Supplementary Information

Effects of Fixed Charge Group Physicochemistry on Anion Exchange Membrane Permselectivity and Ion Transport

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S1. Preparation and Characterization of 1,2-Dimethyl-3-(4-vinylbenzyl)imidazolium Chloride

Synthesis of 1,2-dimethyl-3-(4-vinylbenzyl)imidazolium chloride was completed via the Menshutkin reaction.¹ A mixture of 9.6 g of 4-vinylbenzyl chloride (catalog number 436887, Sigma-Aldrich), 3.5 g of 1,2-dimethyl imidazole (catalog number 136131, Sigma-Aldrich) and 20 mL of anhydrous chloroform were added to a pre-dried flask. The mixture was magnetically stirred at room temperature for 0.5 hr, and then it was heated to 50°C and maintained at this temperature for 8 hr. The reaction mixture was then poured into 100 mL of diethyl ether to precipitate the 1,2-dimethyl-3-(4-vinylbenzyl)imidazolium chloride product. The precipitate was washed three times using 100 mL of ethyl acetate to remove unreacted 4-vinylbenzyl chloride and/or 1,2-dimethyl imidazole. The chemical structure of the final 1,2-dimethyl-3-(4-vinylbenzyl)imidazolium chloride product was verified using ¹H NMR (Figure S1).



Figure S1. Annotated ¹H NMR spectrum of the 1,2-dimethyl-3-(4-vinylbenzyl)imidazolium chloride product. The measurement was performed using a 600MHz Varian NMR at room temperature, and D₂O was used as the solvent.

S2. Estimation of Fixed Charge Group Van der Waals Volume and Enthalpy of Hydration

The van der Waals volumes (V_{vdw}) of the fixed charge groups were estimated using an empirical method adapted from the literature.² According to this method, the van der Waals volume (Å³/molecule) of an organic molecule can be calculated by considering contributions from the atoms, bonds, and ring structures present in the molecule:

$$V_{vdw}(\text{\AA}^3 / \text{molecule}) = \sum (\text{all atom contributions}) - 5.92N_B - 14.7R_A - 3.8R_{NA}$$
(S1)

where the Σ (all atom contributions) term is the sum of the van der Waals volumes of all atoms in the molecule, N_B is the total number of bonds (regardless of bond type), R_A is the number of aromatic rings, and R_{NA} is the total number of non-aromatic rings.²

The "all atom contributions" term is the sum of the individual van der Waals volume of each atom in the molecule. The values for common atoms (e.g., carbon, hydrogen, nitrogen etc.) are tabulated.² To estimate the van der Waals volumes of the trimethyl ammonium and 1,4-dimethyl imidazolium fixed charge groups (of interest to this study), the volumetric contributions from each atom, bond and ring in the two groups were calculated (Table S1).

Trimethyl	Ammonium	n (TMA)	1,4-Dimethyl Imidazolium (DMI)			
Component	Number	Total Contribution (Å ³)	Component	Number	Total Contribution (Å ³)	
Н	9 65.2		Н	8	57.9	
С	3	61.7	С	5	102.9	
Ν	1	15.6	Ν	2	31.2	
Bonds	12	-71.0	Bonds	15	-88.8	
Aromatic Rings	romatic Rings 0 0		Aromatic Rings 0		0	
Non-aromatic Rings	Non-aromatic Rings 0 0		Non-aromatic Rings	1	-3.8	
V_{vdw}		71.5	V _{vdw}		99.4	

Table S1. Estimation of the van der Waals volumes of the trimethyl ammonium and 1,4-dimethyl imidazolium fixed charge groups using tabulated contributions of atoms, bonds, and rings.²

The enthalpy of hydration (ΔH_{hyd}) of the fixed charge group was estimated using a method that relates the thermodynamic hydration properties (e.g., enthalpy of hydration) with the inverse cube root of the unit volume of the ion or a compound.³ According to this method, the enthalpy of hydration of an ion, ΔH_{hyd} , decreases with ionic volume as:

$$\Delta H_{hvd} (\text{kJ/mol}) = -48.2 V_m^{-1/3} (\text{nm}^{-1}) - 154.6$$
(S2)

It should be noted that this method applies to both spherical ions (e.g., Cu^+ , Ag^+ , Au^+ etc.) and nonspherical ions (e.g., tetramethyl ammonium, tetraethyl ammonium, etc.), but the methods used to estimate the ionic volumes are different. For the spherical ions, the volume was calculated using the ion radius. For the non-spherical ions, the best source of ionic volume comes from crystallographic measurements.³ For the purpose of this study, however, a qualitative comparison between the fixed charge group volumes was sufficient, so the van der Waals volumes of the fixed charge groups (Table S1) were used in Equation S2 to estimate the enthalpy of hydration. The final results are reported in Table 1 in the main text.

