

# Supporting Information

## Elucidating the roles of polyamide layer structural properties in permeability-selectivity tradeoff governing aqueous separations

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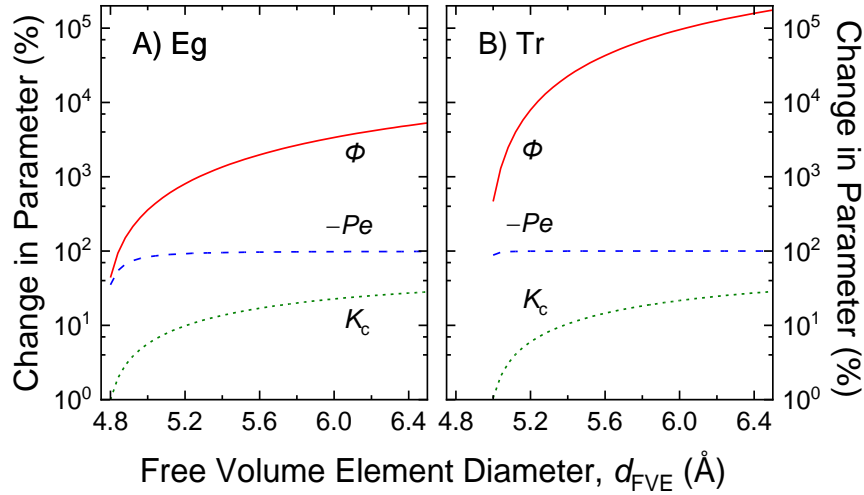
## ■ THE PERMEABILITY-SELECTIVITY TRADEOFF RELATIONSHIP DESCRIBED BY DIFFERENT TRANSPORT MODELS

**Impacts of Free Volume Diameter on Selectivity Parameters of the Hindered Transport Model.** The membrane water-solute selectivity,  $\alpha$ , is formulated in eq. 11 in the main manuscript using the hindered transport model:

$$\alpha = \left[ \frac{1 - \exp(-Pe)(1 - \Phi K_c)}{\Phi K_c} - 1 \right] \times \frac{RT}{v_w (\Delta P - \Delta \pi)} \quad (11)$$

where  $\Phi$  is the water-solute partition coefficient and is related to the ratio of the solute diameter to the effective pore size,  $\omega$  ( $0 < \omega < 1$ ), by  $\Phi = (1 - \omega)^2$ ,  $K_c$  is the convective hindrance factor,  $Pe$  is the membrane Peclet number,  $v_w$  is the molar volume of water,  $\Delta P$  is the applied hydraulic pressure,  $\Delta \pi$  is the transmembrane osmotic pressure difference,  $R$  is the gas constant, and  $T$  is the absolute temperature.

Employing the Hagen-Poiseuille equation,  $J_w = (\Delta P - \Delta \pi) d_p^2 / (32 \eta_w L)$ , in  $Pe$  yields  $Pe = K_c d_p^2 (\Delta P - \Delta \pi) / (32 \eta_w K_d D_s^{aq})$ .<sup>1,2</sup> Hence, the three parameters in  $\alpha$ ,  $-Pe$ ,  $\Phi$ , and  $K_c$ , are all functions of only effective pore size  $d_p$ , and are independent of transport pathway. To analyze the impacts of  $d_p$  on the three parameters, a conversion factor  $f_h$  is applied to account for the polymer hydration effects on the pore size, i.e.,  $d_p = f_h d_{FVE}$ .  $f_h = 1.08$  according to the analysis in the main manuscript. Percentage changes in  $\Phi$ ,  $-Pe$ , and  $K_c$  as a function of the membrane free volume diameter  $d_{FVE}$  are examined in Figure S1. The partition coefficient is defined as ratio of the mean solute concentrations in the membrane phase to that in the aqueous phase,  $\Phi = \langle c_{s,F}^m \rangle / c_{s,F}^{aq} = \langle c_{s,P}^m \rangle / c_{s,P}^{aq}$ , where subscripts “F” and “P” denote feed and permeate in reverse osmosis and nanofiltration and superscripts “m” and “aq” represent membrane and aqueous phases, respectively.<sup>3-5</sup> Enlarging  $d_{FVE}$  by 33% significantly increases the water-solute partition coefficient,  $\Phi$ , by 4 orders of magnitude, which greatly enhances the solute concentration in the membrane matrix and decreases the selectivity. In comparison,  $-Pe$  and  $K_c$  increase by  $\approx 99\%$  and  $\approx 30\%$ , respectively. Overall, increasing FVE size most significantly elevates the partitioning coefficient, thus facilitating the solute to partition into the membrane matrix and decreasing the selectivity.



