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Electronic Supplementary Information

Atomistic Characterization of Hydration-Dependent Fuel Cell Ionomer Nanostructure: Validation by Vibrational Spectroscopy

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Guide to Electronic Supplementary Information

Main Document

This supplementary document is organized as follows:

S1: DFT Geometry Optimizations and Normal Mode Analyses (pg. 1 - pg. 9)

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Nafion Model Compound Vibrational Normal Mode Eigenvector Animations

All model compound animations were produced in Schrodinger Maestro (v. 14.1, ©Schrödinger, LLC, New York, NY, 2024). Animations were recorded and exported as .mp4 files using the free version of Microsoft Clipchamp (v. 3.1, © 2025 Clipchamp). The speed and amplitude of the vibrations were set to 3 and 2, respectively. Values on the top left of each animation refer to the normal mode frequency in cm⁻¹. Atom color codes are specified below. All normal modes were calculated with DFT as specified in the main article (**2.1**).

Animations 1-3: Component models.

Colors: hydrogen (white), carbon (grey), oxygen (red), fluorine (green), sulfur (yellow).

- 1. Triflic Acid (1440, 831 cm⁻¹): DFT_TrflicAcid_720p.mp4
- 2. Triflate Ion: PFME (1016 cm⁻¹): DFT_Triflate_720p.mp4
- 3. **PFME** (1336, 1293, 1263, 1260, 1180, 983, 699 cm⁻¹): DFT_PFME_720p.mp4

Animations 4-9: 1-mer-CF₃ ($\Lambda = 0$).

<u>Colors</u>: hydrogen (white), carbon (dark grey), oxygen (red), sidechain -CF₃ fluorine (green), all other fluorine (light grey), sulfur (yellow).

4.	1-mer-CF₃-$\alpha_{\rm HF}$ (1439 cm ⁻¹):	DFT_1merCF3-alpha-HF_720p.mp4
5.	1-mer-CF₃-α_{NSC} (1011 cm ⁻¹):	DFT_1merCF3-alpha-NSC_720p.mp4
6.	1-mer-CF₃-α_{LF} (835 cm ⁻¹):	DFT_1merCF3-alpha-LF_720p.mp4
7.	1-mer-CF₃-β_{HF} (1032 cm ⁻¹):	DFT_1merCF3-beta-HF_720p.mp4
8.	1-mer-CF₃-β_{NSC} (1009 cm ⁻¹):	DFT_1merCF3-beta-NSC_720p.mp4
9.	1-mer-CF₃-β _{LF} (964 cm ⁻¹):	DFT_1merCF3-beta-HF_720p.mp4

ReaxFF Molecular Dynamics Files

RMD Structure Files: .pdb files corresponding to snapshots at 2 ns.

- 1. $\lambda = 0$: MD_L00-2ns.pdb
- 2. $\lambda = 1$: MD_L01-2ns.pdb
- 3. $\lambda = 2$: MD_L02-2ns.pdb
- 4. $\lambda = 3$: MD_L03-2ns.pdb
- 5. $\lambda = 5$: MD_L05-2ns.pdb
- 6. $\lambda = 7$: MD_L07-2ns.pdb
- 7. $\lambda = 10$: MD_L10-2ns.pdb
- 8. $\lambda = 15$: MD L15-2ns.pdb
- 9. $\lambda = 20$: MD_L20-2ns.pdb

Text Files: Time-dependent MD trajectory data. Each row corresponds to a time step and each column corresponds to a λ value.

- 1. Cell densities: MD_Density-vs-Time.txt
- 2. Number of SO₃H groups (i.e., $N_{S_{\alpha}}$): MD_nAlpha-vs-Time.txt

Excel File: f_{Λ} and $f_{\Lambda_{\alpha}}$ values for each λ at 2 ns.

