutes.

Figure 10: Boron rejection by SWRO membranes as a function of their free-volume hole-radius (Reproduced with permission from Ref. [21]. Copyright 2010 IWA Publishing).

Figure 11: Correlation between the rejection of the uncharged organic compounds and the ratio of the compound size (V_m) to the free-volume hole size (V_f) for the active skin layer in the RO (LF10) and NF (NTR729HF and NTR7250) membranes (Reproduced with permission from Ref. [22]. Copyright 2011 ACS Publications).

In addition to free-volume hole-size, several other membrane properties may influence boron rejection. Sasaki et al., [74] showed that boron rejection by modified SWRO membranes is not clearly correlated with their free-volume hole-radius. Data from other two studies [20, 69] also showed no apparent correlation between free-volume hole-size and boron rejection for LPRO membranes. For example, a large variation in boron rejection (27-69%) was found between three LPRO membranes with the same free-volume hole-radius (i.e., 0.267 nm) [69].

4.2. Other membrane properties

Other potentially important physicochemical properties of RO membranes for neutral solute rejection include free-volume fraction and thickness, which can vary among RO membranes even with identical mean free-volume hole-radius. No previous studies have evaluated the effect of these properties on neutral solute rejection by RO membranes. This is probably in part due to the technical challenges in their accurate quantification. In general, an increase in free-volume fraction of the active skin layer increases the diffusivity of water and solute, enhancing water permeability and solute permeation. A trade-off between water permeability and solute selectivity has been reported in previous studies [75, 76]. Experimental results from a study by Bernstein et al., [77] (Figure 12) indicate that there is a strong correlation between the permeability of several RO membranes and boron rejection. These results imply that free-volume fraction – an important indicator of permeability – can influence solute

rejection. The basic solution-diffusion model described in Section 2.2 indicates that solute rejection is dependent on thickness [78]. In addition, an extended solution-diffusion model that has included the concept of free-volume holes shows that solute rejection is determined with these two parameters (i.e., thickness and free-volume fraction) as well as free-volume hole-radius [36]. As a result, solute transport through RO membranes is likely to depend on multiple factors.

Figure 12: Boric acid passage and membrane permeability of commercial BWRO (grey squares) and SWRO (black triangles) elements as reported by the manufacturers, Empty triangles show results for commercial membranes tested in dead-end cells and empty circles show the dead-end cell results for LE membranes modified with glycidyl methacrylate (GMA) to a different degree (Degree of grafting = 0.67 and 1.1) (Reproduced with permission from Ref. [77]. Copyright 2011 ACS Journal).

The other property that can potentially influence neutral solute rejection is the real surface area of the top active skin layer. RO filtration systems are generally operated under constant water flux (e.g., 20 L/m²h for wastewater recycling applications [49]) which is calculated based on their apparent membrane surface area. While a constant water flux can be employed for different RO membranes, their real local water flux can vary depending on the membrane surface conditions. In general, a rougher membrane has a larger surface area (Section 2.1), leading to a higher permeability (Table 4). Membranes with a small surface roughness have a real surface area similar to the apparent surface area. As a result, their real local water flux can be similar to the tested experimental water flux (Table 4). In contrast, membranes with a rougher surface (i.e., a higher surface area) can have a lower real local water flux under the identical apparent water flux. As a result of the decreased local water flux, solute rejection

also decreases (Table 4) as described in Section 2.2. To evaluate this mechanism, PAS can play an important role in confirming the free-volume hole-radius and thickness of the target membranes.

Table 4: Effects of RO membrane active skin layer surface area on solute rejection. The active skin layers in A and B have the same free-volume hole-radius. Apparent surface area and water flux refer to values that can be measured over a large area of sample without taking into account the local (micrometre scale) surface roughness. Real surface area and water flux refer to values calculated at micrometre scale level taking into account the local surface roughness.

Case	A (Low roughness)	B (High roughness)
Schematic cross-sectional image
Properties		
a. Apparent surface area	S_A	$S_B = S_A$
b. Real local surface area	$S_{A (local)}$	$S_{B (local)} > S_{A (local)}$
c. Permeability	L_A	$L_B > L_A$
Conditions		
a. Apparent water flux	J_A	$J_B = J_A$
b. Real local water flux	$J_{A (local)} \approx J_A$	$J_{B (local)} < J_{A (local)}$
c. Effective pressure	ΔP_A	$\Delta P_B < \Delta P_A$
d. Rejection	R_A	$R_B < R_A$

5. Future research roadmap

5.1. Current challenges

State-of-the-art analytical techniques (e.g., PAS, SEM, TEM, and AFM) have allowed RO membrane properties to be comprehensively evaluated as described earlier. Using experimentally evaluated separation performance (e.g., solute rejection and permeability), previous studies [20-22, 70] revealed that free-volume hole-radius in the active skin layer is a key property governing the rejection of small and neutral solutes. Nevertheless, these rejections are not solely dependent on free-volume hole-radius, and there may still be uncertainties with respect to the impact of several other membrane properties. These include free-volume hole-shape, hole-size distribution, and free-volume fraction. While the contribution of these properties to the rejection of uncharged solutes remains unclear, the

quantification of these membrane properties can greatly assist in furthering our understanding of solute-membrane interaction during RO filtration.

