

Supporting information for:

Transport and co-transport of carboxylate ions and ethanol in anion exchange membranes

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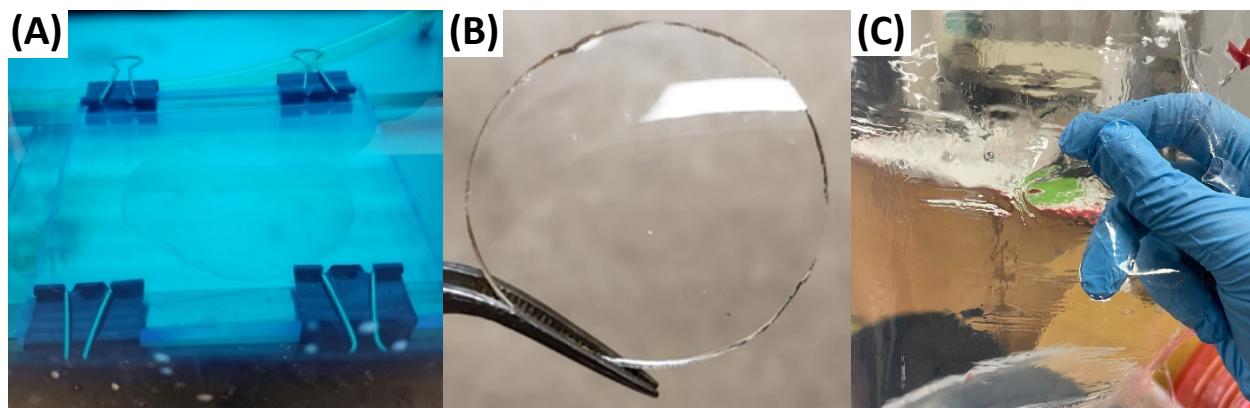


Figure S1. (A) Photopolymerization of a prepolymerization mixture. (B) A hydrated crosslinked film. (C) Selemion® AMVN.

Table S1. Solute diffusivities of select species in water ($\times 10^5 \text{ cm}^2/\text{s}$) at 25 °C in the dilute condition.

Solute	Diffusivity in water
Water	2.45 [1]
EtOH	1.23 [2]
OFm ⁻	1.454 [3]
OAc ⁻	1.089 [3,4]
K ⁺	1.957 [4]
Na ⁺	1.334 [4]

Table S2. Diffusive permeabilities ($\times 10^7$ cm²/s) of A0, A8, A12, and AMVN to EtOH and carboxylate salts in single and EtOH-carboxylate mixture.

A0		K	Na	A0	EtOH
Single	OFm	2.06 ± 0.11	1.44 ± 0.14	Single	5.57 ± 0.27
EtOH	OFm	1.82 ± 0.17	1.75 ± 0.03	KO _{Fm}	6.04 ± 0.03
Single	OAc	1.38 ± 0.03	1.25 ± 0.01	NaOFm	6.56 ± 0.01
EtOH	OAc	1.47 ± 0.02	1.18 ± 0.01	KOAc	5.65 ± 0.04
				NaOAc	5.50 ± 0.08

A8		K	Na	A8	EtOH
Single	OFm	3.64 ± 0.36	2.89 ± 0.16	Single	6.97 ± 0.34
EtOH	OFm	2.64 ± 0.28	1.63 ± 0.13	KO _{Fm}	7.84 ± 0.12
Single	OAc	1.93 ± 0.07	1.27 ± 0.04	NaOFm	7.05 ± 0.26
EtOH	OAc	1.71 ± 0.03	0.65 ± 0.02	KOAc	7.25 ± 0.17
				NaOAc	7.50 ± 0.25

A12		K	Na	A12	EtOH
Single	OFm	3.73 ± 0.24	2.81 ± 0.16	Single	7.94 ± 0.02
EtOH	OFm	2.46 ± 0.26	2.72 ± 0.25	KO _{Fm}	7.87 ± 0.19
Single	OAc	2.45 ± 0.13	1.43 ± 0.02	NaOFm	7.95 ± 0.21
EtOH	OAc	2.19 ± 0.15	0.58 ± 0.15	KOAc	7.62 ± 0.23
				NaOAc	7.25 ± 0.48

AMVN		K	Na	AMVN	EtOH
Single	OFm	0.44 ± 0.02	0.23 ± 0.03	Single	0.92 ± 0.05
EtOH	OFm	0.11 ± 0.01	0.12 ± 0.01	KO _{Fm}	1.60 ± 0.14
Single	OAc	0.13 ± 0.02	0.08 ± 0.00	NaOFm	1.75 ± 0.17
EtOH	OAc	0.14 ± 0.02	0.09 ± 0.00	KOAc	1.68 ± 0.06
				NaOAc	1.30 ± 0.05

Table S3. Solubilities of A0, A8, A12, and AMVN to EtOH and carboxylate salts in single and EtOH-carboxylate mixture.