**Figure S1.** Impacts of free volume element diameter,  $d_{FVE}$ , on selectivity parameters  $-Pe$ ,  $\Phi$ , and  $K_c$  for A) Eg and B) Tr. The vertical axis represents percentage change and is in logarithmic scale.

### Permeability-Selectivity Behaviors under the Solution-Diffusion Framework.

Detailed presentations on the application of the solution-diffusion (S-D) framework in aqueous separation membranes can be found in our previous study and other literature,<sup>6-9</sup> and are succinctly introduced here. The classic S-D model describes the permeability of the membrane to penetrant  $i$  (water or solute),  $P_i$ , as the product of the sorption coefficient,  $K_i$ , and diffusivity,  $D_i$ , i.e.,  $P_i = K_i D_i$ . In aqueous separations, the S-D framework relates the water and solute permeance coefficients,  $A$  and  $B$ , respectively, to membrane permeabilities to water ( $P_w$ ) and solute ( $P_s$ ) by  $A = P_w v_w / LRT$  and  $B = P_s / L$ , where  $v_w$  is the molar volume of water,  $R$  is the gas constant,  $T$  is the absolute temperature, and  $L$  is the effective membrane thickness (equivalent to effective membrane transport pathway in this study).

The tradeoff trend between permeability and selectivity is being increasingly documented for thin-film composite polyamide membranes in aqueous separations<sup>9-12</sup> and is described by an empirical relationship:  $P_w/P_s = \beta/P_w^\lambda$ , where  $\beta$  and  $\lambda$  are fitting parameters. Substituting permeabilities in the empirical equation with membrane permeance coefficients,  $A$  and  $B$ , yields:

$$B = \left( \frac{360L^\lambda}{\beta} \right) \left( \frac{RT}{v_w} \right)^{\lambda+1} A^{\lambda+1} \quad (S1)$$

Eq. S1 indicates a linear relationship between the logarithms of the solute and water permeance coefficients, i.e.,  $\log B \propto (\lambda + 1)\log A$ , which is consistent with the permeability-selectivity trends observed in Figure 1 in the main manuscript.

In gas separation membranes differentiating gas A over gas B, the classic S-D model defines the selectivity as  $\alpha_{A/B} \equiv P_A/P_B = (K_A/K_B) (D_A/D_B)$ . The activation energy model is employed to describe the transmembrane diffusion of permeants, where the diffusivity is proportional to the square of the kinetic diameter of gas molecules, and the logarithmic selectivity can then be expressed as:

$$\ln \alpha_{A/B} = \ln \left( \frac{K_A}{K_B} \right) + \left( \frac{1-a}{RT} \right) c (d_B^2 - d_A^2) \quad (\text{S2})$$

Here,  $a$  is an independent constant, variable  $c$  describes the mobility of polymer chains, and  $d$  is the kinetic diameter of the gas molecules. According to eq. S2, selectivity between a pair of permeants is influenced by permeant sorption into the membrane ( $K_i$ ), i.e., the partition process, as well as polymer-related properties. This is in agreement with the findings of the analyses using the hindered transport model in the main manuscript. Further, the formulation of  $\alpha_{A/B}$  is independent of the effective transport pathway,  $L$ , which is, again, consistent with the hindered transport model analysis of the current study.