1. MD_2ns-Analysis.xlsx

Figure 9 Inner-spheres Animation Panel Video

1. Fig9_1080p.mp4

Nafion 211 Dehydration vs. Time Transmission FTIR Video

1. NafionDehydration_1080p.mp4

S1: DFT Geometry Optimizations and Normal Mode Analyses

Preparation of QM-Calculated Spectra and Eigenvector Normal Mode Animations

All DFT model compounds considered in this study are shown in **Figure S1-1**. Each set of DFT-calculated normal modes was fit with a Lorentzian line shape function using the Schrodinger Maestro Spectrum Plot feature (v. 13.3, ©Schrödinger, LLC, New York, NY, 2024). The half-bandwidth was set to 8 and the scale factor was set to 1.0. Spectra were re-plotted using OriginPro (v. 2017, ©OriginLab Corporation, Northampton, MA). Each spectrum and its corresponding set of normal mode drop-line points were normalized to their maximum intensity peak and point, respectively, in the ~1100-1400 cm⁻¹ range. Vibrational modes with intensities below 1% of the maximum were not considered. In **Figures S1-3**, **S1-4**, and **S1-5**, drop-line points from ~1050-1350 cm⁻¹ are hidden, and all other points are reduced by half for visual clarity. Filled and open points represent normal modes with and without labeled assignments, respectively. Calculated normal mode frequencies are followed by a * symbol.

Component Model Normal Mode Analysis

Nonlinear molecules have 3N-6 orthogonal normal modes, each characterized by a unique set of motions, where every atom oscillates (or vibrates) with respect to an equilibrium position (e.g., angle or bond length) at a fixed frequency and phase.¹ For any normal mode, the vibrational internal coordinates of each molecular fragment (e.g. sidechain COC or -SO₃H groups) are mechanically coupled²⁻⁴ to the vibrations of neighboring fragments, giving rise to group modes (i.e., molecular fragments do not vibrate in isolation).^{5–13} Normal modes are, however, generally dominated by one, or a small number of, fragment(s) that undergo particularly large changes in their instantaneous dipole moments (IR active modes) and/or instantaneous polarizabilities (Raman active modes).^{1,14} Identification of these fragments is facilitated by normal mode analyses of 'component models' that minimally represent fragments of a larger 'parent' molecule. For example, triflic acid, triflate ion, and perfluorinated dimethyl ether (PFME) are all component models of the three Nafion monomer models (**Fig. S1-1**). Component model normal modes with high intensities, and whose eigenvector animations show large atomic displacements, typically result in large contributions to the corresponding monomer group modes.



Figure S1-1. DFT model compounds. Ether oxygens are labeled (A) and (B) to differentiate sidechain and backbone proximal fragments, respectively.





Figure S1-2. Component model normal mode analysis. (left) QM-calculated IR spectra with corresponding normal modes as drop-line points. Magnitudes of points are reduced by factors of 2, 3, and 2.5 for (a), (b), and (c), respectively; (right) Extrema snapshots of select normal mode animations. -CF₃ groups are hidden from the α - and β -mode snapshots for visual clarity.

It is noteworthy that that all our component models exhibit some degree of mechanical coupling. For example, all triflate modes are coupled $-SO_3^-$ and $-CF_3$ oscillations and all PFME modes are coupled COC and $-CF_3$ motions.

Figure S1-2 shows the calculated IR spectra and normal mode frequencies for triflic acid (α, protonated), triflate (β, deprotonated), and PFME. The triflic acid 1440* and 831* are both dominated by the -SO₃H group, and correspond to the Nafion α_{HF} (1414 cm⁻¹) and α_{LF} (910 cm⁻¹) bands, respectively (**Fig. 4b**). The 1440* mode is primarily v_{as} (O=S=O) and δ (SOH). The 831* mode is primarily v(S-OH), δ (O=S=O), δ (SOH), and v_s (CF₃). The triflate ion only yields a single 1016* near the observed β_{HF} (1058 cm⁻¹) and β_{LF} (971 cm⁻¹) bands (**Fig. 4b**). The 1016* mode is primarily a $v(SO_3^-)$ mode with some δ_u (CF₃) contribution. The absence of a second calculated β-mode for the triflate ion is unsurprising, given that the two observed β -modes for Nafion are group modes consisting of strongly coupled COC and SO₃⁻ motions.⁵⁻²¹ The PFME 983* mode is a perfect fit to the NSC band at 983 cm⁻¹ (**Fig. 4b** red and blue spectra). This mode is dominated by v_s (CF₃), where the -CF₃ stretching modes are out of phase. A concurrent ρ (COC) is a consequence of the -CF₃ motions. The v_s (COC) and v_{as} (COC) modes, known to contribute to Nafion α - and β -bands, appear at 1293* and 1180*, respectively.