A0		K	Na	A0	EtOH
Single	OFm	0.172 ± 0.007	0.133 ± 0.013	Single	0.298 ± 0.004
EtOH	OFm	0.168 ± 0.010	0.107 ± 0.000	KOFm	0.379 ± 0.001
Single	OAc	0.155 ± 0.015	0.094 ± 0.005	NaOFm	0.386 ± 0.001
EtOH	OAc	0.144 ± 0.001	0.095 ± 0.000	KOAc	0.413 ± 0.001
				NaOAc	0.407 ± 0.001

A8		K	Na	A8	EtOH
Single	OFm	0.222 ± 0.008	0.143 ± 0.002	Single	0.332 ± 0.014
EtOH	OFm	0.195 ± 0.016	0.134 ± 0.004	KOFm	0.393 ± 0.025
Single	OAc	0.159 ± 0.007	0.106 ± 0.004	NaOFm	0.385 ± 0.016
EtOH	OAc	0.164 ± 0.004	0.112 ± 0.006	KOAc	0.388 ± 0.016
				NaOAc	0.407 ± 0.032

A12		K	Na	A12	EtOH
Single	OFm	0.260 ± 0.007	0.134 ± 0.006	Single	0.360 ± 0.029
EtOH	OFm	0.192 ± 0.013	0.133 ± 0.010	KOFm	0.394 ± 0.020
Single	OAc	0.166 ± 0.010	0.119 ± 0.006	NaOFm	0.395 ± 0.002
EtOH	OAc	0.152 ± 0.003	0.117 ± 0.004	KOAc	0.396 ± 0.017
				NaOAc	0.396 ± 0.014

AMVN		K	Na	AMVN	EtOH
Single	OFm	0.087 ± 0.014	0.064 ± 0.006	Single	0.139 ± 0.019
EtOH	OFm	0.076 ± 0.030	0.070 ± 0.006	KOFm	0.306 ± 0.060
Single	OAc	0.068 ± 0.002	0.047 ± 0.011	NaOFm	0.274 ± 0.007
EtOH	OAc	0.048 ± 0.010	0.056 ± 0.002	KOAc	0.395 ± 0.005
				NaOAc	0.168 ± 0.004

Table S4. Diffusivities ($\times 10^7$ cm 2 /s) of A0, A8, A12, and AMVN to EtOH and carboxylate salts in single and EtOH-carboxylate mixture.

A0		K	Na	A0	EtOH
Single	OFm	11.9	10.8	Single	18.7
EtOH	OFm	10.8	16.3	KOFm	15.9
Single	OAc	8.9	13.2	NaOFm	17.0
EtOH	OAc	10.2	12.4	KOAc	13.7
				NaOAc	13.5

A8		K	Na	A8	EtOH
Single	OFm	16.4	20.1	Single	21.0
EtOH	OFm	13.5	12.2	KOFm	20.0
Single	OAc	12.1	11.9	NaOFm	18.3
EtOH	OAc	10.4	5.8	KOAc	18.7
				NaOAc	17.1

A12		K	Na	A12	EtOH
Single	OFm	14.3	21.1	Single	22.1
EtOH	OFm	12.9	20.4	KOFm	20.0
Single	OAc	14.8	12.1	NaOFm	20.1
EtOH	OAc	14.4	5.0	KOAc	19.3
				NaOAc	18.3

AMVN		K	Na	AMVN	EtOH
Single	OFm	5.1	3.6	Single	6.6
EtOH	OFm	1.4	1.7	KOFm	5.2
Single	OAc	2.0	1.7	NaOFm	6.4
EtOH	OAc	3.0	1.6	KOAc	4.3
				NaOAc	7.7

Table S5. Weight percent (wt.%) of AEMs (A8, A12, and AMVN) in Cl⁻ and HCO₃⁻ forms.

		Measured			Theoretical*		
		C	O	Cl	C	O	Cl
Cl-form	A8	57.8 ± 0.7	41.6 ± 0.6	0.6 ± 0.1	59.9	37.8	2.3
	A12	57.7 ± 0.3	41.1 ± 0.3	1.2 ± 0.1	59.8	36.8	3.4
	AMVN	89.6 ± 0.4	6.2 ± 0.3	4.1 ± 0.1	-	-	-
HCO ₃ ⁻ form	A8	59.5 ± 0.2	40.5 ± 0.2	-	59.7	40.3	-
	A12	58.9 ± 0.5	41.1 ± 0.5	-	59.6	40.4	-
	AMVN	91.3 ± 0.3	8.7 ± 0.3	-	-	-	-

*Theoretical values of A8 and A12 were calculated based on the compositions in prepolymerization mixtures.

