Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supplementary Information

for

Asymmetric Nanoporous Membranes for ethanol/water Pervaporation Separation and Their Design

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1. Free Energy Calculation

The Helmholtz free energy profiles for ethanol molecules are calculated to shed light on the diffusion behavior of ethanol near the permeate-side surface. Provided that ethanol is a dominant phase in the system, their free energy profiles are computed directly from the concentration profiles along the z-axis. The calculation of free energy is based on Equation 1:

$$\Delta A = -k_b T \ln \frac{C_i(z)}{C_{i,ref}} \tag{1}$$

Where k_b is the Boltzmann constant, T is the temperature, $C_i(z)$ is the ethanol concentration at a specific position, and $C_{i,ref}$ denotes the maximum concentration of ethanol molecules along the z-axis.

Table S1. The results for the four types of membrane separation factor and thickness-normalized flux are presented per four independent calculations.

Membrane type	Separation factor (α)	Thickness normalized flux (Kg Å/m^2 h) (J)
MFI (random seed 1)	21.61	6.24×10^5
MFI (random seed 2)	27.68	7.70×10^5
MFI (random seed 3)	21.29	7.04×10^5
MFI (random seed 4)	23.69	6.14×10^5
Zigzag (random seed 1)	118.32	8.76×10^5
Zigzag (random seed 2)	85.83	9.24×10^5
Zigzag (random seed 3)	110.29	9.43×10^5
Zigzag (random seed 4)	115.28	9.85×10^5
Zigzag-MFI (random seed 1)	268.14	1.18×10^6
Zigzag-MFI (random seed 2)	645.21	1.03×10^6
Zigzag-MFI (random seed 3)	176.11	1.12×10^6
Zigzag-MFI (random seed 4)	204.60	1.07×10^6
MFI-Zigzag (random seed 1)	29.58	7.46×10^5
MFI-Zigzag (random seed 2)	36.18	8.98×10^5
MFI-Zigzag (random seed 3)	21.96	9.00×10^5
MFI-Zigzag (random seed 4)	25.68	7.53×10^5

Table S2. Performance comparison between experiments and simulations. The simulation results obtained in this work are the averaged values of four independent simulations with different random seeds.

Membrane type	separation factor (α)	Thickness normalized flux (Kg Å/m^2 h) (J)	ref
MFI/mullite tube	30-72	8.00×10^4-2.26×10^5	1
MFI/YSZ fiber	47	2.22×10^5	2
silicalite-1/α- Al_2O_3 tube	23-45	1.01×10^5-1.92×10^5	3
MFI (simulation)	20.17	5.88×10^5	4, 5
Zigzag (simulation)	136.00	6.77×10^5	4, 5
MFI	23.57	6.78×10^5	This work
Zigzag	107.43	9.32×10^5	This work
Zigzag-MFI	323.52	1.10×10^6	This work
MFI-Zigzag	28.35	8.49×10^5	This work