Firstly, free-volume hole-shape can play an important role in the rejection of solutes. Kiso et al., [79] investigated the effects of compound shape on their rejection and reported that the shape of compounds is an important parameter governing their rejections. Thus, a large variation in separation performance is expected among RO membranes with identical free-volume hole-radii but with different shapes. In addition, local segmental dynamics of the polymer chain surrounding a free-volume hole in water, which cannot be evaluated by PALS, but is of great interest. The impact of the local segmental dynamics on the shape and size of free-volume holes, in particular at a high temperature, may be significant. It is noteworthy that free-volume holes analysed using PALS are assumed to be spherical and their shapes cannot be determined by PALS; thus, another analytical technique needs to be developed to clarify the impact of hole geometry on the measurements.

The size distribution of free-volume holes is another potential factor. Given that free-volume hole-size is one of the most important factors, quantification of the hole-size distribution rather than the mean value is required. In typical PALS, free-volume hole-radius is determined as the mean value as described in Section 3.1. The distribution of *o*-Ps lifetime and corresponding free-volume hole-radius can be estimated by processing the PALS spectrum with inverse Laplace transformation [21, 64, 65, 80]. The lifetime distribution analytical software includes MELT and CONTIN [65, 73, 81]. In some cases, positron annihilation lifetime can be analysed with 4 component lifetimes. For example, the large holes named as nanocavities have been evaluated by using τ_4 (>30 ns), resulting in free-volume hole-radii of 1.6-4.6 nm [82]. Kim et al., [23] divided annihilation lifetime (1-5 ns) into two regions – a shorter lifetime (τ_3) and a longer lifetime (τ_4) – which in the study corresponded to small ($r = 0.21$ - 0.24 nm) and large ($r = 0.35$ - 0.45 nm) free-volume holes, respectively. Despite the difficulty in understanding the complete annihilation process of all of positrons through *o*-Ps formation in a sample, it is necessary to reconcile the difference between the actual properties (i.e., hole-shape and hole-size distribution) and the underlying assumption of current PALS techniques (i.e., spherical shape and uniform size).

In addition, the free-volume fraction of the active skin layer could also be key factors that influence solute rejection. PAS techniques available to date are not able to quantify the free-volume fraction. This suggests that analytical techniques other than PAS may be required to quantify the free-volume fraction of the active skin layer. Additionally, hole-connectivity is of great interest for understanding solute transport, given that the difference in solute transport phenomenon between the representative two models (i.e., solution-diffusion and pore-flow models) is essentially the permanency of free-volume holes [31]. Some free-volume holes may be independently present as closed holes which clearly are not involved in solute separation.

Another challenge is associated with sample condition. Almost all previous PAS studies using slow positron methods have been performed under vacuum. [Membrane sample preparation with drying may cause physical damage to the active skin layer. More importantly, considering RO membranes for water treatment applications are utilised in water under high pressure conditions, free-volume hole-size obtained through the current PALS may be different from actual free-volume hole-size within TFC membranes during filtration. For example, a previous study using RI-based PALS reported that the free-volume hole-radius of SWRO \(SW30, Dow/Filmtec\) membranes can increase by approximately 0.02 nm by increasing relative humidity from 0 to 100% due possibly to hole swelling effects \[24\]. Swelling may expand the polymer network, hence, influencing the membrane permeability and selectivity \[66, 83\]. Although PALS analysis with a slow positron beam under water may be impossible, the impact can be partly clarified by utilising a pulsed beam PALS which is designed to analyse membranes under atmospheric conditions with high humidity \[84\]. A recent development in PALS allows thin films to be successfully analysed under a range of humidity \[85\]. There are only a few studies to date where polyamide-based TFC membranes were analysed in a wet state using a slow positron beam \[62, 66\]. They developed a method that membrane samples are maintained under wet conditions with multiple additional layers placed on the membrane in sealable membrane sample folder. The effect of using a membrane in a wet state in the study \[62\] was consistent with the previous study where relative humidity was adjusted \[24\]; that is, free-volume hole enlarges with water content by hole swelling.](#)

588 5.2. Complementary techniques

589 As described in Section 5.1, solute rejection by RO membranes can be governed by not only
590 the free-volume hole-radius but also other factors such as hole-shape, hole-size distribution,
591 and free-volume fraction of the active skin layer that may not be measured by PALS.
592 Molecular dynamics (MD) simulation has significant potential to fill the gap and may achieve
593 a breakthrough in understanding the mechanisms of solute rejection. MD simulation has
594 increasingly used to predict solute and water transport through RO membranes at the
595 molecular level [86, 87]. MD simulations, which are based on computational models of
596 molecular systems, are capable of describing the solution- and solute-diffusion through
597 membrane polymer chains.