S3. Parameters used in the Apparent Permselectivity Calculations

The experimental temperature (*T*), ion transport numbers (t_j^i) , and activity $(a_{\pm}^{s0} \text{ and } a_{\pm}^{sL})$ values for aqueous solutions of lithium chloride, sodium chloride, ammonium chloride, sodium bromide and sodium nitrate were used in the apparent permselectivity calculations (Equation 6 in the main text). A summary of these values and the calculated apparent permselectivity values for PVBAN-TMA[X] is provided as Table S2.

Table S2. Summary of the parameters used in the apparent permselectivity calculations for the PVBAN-TMA[X] materials. The measurements were made at room temperature $(23\pm2^{\circ}C)$, and the apparent permselectivity (α), was calculated at 23°C. The measured electric potential difference across the membrane (E_m) was corrected for the electrode offset potential and averaged over three measurements. The uncertainty was taken as one standard deviation from the average.

Electrolyte	Т	Transport Numbers		Activity		Measured E_m	
	(°C)	t_{M}^{s}	t_X^s	a^{s0}_{\pm}	$a_{\scriptscriptstyle{\pm}}^{\scriptscriptstyle{sL}}$	(mV)	a
LiCl	23	0.664	0.336	0.079	0.370	31.1±0.3	0.69±0.01
NaCl	23	0.604	0.396	0.078	0.340	31.9±0.6	0.81 ± 0.02
NH ₄ Cl	23	0.506	0.494	0.077	0.320	31.4±0.7	0.86 ± 0.02
NaBr	23	0.574	0.426	0.078	0.348	32.3±0.6	0.81 ± 0.02
NaNO ₃	23	0.588	0.412	0.076	0.308	28.4±0.2	0.75±0.01

S4. The Influence of the Liquid Junction Potential on Apparent Permselectivity

Electrodes filled with 1 mol/L aqueous potassium nitrate were used to measure the membrane potential, and ultimately, apparent permselectivity. The electrodes were exposed to 0.1 and 0.5 mol/L aqueous solutions of lithium chloride, sodium chloride, ammonium chloride, sodium bromide and sodium nitrate solutions, respectively (thermodynamic activity values for these solutions are provided in Table S2). A liquid junction potential can form between the electrode filling and external solutions, and this potential may bias the measurement results.⁴ This junction potential can be estimated using a theoretical method

based on the Henderson Equation.⁴ By applying this correction, we estimate that the junction potential may reduce the measured membrane potential by 3.7, 2.2, 1.6 and 2.4 mV for lithium chloride, sodium chloride, sodium nitrate and sodium bromide, respectively. The junction potential may increase the measured membrane potential by 0.1 mV for ammonium chloride.

The liquid junction potential-corrected apparent permselectivity values are presented in Figure S2. Comparing the data in Figure S2 with that in Figure 3 from the main text, it was observed that first, incorporating the liquid junction potential correction could enlarge the apparent permselectivity difference between electrolytes with different co-ions, i.e., lithium chloride, sodium chloride and ammonium chloride (i.e., compare Figure S2A and Figure 3A). Secondly, incorporating the liquid junction potential correction reduced the absolute values of the apparent permselectivity for electrolytes with different counter-ions, i.e., sodium chloride, sodium bromide and sodium nitrate (i.e., compare Figure S2B and Figure 3B). Overall, the liquid junction potential correction influences the absolute values of the membrane potential and apparent permselectivity, but the observed qualitative trends, with respect to the ions of interest in this study, were not significantly affected by incorporating the liquid junction potential correction (i.e., compare Figure 3).



Figure S2. Apparent permselectivity values of the two AEMs including the liquid junction potential correction. The liquid junction potential correction was estimated using a theoretical method based on the Henderson Equation.⁴

S5. Kinetic Desorption Measurement and Data Analysis

To minimize the effects of atmospheric carbon dioxide on the salt sorption coefficients, the kinetic desorption measurements were all conducted under a nitrogen blanket. As such, the conductivity (thus the electrolyte concentration of the desorption solution) not only increased due to the progress of the kinetic desorption process, but it also increased due to evaporation of water caused by the nitrogen purge. The nitrogen purge gas flow rate was controlled, so this evaporation effect could be subtracted from the measured data using background curves that captured the consistent change in the conductivity of the solution due to the nitrogen purge. Using these background curves, we determined "evaporation-corrected" desorption curves, and these data were ultimately used to calculate the membrane salt sorption and diffusion coefficients.