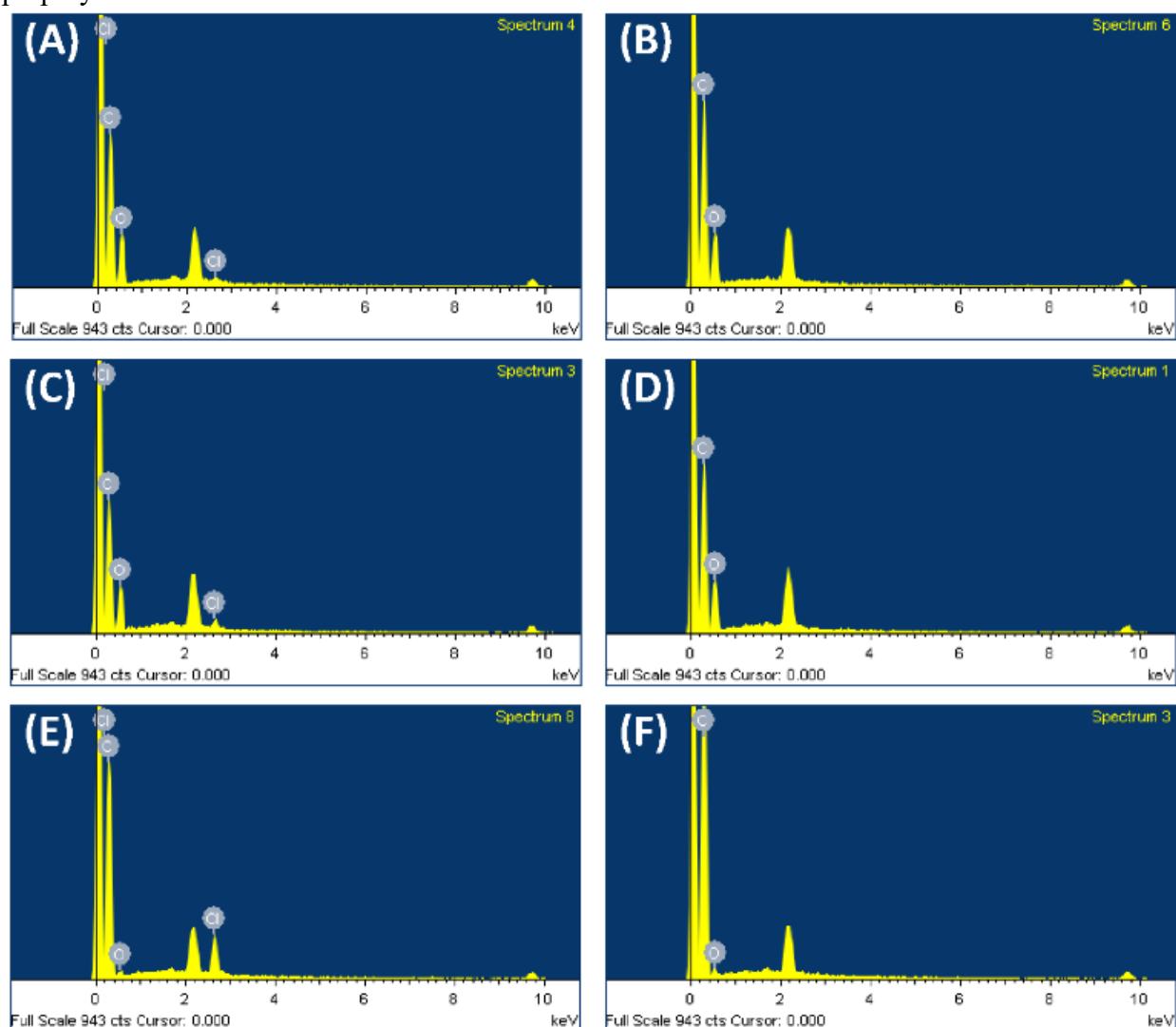


Figure S2. Exemplary EDS spectra for AEMs, (A,B) A8, (C,D) A12, (E,F) AMVN, in (A,C,E) Cl⁻ and (B,D,F) HCO₃⁻ forms.

Table S6. Normalized film thickness to hydrated membrane after permeability measurements.