598 A three-dimensional representation of the active skin layer for MD simulation using
599 physicochemical properties (e.g., material compositions, charge density of functional groups,
600 and cross-linking degree) can be constructed. By optimising the polymer chain energy, the
601 three-dimensional representation can then provide further insight about free-volume shape,
602 free-volume fraction, and connectivity of free-volume, which cannot be currently determined
603 by PAS including PALS. The change of molecular structure in pure water as well as in saline
604 water that could occur due to the local segmental dynamics of the polymer chain may also be
605 simulated.

606 An example of MD simulation of the transport of Na^+ , Cl^- , and water in a polyamide layer is
607 shown in Figure 13 [13]. The diffusivity of water and target compounds in the membrane can
608 be quantified through the MD simulation. As summarised in Table 5, the calculated Na^+
609 diffusivity (D_{Na^+}) in the polyamide is much smaller than that for the calculated water
610 diffusivity (D_{water}) leading to a very large selectivity ($D_{\text{water}}/D_{\text{Na}^+}$), an order of magnitude
611 greater than for an aqueous NaCl solution. Because hydrated Na^+ is larger than water
612 molecule in size, the number of free-volume holes in the molecular model that hydrated Na^+
613 can occupy was far less than that of water molecule. In fact, the mean radius of free-volume
614 holes determined by PALS ($r = 0.24\text{-}0.27$ nm) was smaller than the first hydration shell size
615 of Na^+ , which is approximately 0.35 nm [13]. It was postulated that the size of the solute
616 (Na^+) being larger than most of free-volume holes contributed to the large selectivity
617 ($D_{\text{water}}/D_{\text{Na}^+}$) in the membrane [13]. Similarly, the impact of free-volume holes on neutral

solute rejection can also be evaluated by calculating the diffusion coefficients of the solute in the membrane and identifying free-volume holes in the molecular model that are available for the solute to diffuse through. Despite the progressive development and the versatility of MD simulation, it is still necessary to cross-check free-volume hole-size determined by PALS with that calculated by the model. The molecular model used for MD simulation is typically developed by three dimensionally interconnecting a certain length of polymer chains; thus, ensuring the modelled structure represents realistically the molecular structure. In fact, several previous studies [13, 19, 66, 88] have attempted to simulate NaCl permeation through TFC membranes using MD simulations and PAS data. To the best of our knowledge, no studies have simulated the transport of small and neutral solutes (e.g., boric acid) through RO membranes.

Figure 13: Schematics of typical molecular model used for MD simulations. Yellow sphere: Na^+ , Blue sphere: Cl^- , Small molecule consisting of red and white lines: Water (Reproduced with permission from Ref. [13]. Copyright IOP Publishing Ltd).

Table 5: Diffusion coefficient ($\times 10^{10} \text{ m}^2/\text{s}$) of water and Na^+ at 25 °C that is calculated by MD simulation using the model described in Figure 14 (Reproduced with permission from Ref. [13]. Copyright IOP Publishing Ltd).

Material	D_{water}	D_{Na^+}	$D_{\text{water}} / D_{\text{Na}^+}$
NaCl aqueous solution	26.7	10.2	2.61
Polyamide	3.86	0.0181	213

6. Conclusions

Further improvements of the RO membrane require a comprehensive understanding of interactions between solute and membrane at near molecular level. Positron annihilation spectroscopy (PAS) using a slow positron beam revealed that RO membranes have a very thin active skin layer with sub-nanometre-sized free-volume holes. Until recently the difficulty in analysing the internal membrane structure has been a major obstacle in elucidating RO membrane transport mechanisms. PAS using a slow positron beam is a powerful tool to investigate the subnanometre-scale inner structure of the active skin layer. Positron annihilation lifetime spectroscopy (PALS) data corroborated in this review showed that commercially available RO membranes have a mean free-volume hole-radius of 0.20-0.29 nm in the active skin layer with the thickness of approximately 100 nm. PALS experimental results clearly show that free-volume hole-size can be the most important parameter determining the rejection of boron which is neutral at environmental pH. The literature data also suggests that, in addition to the free-volume hole-size, the free-volume fraction of the active skin layer may also have an important role in solute rejection. This review article also proposes that another membrane property (i.e., thickness) is a factor influencing solute transport. Major limitations to further understand the solute transport lies in the measurement of free-volume fraction, free-volume hole-shape and hole-size distribution. A better understanding of membrane transport is possible through MD simulation in combination with free-volume hole-size measured by PALS.

7. References

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