As discussed in the main text, the kinetic desorption was conducted by immersing an electrolyte solution-equilibrated membrane sample into DI water and subsequently recording the conductivity of the desorption solution as a function of time. The background curve was obtained by recording the conductivity change of an electrolyte solution of similar concentration compared to the desorption solutions used (e.g. 1 to 5 ppm in this study), without having a membrane sample placed in the solution. The nitrogen purge gas pressure was precisely controlled to be 2 psig to ensure constant and consistent gas flow rates during the processes of obtaining the background curves and kinetic desorption measurements themselves. The background curves for the five electrolytes, i.e., lithium chloride, sodium chloride, ammonium chloride, sodium nitrate, were obtained using their aqueous solutions of 1 to 5 ppm. For all of the electrolytes considered, the conductivity increased linearly with time as water evaporation occurred. Specifically, the average background conductivity increases for lithium chloride, sodium chloride, ammonium chloride, and sodium nitrate were 0.05, 0.04, 0.10, 0.05, 0.05 μ S/cm per 100 min, respectively. These background conductivity increase rates were used to define the endpoint of the kinetic desorption measurements, as the end of the experiment was indicated when the increase in conductivity over time matched the background rate.

The "evaporation-corrected" desorption conductivity curves were obtained as follows. Here, an ammonium chloride desorption measurement using PVBAN-TMA[Cl] is provided as a representative example. During the kinetic desorption measurement, the first conductivity point recorded without desorption of any salt was 0.18 μ S/cm. As the desorption of salt proceeded, the conductivity increased to 8.27 μ S/cm and ultimately only increased by 0.01 μ S/cm during the subsequent 10 min. It took 259 min for the conductivity to reach to 8.27 μ S/cm and another 10 min to reach to 8.28 μ S/cm. The point where the conductivity reached to 8.28 μ S/cm was regarded as the final point of the kinetic desorption. Throughout the desorption measurement, an increase in conductivity of 0.27 μ S/cm could be attributed to the

evaporation effects (according to the background conductivity curve for ammonium chloride). This total conductivity change was taken into account by subtracting it from the final desorption point, i.e., the conductivity corresponding to the final desorption point was calculated to be 8.01 μ S/cm. The corrected final desorption point was then used for further data analysis, i.e., the value 8.01 μ S/cm was converted to M_{∞} to calculate the $M_t/M_{\infty} \sim t$ and $M_t/M_{\infty} \sim t^{1/2}$ curves. Alternatively, when evaporation was not accounted for, the value 8.28 μ S/cm was converted to M_{∞} for the $M_t/M_{\infty} \sim t$ and $M_t/M_{\infty} \sim t^{1/2}$ curves before and after the evaporation correction are presented in Figure S3. The slopes of the initial portion of the curves were 0.027 and 0.028 before and after the evaporation correction, respectively, and these slopes are critical for determining the salt diffusion coefficient in the membrane. As such, the effects of water evaporation on the desorption measurements were relatively minor.



Figure S3. The $M_t/M_{\infty} \sim t$ curves before (\bigcirc) and after (\bigcirc) the evaporation correction (A), and the $M_t/M_{\infty} \sim t^{1/2}$ curves before (\square) and after the evaporation correction (\blacksquare) (B). The data shown here were recorded during an ammonium chloride desorption measurement using the PVBAN-TMA[C1] membrane.

S6. The Influence of $k_{X/M}^m$, $D_{X/M}^m$ and $D_{X/M}^s$ on Apparent Permselectivity

The parameters $k_{X/M}^m$, $D_{X/M}^m$ and $D_{X/M}^s$ describe co-ion and counter-ion transport in the membrane and solution phases, and each of the parameters affect the apparent permselectivity to a different extent. The subsequent analysis discusses the magnitude of the influence of each parameter on permselectivity. The analysis was conducted based on:

$$\alpha = 1 - \frac{k_{X/M}^m D_{X/M}^m (1 + \frac{1}{D_{X/M}^s})}{k_{X/M}^m D_{X/M}^m + 1}$$
(S3)

$$\Delta \alpha = f\left(\Delta k_{X/M}^m, \Delta D_{X/M}^m, \Delta D_{X/M}^s\right)$$
(S4)