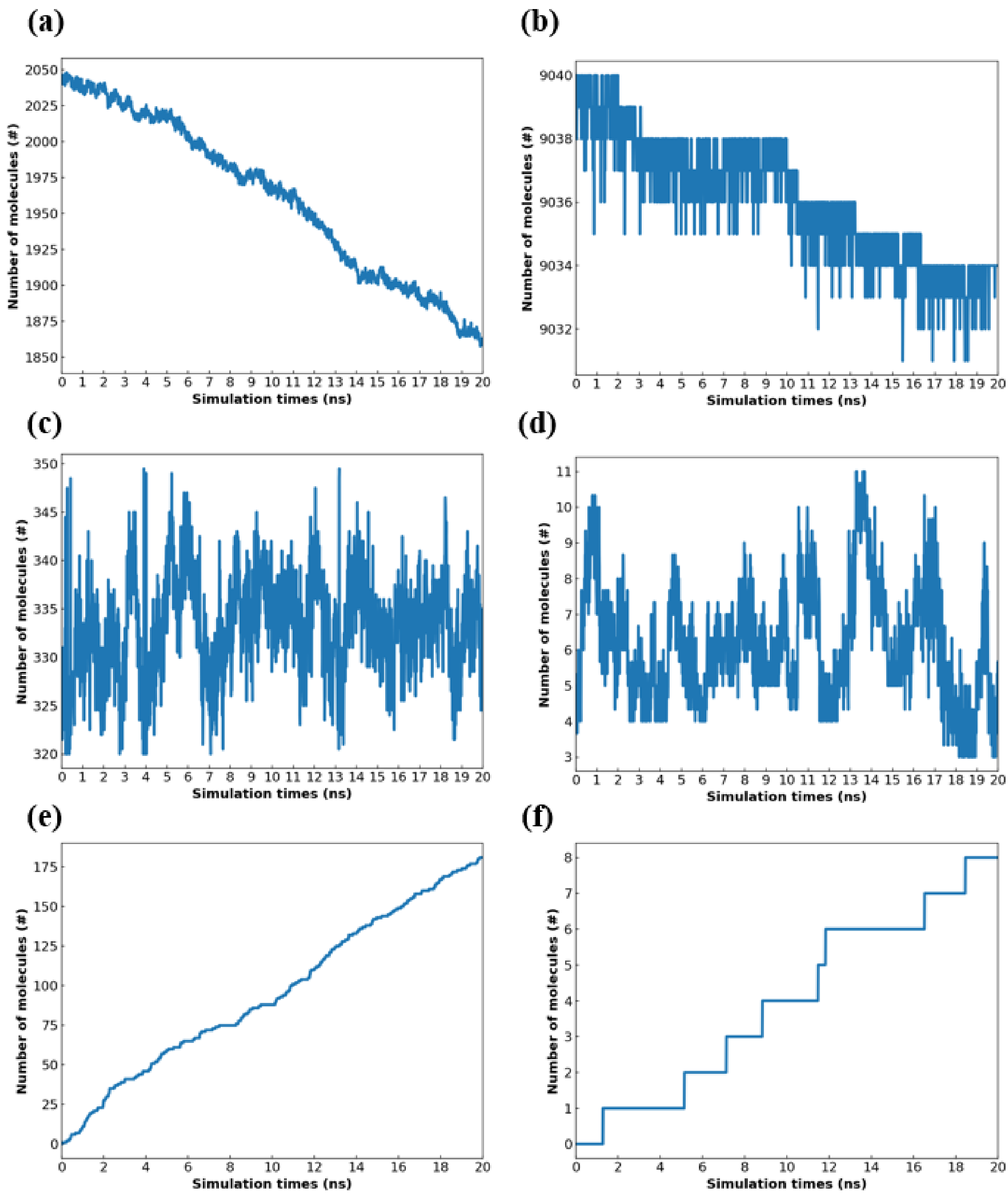

Figure S1. The number of (a) ethanol and (b) water molecules in the feed-side region, the number of (c) ethanol (d) water molecules within the membrane, the number of (e) ethanol and (f) water molecules on the adsorbing plate as a function of simulation time.

