



# Effects of water chemistry on structure and performance of polyamide composite membranes



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## ABSTRACT

The effects of feed solution ionic strength, pH and divalent cation content on NF/RO membrane structure and performance were elucidated experimentally and fitted with a modified solution–diffusion transport model that describes polyamide thin film free volume through an effective pore radius and structure factor. All the membranes tested became more hydrophilic and swollen with increasing feed solution ionic strength, pH, and divalent cation concentrations. Generally, water permeabilities of all three membranes decreased with ionic strength and divalent cation content, but increased with pH. For RO membranes, neutral solute rejection decreased with pH and divalent cation content, but increased with ionic strength and the salt rejection remained independent with water chemistry except for very low pH of 3; for a NF membrane, solute rejection was more sensitive to water chemistry and neutral solute rejection decreased with ionic strength and pH, but increased with divalent cation content. The results presented herein provide new insight into the fundamental relationship between changes in NF/RO membrane structure and performance. Ultimately, these new insights may be useful in selection of already commercial or design of new NF/RO membranes for removal of chemicals of emerging concern in water treatment.

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## 1. Introduction

The excellent separation performance and broad applicability of nanofiltration (NF) and reverse osmosis (RO) membranes have led to widespread employment in drinking water production, wastewater treatment and industrial separations [1]. These are well-studied materials and processes. One remaining challenge is a quantitative understanding of the relationship between NF/RO membrane structure, separation performance and feed solution chemistry. In a recent review, Luo and Wan comprehensively summarized the effect of solution pH and salt content on NF membrane transport [2]. Different mechanisms are proposed depending on solute type [1,3–8]. For charged solutes, it is thought that increasing ionic strength, divalent cation content and lower pH all reduce Donnan exclusion, and hence, enhance ion permeation through by charged NF/RO membranes [9,10]. However, charge interactions cannot explain changes in neutral solute rejection, which have been also observed with changes in feed

water chemistry. Some researchers suggest reduction in the Stokes radius of neutral solutes due to salt ions with higher hydration energy outcompeting neutral solutes for water molecules [11,12]. Membrane swelling and de-swelling have also been proposed to explain changes in neutral solute rejection with differences in feed water pH and ionic strength [5]. Freger and co-workers measured changes in polyamide layer thickness using atomic force microscopy (AFM) after soaking membrane in solution with different salt concentrations and pH [6]. They observed a correlation between the changes in polyamide layer thickness, permeability and solution chemistry (salinity and pH).

Historically, it has been difficult to directly characterize NF/RO membrane structure (pore size, film thickness, porosity) when exposed to different water chemistries. Current dense polymer film structure characterization techniques may not be accurate enough to resolve subtle changes [2]. Also, most structural characterization techniques are not conducted in representative process conditions (saturated with water and solute, wet, flowing and under positive feed pressure). Many researchers have attempted to calculate membrane structure parameters with neutral solute rejection data based on membrane transport models [2,13,14]. Luo and Wan fitted experimental glucose rejection data with a membrane transport model considering steric exclusion to estimate an apparent

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membrane pore size and structure factor (the ratio of membrane thickness to porosity) for high salinity feeds [9]. Verliefe et al. claimed that solute transport predictions made by assuming only steric exclusion significantly overestimated solute rejection. They established a “solute–membrane affinity” model (essentially an extended solution–diffusion model), which considered both steric effects and solute–membrane interactions, to predict neutral solute rejection by NF membranes [14]. However, in these studies only one background water chemistry was evaluated. Moreover, two structure parameters (pore size and structure factor) were estimated by one transport equation (solute rejection). With only one equation and two unknowns the structure factor was assumed to extract a relative pore size.

The main goal of this study was to expand upon the extended solution–diffusion model of Verliefe et al. [14] to more accurately quantify changes in membrane structure and solute–solvent–membrane interactions due to changes in feed water chemistry (ionic strength, pH and divalent cation content). Ultimately, this work provides new structure–performance insights into polyamide NF/RO membrane separation performance. Herein, the extended solution–diffusion model accounts for both water flux and (neutral) solute rejection. Therefore, we provide two equations that allow one to directly solve for the two membrane structural descriptors (i.e., effective pore radius and structure factor) by properly fitting to experimentally observed flux and rejection data.

## 2. Model development

In the classical solution–diffusion transport model, water and solute are understood to partition into and diffuse through a “nonporous” membrane skin layer. However, according to molecular dynamic simulations and advanced characterization techniques (e.g., AFM, TEM, NMR, PALS) the free volume throughout the dense polyamide layer contains interconnected pore-like voids with characteristic dimensions in the size range of 0.2–0.6 nm [15–18]. Herein, we model dense polymer film fractional free volume (FFV) with a hypothetical cylindrical capillary pore size ( $r_p$ ), porosity ( $\epsilon$ ) and pore length ( $\Delta x = \tau l$ ,  $\tau$  is the tortuosity and  $l$  is the membrane thickness). Among a number of possible errors introduced by such simplified free volume geometry, one of the more obvious issues is that this model ignores the possibility of having free volume spaces that are partially or wholly inaccessible by either solvent or solute. This model also ignores the well known rugose morphology of polyamide RO membranes, the effects of which are only beginning to be studied theoretically and quantitatively [19,20].