considering a base scenario where the membrane properties are $c_A^m = 3 \text{ mol/L}$, $k_{X/M}^m = 0.162$, $D_{X/M}^m = 0.66$ and $D_{X/M}^s = 0.66$. The value of $c_A^m = 3 \text{ mol/L}$ was chosen as a representative value for AEMs;⁵ $k_{X/M}^m$ was calculated by assuming that ideal Donnan exclusion occurred in a membrane exposed to a 0.5 mol/L external solution; the value of $D_{X/M}^s$ was calculated using the sodium and chloride diffusivities in aqueous solution at infinite dilution.⁶ Finally, the value of $D_{X/M}^m$ was determined by assuming sodium and chloride diffusion was suppressed to the same extent in the membrane phase (i.e., $D_{X/M}^m = D_{X/M}^s$) relative to that in the solution phase.

Varying $k_{X/M}^m$, $D_{X/M}^m$, or $D_{X/M}^s$ by some amount $\Delta k_{X/M}^m$, $\Delta D_{X/M}^m$, or $\Delta D_{X/M}^s$ changes the membrane apparent permselectivity. This change in apparent permselectivity, $\Delta \alpha$, was calculated using Equation S4 and normalized to the base case permselectivity, α , calculated using Equation S3. The permselectivity decreased by 5.7%, 1.9% and increased by 3.2% when $k_{X/M}^m$, $D_{X/M}^m$, or $D_{X/M}^s$ increased by 20%, respectively (Figure S4).



Figure S4. Membrane permselectivity decreases with increasing $k_{X/M}^m$ or $D_{X/M}^m$ but increases with increasing $D_{X/M}^s$. These data were calculated relative to a base case scenario where a hypothetical membrane is assumed to have $c_A^m = 3 \text{ mol/L}$, $k_{X/M}^m = 0.162$, $D_{X/M}^m = 0.66$ and $D_{X/M}^s = 0.66$.

S7. Measured Values of k_s^m , c_A^m , D_s^m and σ_s^m for the AEMs Considered in this Study

The k_s^m , c_A^m , D_s^m and σ_s^m values for the two AEMs considered in this study were measured using the methods specified in the main text, and they were used to calculate the $k_{X/M}^m$ and $D_{X/M}^m$ values. The measured k_s^m , c_A^m , D_s^m and σ_s^m values of the two AEMs are summarized in Table S3.

Table S3. The measured k_s^m , c_A^m , D_s^m and σ_s^m values for the PVBAN-TMA[X] and PVBAN-DMI[X] membranes determined using the methods specified in the main text. The units of k_s^m are [(mol salt / L external solution) / (mol salt / L water sorbed by the membrane)]. The units of c_A^m are [(mol fixed charge groups) / (L water sorbed by the membrane)]. The units of c_s^m are [(mol fixed charge groups) / (L water sorbed by the membrane)]. The units of σ_s^m are [S/m]. The values for k_s^m and D_s^m are reported as the average and standard deviation of four to five measurements. The values of σ_s^m are reported as the average and standard deviation of three measurements.

Electrolyte	PVBAN-TMA[X]				PVBAN-DMI[X]			
	k_s^m	C_A^m	D_s^m	$\sigma^{\scriptscriptstyle m}_{\scriptscriptstyle s}$	k_s^m	\mathcal{C}_A^m	D_s^m	$\sigma^{\scriptscriptstyle m}_{\scriptscriptstyle s}$
LiCl	0.26±0.01	2.6±0.3	4.8±0.9	2.4±0.05	0.29±0.02	3.8±0.4	0.9±0.1	0.6±0.01
NaCl	0.18 ± 0.01	2.7±0.3	4.6±1.1	1.3 ± 0.001	0.22 ± 0.02	3.8±0.4	0.9 ± 0.6	$0.4{\pm}0.01$
NH4Cl	0.15±0.003	2.7±0.4	6.7±0.1	1.6 ± 0.02	$0.20{\pm}0.02$	4.0±0.4	1.4 ± 0.3	0.6 ± 0.01
NaBr	0.22 ± 0.08	3.2±0.4	1.5 ± 0.6	$0.4{\pm}0.07$	0.23 ± 0.02	4.4±0.6	$0.4{\pm}0.1$	0.1 ± 0.01
NaNO ₃	0.17±0.03	3.3±0.4	0.8 ± 0.03	0.5 ± 0.02	0.20 ± 0.09	5.3±1.8	0.3±0.1	$0.2{\pm}0.01$

S8. References

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