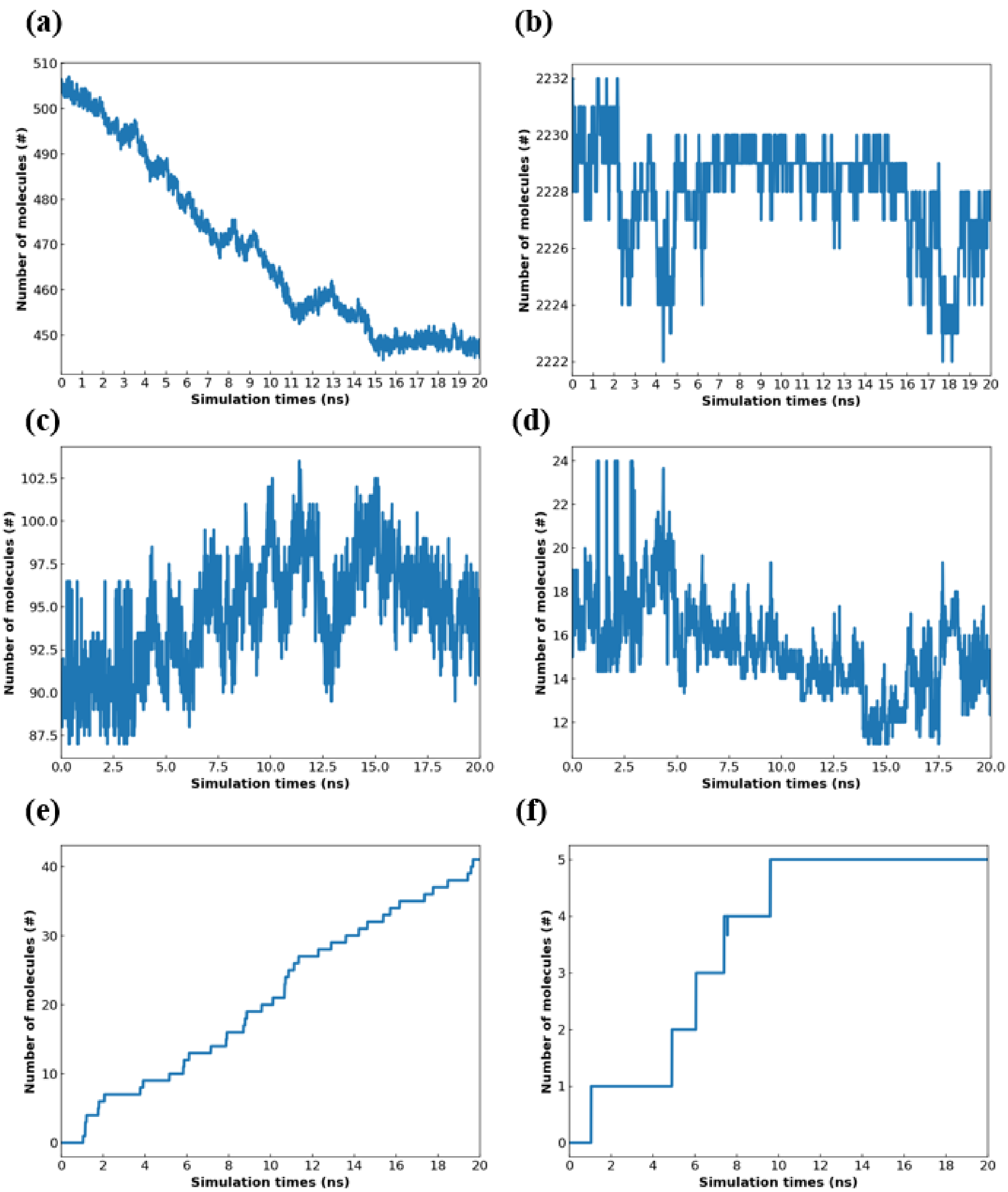

Figure S2. The number of (a) ethanol and (b) water molecules in the feed-side region, the number of (c) ethanol and (d) water molecules within the membrane, the number of (e) ethanol and (f) water molecules on the adsorbing plate as a function of simulation time observed in simulation of a smaller domain (i.e., 4-fold smaller than the simulation domain adopted to obtain all the reported main results in this work).