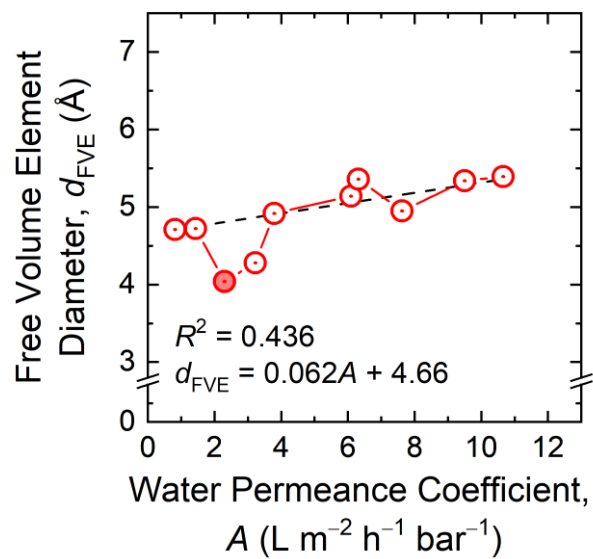
## ■ SUPPLEMENTARY DATA

**Table S1.** van der Waals diameters of solutes, pH of the feed solutions, and  $pK_a$  values of the solutes at 25 °C. Data of van der Waals diameters,  $d_s^{aq}$ , are analyzed using software MarvinSketch.<sup>13</sup> Note that trioxane does not deprotonate in aqueous solutions.  $pK_a$ s of Eg is obtained from reference.<sup>14</sup>

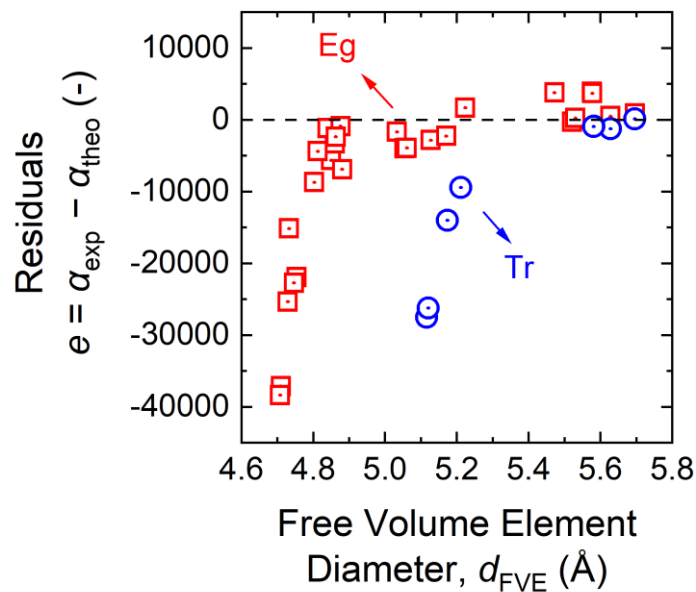
<b>Solute</b>	<b>Abbreviation</b>	<b>van der Waals diameter, <math>d_s^{aq}</math> (Å)</b>	<b>Feed Solution pH</b>	<b><math>pK_a</math></b>
Ethylene glycol	Eg	4.92	$5.87 \pm 0.18$	15.10
Trioxane	Tr	5.31	$6.23 \pm 0.37$	N/A

**Table S2.** Diameters of free volume elements of membranes ( $d_{\text{FVE}}$ ) of different water permeance coefficients,  $A$ , with lifetimes ( $t$  and  $\tau$ ) and intensities ( $I$ ) of positronium components using PALS. Subscripts “p-Ps” and “fp” denote para-positronium and free positrons, respectively, and shorter and longer ortho-positroniums components are represented by subscripts “o-Ps” and “o-Ps-l”, respectively. Note that  $\tau_{\text{o-Ps}}$  is employed to calculate the  $d_{\text{FVE}}$  values in this study. Only one  $d_{\text{FVE}}$  out of two duplicate measurement is reported for each membrane sample (data were highly reproducible and standard deviations were imperceptible). Note that standard deviations of lifetimes and intensities originate from the statistics of fitting the positron annihilation lifetime spectra.