	AMVN	A0	A8	A12
Hydrated	1.00	1.00	1.00	1.00
1. EtOH	1.05	0.93	0.91	0.85
2. KOFm	0.99	0.93	0.90	0.83
3. NaOFm	0.95	0.92	0.88	0.85
4. KOAc	1.02	0.91	0.90	0.83
5. NaOAc	1.05	0.93	0.89	0.83
6. EtOH/KOFm	1.01	0.92	0.91	0.87
7. EtOH/NaOFm	1.03	0.93	0.90	0.85
8. EtOH/KOAc	1.03	0.93	0.90	0.84
9. EtOH/NaOAc	1.03	0.93	0.90	0.84

Table S7. Volume of hydrated films and volume of swollen films (mm^3) after sorption experiments measured from photographs and a digital caliper. Normalized to the volume of the hydrated films.

	A0	A8	A12	AMVN
Hydrated	1.000	1.000	1.000	1.000
1. EtOH	0.988	0.904	0.899	1.085
2. KOFm	0.976	0.926	0.926	1.081
3. NaOFm	0.994	0.885	0.959	1.078
4. KOAc	0.968	0.885	0.880	1.068
5. NaOAc	0.946	0.899	0.876	1.084
6. EtOH/KOFm	1.090	1.016	0.993	1.070
7. EtOH/NaOFm	1.074	0.975	0.975	1.082
8. EtOH/KOAc	1.022	0.980	1.005	1.093
9. EtOH/NaOAc	1.002	0.969	0.984	1.078

Table S8. Volume fraction among the solution, EtOH (ϕ_e)-carboxylate salt (ϕ_c), inside the membranes after sorption experiments, where the remaining is the volume fraction of water (ϕ_w) from the solution.

	External, 1 M		AMVN		A0		A8		A12	
	ϕ_e	ϕ_c	ϕ_e	ϕ_c	ϕ_e	ϕ_c	ϕ_e	ϕ_c	ϕ_e	ϕ_c
1. EtOH	0.058	-	0.038	-	0.033	-	0.051	-	0.047	-
2. KOFm	-	0.044	-	0.017	-	0.016	-	0.025	-	0.025
3. NaOFm	-	0.035	-	0.010	-	0.009	-	0.014	-	0.010
4. KOAc	-	0.063	-	0.022	-	0.018	-	0.027	-	0.024
5. NaOAc	-	0.054	-	0.012	-	0.010	-	0.015	-	0.015
6. EtOH/KOFm	0.058	0.044	0.044	0.015	0.076	0.014	0.051	0.019	0.046	0.017
7. EtOH/NaOFm	0.058	0.035	0.045	0.008	0.081	0.010	0.053	0.011	0.047	0.010
8. EtOH/KOAc	0.058	0.063	0.051	0.019	0.070	0.012	0.053	0.024	0.046	0.019
9. EtOH/NaOAc	0.058	0.054	0.052	0.011	0.087	0.013	0.056	0.014	0.047	0.013

Table S9. Water volume fractions (ϕ_w) and solution volume fractions (ϕ_s) of films after sorption experiments, where the remaining is the polymer volume fraction (ϕ_p) from the dry polymer density.

	AMVN, ϕ_s	A0, ϕ_s	A8, ϕ_s	A12, ϕ_s
Water volume fractions, ϕ_w	0.217	0.452	0.492	0.504
1. EtOH	0.245	0.452	0.382	0.446
2. KOFm	0.242	0.445	0.397	0.462
3. NaOFm	0.240	0.455	0.369	0.481
4. KOAc	0.233	0.441	0.369	0.434
5. NaOAc	0.244	0.428	0.380	0.432
6. EtOH/KOFm	0.235	0.503	0.451	0.499
7. EtOH/NaOFm	0.243	0.496	0.427	0.489
8. EtOH/KOAc	0.250	0.470	0.430	0.505
9. EtOH/NaOAc	0.240	0.460	0.424	0.494

References

1. Hayduk, W.; Laudie, H. Prediction of Diffusion Coefficients for Nonelectrolytes in Dilute Aqueous Solutions. *Aiche J* **1974**, *20*, 611–615, doi:10.1002/aic.690200329.
2. Hao, L.; Leaist, D.G. Binary Mutual Diffusion Coefficients of Aqueous Alcohols. Methanol to 1-Heptanol. *J Chem Eng Data* **1996**, *41*, 210–213, doi:10.1021/je950222q.
3. Vany'sek, P. Ionic Conductivity and Diffusion at Infinite Dilution. *CRC Handbook of Chemistry and Physics, 93rd Edition* **2012**.
4. Hills, E.E.; Abraham, M.H.; Hersey, A.; Bevan, C.D. Diffusion Coefficients in Ethanol and in Water at 298K: Linear Free Energy Relationships. *Fluid Phase Equilibr* **2011**, *303*, 45–55, doi:10.1016/j.fluid.2011.01.002.