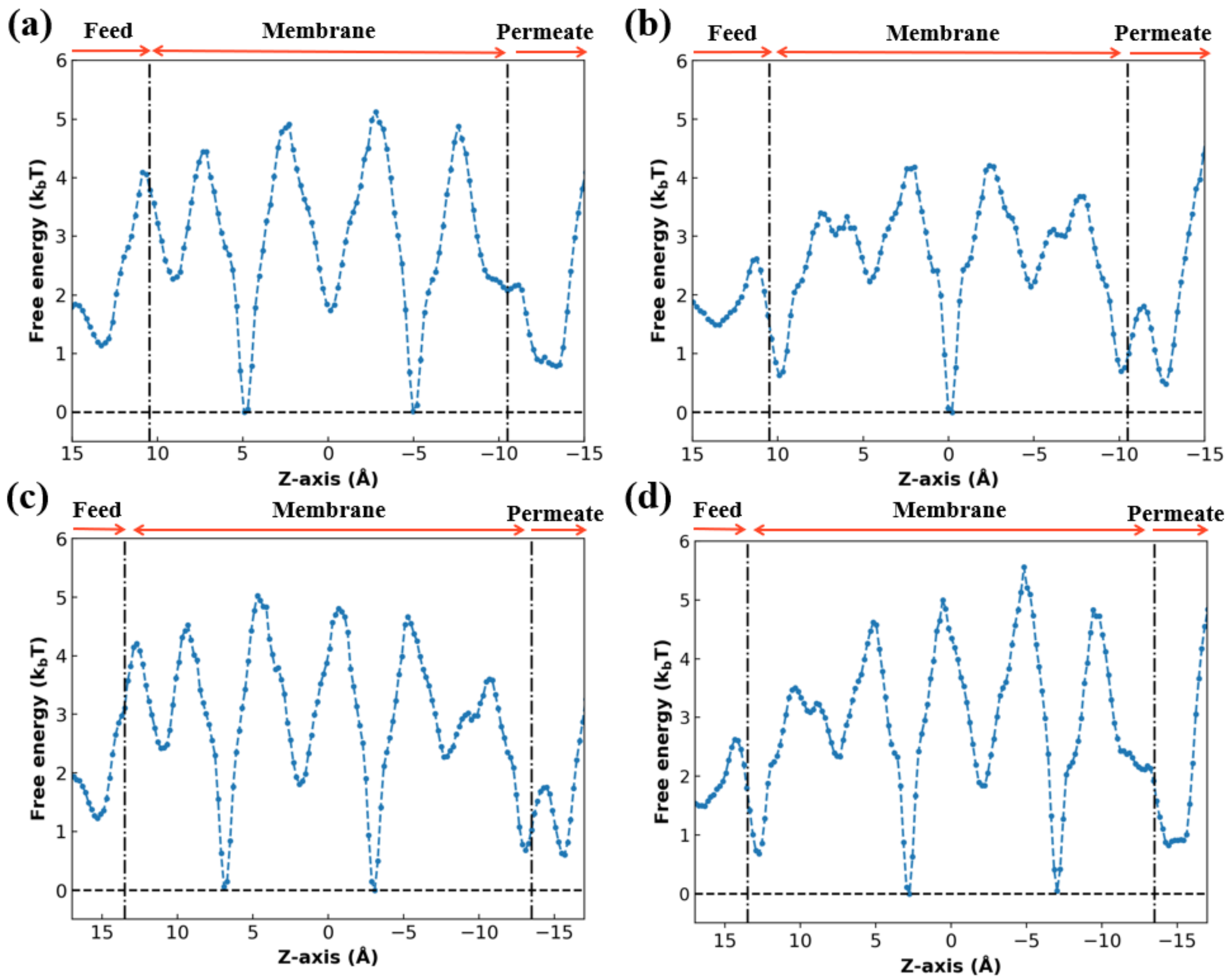

Figure S3. The free energy profiles along the permeation z-direction for ethanol in (a) MFI, (b) Zigzag, (c) MFI-Zigzag, and (d) Zigzag-MFI membranes.

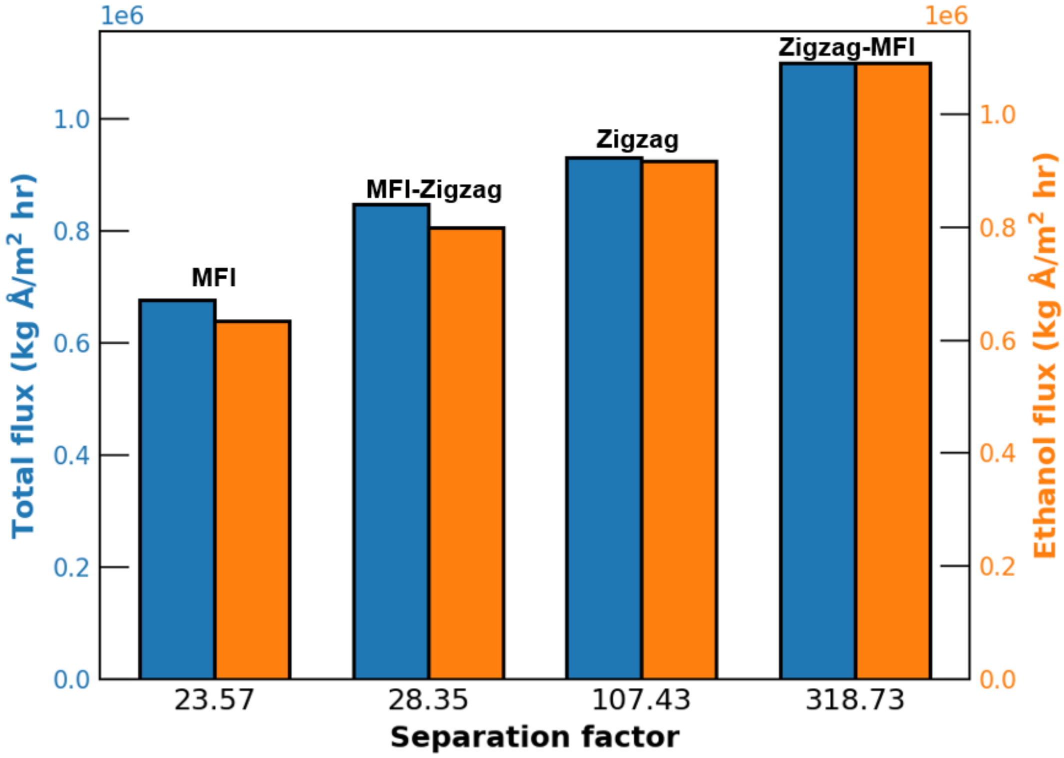

Figure S4. Total and ethanol flux with separation factors of the four studied membranes.

References

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