#	$c_{\text{NaOCl}}$ (ppm)	NaOH treat ment	$A$ ( $\text{L m}^{-2} \text{h}^{-1}$ $\text{bar}^{-1}$ )	$t_{\text{p-Ps}}$ (ns)	$I_{\text{p-Ps}}$ (%)	$t_{\text{fp}}$ (ns)	$I_{\text{fp}}$ (%)	$\tau_{\text{o-Ps}}$ (ns)	$I_{\text{o-Ps}}$ (%)	$\tau_{\text{o-Ps-l}}$ (ns)	$I_{\text{o-Ps-l}}$ (%)	$d_{\text{FVE}}$ ( $\text{\AA}$ )
1	0	No	0.82	$0.16 \pm 0.004$	$18.97 \pm 0.77$	$0.41 \pm 0.003$	$65.91 \pm 0.67$	$1.51 \pm 0.008$	$14.59 \pm 0.14$	$21.30 \pm 1.00$	$0.53 \pm 0.008$	4.71
2	0	Yes	1.43	$0.16 \pm 0.005$	$20.20 \pm 0.88$	$0.41 \pm 0.003$	$64.81 \pm 0.78$	$1.52 \pm 0.009$	$14.46 \pm 0.15$	$21.25 \pm 1.00$	$0.53 \pm 0.008$	4.72
3	200	Yes	2.30	$0.11 \pm 0.004$	$13.28 \pm 0.47$	$0.37 \pm 0.002$	$70.86 \pm 0.36$	$1.24 \pm 0.009$	$15.58 \pm 0.19$	$6.49 \pm 0.36$	$0.28 \pm 0.019$	4.04
4	100	Yes	3.22	$0.14 \pm 0.005$	$9.99 \pm 0.53$	$0.39 \pm 0.002$	$81.73 \pm 0.44$	$1.33 \pm 0.01$	$7.97 \pm 0.14$	$13.60 \pm 0.68$	$0.30 \pm 0.010$	4.28
5	1,500	Yes	3.79	$0.13 \pm 0.006$	$8.66 \pm 0.40$	$0.38 \pm 0.001$	$89.09 \pm 0.37$	$1.60 \pm 0.05$	$1.33 \pm 0.06$	$36.51 \pm 1.87$	$0.92 \pm 0.020$	4.92
6	8,000	Yes	6.09	$0.13 \pm 0.006$	$9.12 \pm 0.42$	$0.38 \pm 0.001$	$88.57 \pm 0.39$	$1.71 \pm 0.05$	$1.14 \pm 0.05$	$38.39 \pm 1.87$	$1.17 \pm 0.024$	5.14
7	1,500	Yes	6.32	$0.13 \pm 0.006$	$5.91 \pm 0.32$	$0.39 \pm 0.0009$	$92.57 \pm 0.30$	$1.82 \pm 0.07$	$0.91 \pm 0.04$	$27.30 \pm 1.71$	$0.62 \pm 0.011$	5.36
8	3,000	Yes	7.63	$0.15 \pm 0.007$	$7.81 \pm 0.49$	$0.40 \pm 0.001$	$90.08 \pm 0.45$	$1.62 \pm 0.04$	$1.65 \pm 0.06$	$24.67 \pm 1.62$	$0.46 \pm 0.008$	4.95
9	3,000	Yes	9.50	$0.15 \pm 0.008$	$6.51 \pm 0.45$	$0.40 \pm 0.001$	$91.96 \pm 0.43$	$1.81 \pm 0.06$	$1.01 \pm 0.04$	$26.17 \pm 1.74$	$0.52 \pm 0.009$	5.34
10	5,000	Yes	10.65	$0.12 \pm 0.005$	$6.39 \pm 0.27$	$0.39 \pm 0.0008$	$92.20 \pm 0.25$	$1.83 \pm 0.06$	$0.94 \pm 0.04$	$25.49 \pm 1.75$	$0.48 \pm 0.009$	5.39