Notwithstanding these simplifications, volumetric water flux ( $J_w$ ) can be derived from the classical solution–diffusion model as

$$J_w = A(\Delta p - \Delta \pi) = \frac{K_w D_{w,m} V_w}{\Delta x R_g T} (\Delta p - \Delta \pi) \quad (1)$$

where  $A$  is the water permeability,  $\Delta p$  and  $\Delta \pi$  are applied pressure and osmotic pressure difference across membrane, respectively,  $D_{w,m}$  is the water diffusion coefficient in membrane,  $V_w$  is the molar volume of water,  $R$  is the gas constant and  $T$  is the temperature. The water solubility ( $K_w$ ) in the membrane is defined as [21]

$$K_w = \frac{C_{w,m}}{C_{w,f}} \quad (2)$$

where  $C_{w,m}$  is the equilibrium water concentration in the membrane,  $C_{w,f}$  is the equilibrium water concentration in the feed side of membrane and  $C_{w,m}$  can be defined as

$$C_{w,m} = C_{w,p} \epsilon \quad (3)$$

where  $C_{w,p}$  is the equilibrium water mass concentration in membrane pores (free volume). The ratio of  $C_{w,p}$  to  $C_{w,f}$  can be defined as water–membrane pore partition coefficient ( $\phi_w$ ) [14]

$$\phi_w = \frac{C_{w,p}}{C_{w,f}} \quad (4)$$

Combining Eqs. (1)–(4) yields

$$K_w = \phi_w \epsilon \quad (5)$$

According to water–membrane partition model [14,22].

$$\phi_w = (1 - \lambda_w)^2 \exp\left(-\frac{\Delta G_{mw}}{kT}\right) \quad (6)$$

where  $\Delta G_{mw}$  is the water–membrane interaction energy,  $k_B$  is the Boltzmann constant, and  $\lambda_w$  is the ratio of water Stokes radius,  $r_w$ , to membrane pore radius,  $r_p$ .

Water diffusion coefficient in membrane ( $D_{w,m}$ ) can be related to water diffusivity in bulk ( $D_{w,\infty}$ ) by diffusive hindrance factor ( $K_d$ ) [23].

$$D_{w,m} = K_d D_{w,\infty} \quad (7)$$

Combining Eqs. (1)–(7) yields

$$J_w = \frac{K_d D_{w,\infty} \epsilon}{\Delta x} (1 - \lambda_w)^2 \exp\left(-\frac{\Delta G_{mw}}{kT}\right) \frac{V_w}{R_g T} (\Delta p - \Delta \pi) \quad (8)$$

where

$$A = \frac{K_d D_{w,\infty} \epsilon}{\Delta x} (1 - \lambda_w)^2 \exp\left(-\frac{\Delta G_{mw}}{kT}\right) \frac{V_w}{R_g T} \quad (9)$$

From Eq. (9), it becomes apparent that a membrane's water permeability is determined from membrane and water physical properties ( $r_w$ ,  $r_p$ ,  $\epsilon$ ,  $\Delta x$ ) and chemical affinity ( $\Delta G_{mw}$ ). The porosity ( $\epsilon$ ) and effective pore length ( $\Delta x$ ) may be lumped together to describe a membrane “structure factor ( $S$ )” that in other models is the combination of thickness, porosity and tortuosity ( $\tau$ ) (i.e.,  $S = \tau l / \epsilon$  where our  $\Delta x = \tau l$ ) [24,25].

Water–membrane interaction energy ( $\Delta G_{mw}$ ) can be related to the interfacial tension between water and the membrane [26]

$$\Delta G_{mw} = -2A_w \left( \sqrt{\gamma_w^{LW} \gamma_m^{LW}} + \sqrt{\gamma_w^+ \gamma_m^-} + \sqrt{\gamma_w^- \gamma_m^+} \right) \quad (10)$$

where  $\gamma^{LW}$  is the apolar (Lifshitz–van der Waals) component of the surface tension,  $\gamma^+$  and  $\gamma^-$  are the polar (electron-acceptor and electron-donor) components of the surface tension (subscripts  $w$  and  $m$  refers to water and membrane, respectively) and  $A_w$  ( $= \pi r_w^2 / 2$ ) is the contact area between water molecular and membrane.

Solute transport occurs by solute diffusion and coupled transport with solvent permeation [14,27]. Solute flux,  $J_s$ , across the membrane can be described as

$$J_s = -K_d D_{s,\infty} \frac{dc}{dx} + \frac{J_w}{\epsilon} K_c c \quad (11)$$

where  $c$  is the solute concentration within membrane pore and  $K_c$  is the convective hindrance factor. Observed rejection,  $R_o$ , can be obtained by integrating Eq. (11) across the membrane thickness, using the boundary conditions

$$\begin{aligned} c &= \phi_s \beta C_f \quad \text{at } x = 0; \\ c &= \phi_s C_p \quad \text{at } x = \Delta x; \end{aligned}$$

$$R_o = 1 - \frac{C_p}{C_f} = 1 - \frac{\beta \phi_s K_c}{1 - (1 - \phi_s K_c) \exp\left(-\left(\frac{J_w K_c S}{K_d D_{s,\infty}}\right)\right)} \quad (12)$$

where  $\beta$  is the concentration polarization factor,  $\lambda_s$  is the ratio of solute radius,  $r_s$ , to membrane pore radius,  $r_p$ . Here,  $\phi_s = (1 - \lambda_s)^2 \exp(-(\Delta G_{mws}/kT))$  and solute–membrane interaction energy ( $\Delta G_{mws}$ ) is calculated from [26]

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