Supporting Information: Cation-ligand interactions dictate salt partitioning and diffusivity in ligand-functionalized polymer membranes

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Figure S1: Computed single ion hydration free energies of Joung-Cheatham ions in TIP4P2005 water (green) compared to literature values of $Marcus^1$ (red) and Schmid² (blue).

| Table S1: Ion diffusivities, standard error, scaling parameters, and coefficient of determin | ıa- |
|--|-----|
| tion obtained from MSD fitting procedures. Diffusion coefficients are averaged over N | at |
| least 5 independent simulation runs. Values following \pm indicate the standard error. | |

| Species | $\langle D^{(i)} angle~({ m cm}^2/{ m s})$ | $\mid \sigma_D \mid /\sqrt{N} \; ({ m cm}^2/{ m s})$ | α | R^2 | |
|--------------------------|--|--|-------------------|---------------------|--|
| Li ⁺ Membrane | 3.32×10^{-7} | 3.14×10^{-8} | 0.992 ± 0.006 | 0.998 ± 0.001 | |
| Na ⁺ Membrane | $6.43 	imes 10^{-8}$ | 4.8×10^{-9} | 1.00 ± 0.02 | 0.997 ± 0.001 | |
| ${\rm K}^+$ Membrane | 2.62×10^{-8} | 1.3×10^{-9} | 1.029 ± 0.007 | 0.996 ± 0.002 | |
| Rb^+ Membrane | 1.23×10^{-8} | 3.1×10^{-9} | 1.035 ± 0.006 | 0.9973 ± 0.0009 | |
| Cs^+ Membrane | 2.22×10^{-8} | 5.7×10^{-9} | 1.01 ± 0.01 | 0.987 ± 0.006 | |
| Cl ⁻ Membrane | 4.32×10^{-7} | 2.5×10^{-8} | 0.991 ± 0.006 | 0.9973 ± 0.0006 | |
| Li^+ Solution | 1.06×10^{-5} | $5.5 	imes 10^{-7}$ | 1.036 ± 0.006 | 0.9989 ± 0.0003 | |
| Na ⁺ Solution | 9.53×10^{-6} | 9.5×10^{-7} | 1.01 ± 0.01 | 0.9979 ± 0.0009 | |
| K^+ Solution | 1.32×10^{-5} | $6.7 	imes 10^{-7}$ | 1.002 ± 0.008 | 0.998 ± 0.001 | |
| \mathbf{Rb}^+ Solution | 1.65×10^{-5} | 4.3×10^{-7} | 1.026 ± 0.008 | 0.9974 ± 0.0008 | |
| Cs^+ Solution | 1.93×10^{-5} | 1.6×10^{-6} | 1.019 ± 0.008 | 0.996 ± 0.001 | |
| Continued on next page | | | | | |

| Species | $\langle D^{(i)} angle ~({ m cm}^2/{ m s})$ | $\mid \sigma_D \mid /\sqrt{N} \; ({ m cm}^2/{ m s})$ | lpha | R^2 |
|-----------------------------------|--|--|-----------------|---------------------|
| $\mathrm{Cl}^{\text{-}}$ Solution | $1.36 	imes 10^{-5}$ | $4.0 	imes 10^{-7}$ | 1.006 ± 0.004 | 0.9987 ± 0.0003 |

Table S1 - continued from previous page



Figure S2: Average fraction of (blue) free cations, (orange) cations complexed to a single crown ether, and (red) cations complexed to two crown ethers.



Figure S3: Radial distribution (top) and coordination distribution (bottom) functions for cations and anions within the membrane phase. We attribute the first and second peak of the radial distribution functions to contact and solvent separated ion pairs, respectively. The relatively small intensity $(n_{\rm M^+Cl^-}(r) < 1)$ of the coordination distribution function in these regions indicates that, on average, there are few (< 1) anions coordinated to cations in the membrane.



Figure S4: Cation diffusion coefficients (squares) plotted as a function of ligand-cation interaction free energy. Chloride and water diffusivities, as well as the Mackie-Meares diffusivity predictions $(\phi_w^2/(2-\phi_w)^2, \phi_w = 0.39)$ are presented as the black, blue, and red dashed lines for comparison. The black curve indicates diffusivity predictions made using Equations 6 and 8 with $\tau(\phi_w) = D^{(C\Gamma)}/D_o^{(C\Gamma)}$ (a non-interacting penetrant). Error bars represent the standard error of at least 5 independent simulations.



Figure S5: Cation permeability coefficients (squares) normalized by cation diffusivity in solution plotted as a function of ligand-cation interaction free energy. The black curve indicates permeability predictions made using Equation 12. Error bars represent the standard error of at least 5 independent simulations.



Figure S6: Computed salt partition coefficients (squares) compared to model predictions (circles) using cation Born radii deduced from the second solvation shell of the cation-water rdf. The black curve indicates predictions made using the Born radius of a lithium ion (also taken as the second solvation shell). Error bars represent the standard error of at least 5 independent simulations.



Figure S7: Cation-water radial distribution (top) and coordination (bottom) functions in the membrane. The coordination distribution functions from solution are shown in gray for comparison.



Figure S8: Chloride-water radial distribution (top) and coordination (bottom) functions in the membrane. The coordination distribution functions from solution are shown in gray for comparison and are nearly superimposed over the membrane results, indicating that Cl⁻ retains its hydration shell in the membrane.



Figure S9: Free energies of ions within the membrane computed from the BAR procedure. Error bars represent the standard error of 5 independent simulations and are generally smaller than width of the marker. Electrostatic interactions are decoupled from windows 0 through 19 while LJ interactions are decoupled from windows 20 through 40.



Figure S10: Example MSDs for ions in solution. Red lines indicate linear fits to the long-time MSD data. Data regarding MSD fits can be found in Table S1.



Figure S11: Comparison of ion self-diffusivities computed in this study and literature values for TIP4P/2005 water + Joung-Cheatham ions at infinite dilution.³



Figure S12: Example MSDs for ions in the membrane. Red lines indicate linear fits to the long-time MSD data. Data regarding MSD fits can be found in Table S1.

References

- (1) Marcus, Y. Ion Properties; Taylor & Francis, 1997.
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- (3) Döpke, M. F.; Moultos, O. A.; Hartkamp, R. On the transferability of ion parameters to the TIP4P/2005 water model using molecular dynamics simulations. J. Chem. Phys. 2020, 152, 024501.