**Figure S2.** Diameter of the free volume element,  $d_{FVE}$ , of membranes with different water permeance coefficient,  $A$ , by PALS characterizations. Data are summarized in Table S2. Dashed line indicates the linear regression of  $d_{FVE}$  on  $A$ , passing through the pristine membrane data point (one outlier, indicated by the red filled symbol was excluded as the studentized residual is  $> 2$ ).<sup>15</sup>



**Figure S3.** Residual analysis of the selectivity prediction using the hindered transport model (Figure 4 in the main manuscript),  $e = \alpha_{\text{exp}} - \alpha_{\text{theo}}$ . The black horizontal dashed line denotes zero value. Data points close to zero indicate good predictions, whereas values  $\ll 0$  represent overpredictions. Note that  $\alpha_{\text{theo}}$  of  $d_p < \text{solute size of Tr}$  approaches  $\infty$  and are not presented.



## ■ REFERENCES

- (1) Baker, R. W. *Membrane technology and applications*; John Wiley & Sons: Chichester, West Sussex; Hoboken, 2012.
- (2) Bird, R. B.; Stewart, W. E.; Lightfoot, E. N. *Transport phenomena*; John Wiley & Sons: Chichester, West Sussex; Hoboken, 2007.
- (3) Bowen, W. R.; Welfoot, J. S. Modelling the performance of membrane nanofiltration—critical assessment and model development. *Chem. Eng. Sci.* **2002**, *57* (7), 1121-1137.
- (4) Deen, W. M. Hindered transport of large molecules in liquid - filled pores. *AIChE J.* **1987**, *33* (9), 1409-1425.
- (5) Nghiem, L. D.; Schäfer, A. I.; Elimelech, M. Removal of natural hormones by nanofiltration membranes: measurement, modeling, and mechanisms. *Environ. Sci. Technol.* **2004**, *38* (6), 1888-1896.
- (6) Chen, X.; Boo, C.; Yip, N. Y. Transport and structural properties of osmotic membranes in high-salinity desalination using cascading osmotically mediated reverse osmosis. *Desalination* **2020**, *479*, 114335. DOI: <https://doi.org/10.1016/j.desal.2020.114335>.
- (7) Freeman, B. D. Basis of permeability/selectivity tradeoff relations in polymeric gas separation membranes. *Macromolecules* **1999**, *32* (2), 375-380.
- (8) Geise, G. M.; Paul, D. R.; Freeman, B. D. Fundamental water and salt transport properties of polymeric materials. *Prog. Polym. Sci.* **2014**, *39* (1), 1-42.
- (9) Yip, N. Y.; Elimelech, M. Performance limiting effects in power generation from salinity gradients by pressure retarded osmosis. *Environ. Sci. Technol.* **2011**, *45* (23), 10273-10282.
- (10) Ritt, C. L.; Stassin, T.; Davenport, D. M.; DuChanois, R. M.; Nulens, I.; Yang, Z.; Ben-Zvi, A.; Segev-Mark, N.; Elimelech, M.; Tang, C. Y. The open membrane database: Synthesis–structure–performance relationships of reverse osmosis membranes. *J. Membr. Sci.* **2021**, 119927.
- (11) Yang, Z.; Guo, H.; Tang, C. Y. The upper bound of thin-film composite (TFC) polyamide membranes for desalination. *J. Membr. Sci.* **2019**, 117297.
- (12) Geise, G. M.; Park, H. B.; Sagle, A. C.; Freeman, B. D.; McGrath, J. E. Water permeability and water/salt selectivity tradeoff in polymers for desalination. *J. Membr. Sci.* **2011**, *369* (1-2), 130-138.
- (13) *MarvinSketch* ChemAxon: 2019. <http://www.chemaxon.com> (accessed 05-16, 2019).
- (14) Lide, D. R. *CRC handbook of chemistry and physics*; CRC Press: Boca Raton, 2004.
- (15) Pope, A. J. *The statistics of residuals and the detection of outliers*; US Department of Commerce, National Oceanic and Atmospheric Administration, National Ocean Survey, Geodetic Research and Development Laboratory: Washington, DC, 1976.