Normal Mode Analyses of Nafion Monomers

Calculated normal mode frequencies of the three Nafion monomers are contrasted with observed FTIR band frequencies (**Table S1-1**). The QM-calculated spectra for the short backbone (1-mer-sbb), methyl-terminated backbone (1-mer-CH₃), and perfluoromethyl-terminated backbone (1-mer-CF₃) monomers are shown in **Figures S1-3**, **S1-4**, **S1-5**, respectively.

The effect of the functional and backbone terminal groups on the long backbone monomers (i.e., 1-mer-CH₃ and 1-mer-CF₃) are discussed in the main article (**3.1**). The PBE0-D3 frequencies across all three Nafion monomers are nearly identical. The notable difference between 1-mer-SBB and the long backbone monomers is the complete insensitivity of its NSC group modes to protonation state (i.e., NSC mode is 1007* for both the α - and β -forms). Thus, we performed normal mode analyses of incrementally hydrated 1-mer-CF₃, which has the closest structural resemblance to the real ionomer repeat unit (**Fig. 1**). The Λ -dependent 1-mer-CF₃ β _{HF}-band frequencies are shown in **Table S1-2**. For all Λ , the β _{HF} group mode is dominated by v_s(SO₃⁻) and has major contributions from v_s(COC-A), v(CS), v_s(COC-B).

		P	X3LYP ^{†,‡}	transmission-IR [‡]			
		1-mer-SBB	1-mer-CF ₃ 1-mer-CH ₃		1-mer-CH ₃	NR212	
<u>neutral</u>	α_{HF}	1440* (+1.8%)	1439* (+1.7%)	1439* (+1.7%)	1405* (-0.7%)	ਤੂ ∫1414 cm ⁻¹	
	$\alpha_{\rm LF}$	835 * (-8.2%)	835 * (-8.2%)	834* (-8.4%)	786* (-13.6%)	$\int_{1}^{1} dr_{a} dr_{a}$	
	$\alpha_{\rm NSC}$	1007* (+2.4%)	1011* (+2.8%)	1009* (+2.6%)	981* (-0.2%)	983 cm ⁻¹	
ionized	$\beta_{\rm HF}$	1032* (-2.5%)	1032* (-2.5%)	1032* (-2.5%)	1059* (+0.1%)	$\sim \frac{1058 \text{ cm}^{-1}}{2}$	
	$\beta_{\rm LF}$	955* (-1.8%)	964 * (-0.9%)	963* (-1.0%)	983* (+1.0%)	113 erb 1 971 cm ⁻¹	
	β_{NSC}	1007* (+2.4%)	1009* (+2.6%)	1011* (+2.8%)	973 * (-1.0%)	$=$ 983 cm^{-1}	

Table S1-1. Observed and QM-calculated IR frequencies for NR212 membrane and model Nafion monomers, respectively. X3LYP-based frequencies and observed bands were obtained with permission from Loupe et al.² Copyright 2020 American Chemical Society.

*DFT calculated frequencies (cm⁻¹) with 0 waters ($\Lambda = 0$). *Values taken from Loupe et al. (**Ref. 13**).

Values in parenthesis are percent differences with respect to FTIR. (**bold** values: smallest errors). *basis set: 6-311G**++



Figure S1-3. Dry 1-mer-SBB QM-calculated spectra and select corresponding normal modes (droplines).



Figure S1-4. Dry 1-mer-CH₃ QM-calculated spectra and select corresponding normal modes (droplines).



Figure S1-5. Dry 1-mer-CF₃ QM-calculated spectra and select corresponding normal modes (droplines).

	$\boldsymbol{\beta}_{\mathbf{HF}}$ (cm ⁻¹)	$\boldsymbol{\beta}_{\mathrm{HF},\Lambda} - \boldsymbol{\beta}_{\mathrm{HF},\Lambda-1} (\mathrm{cm}^{-1})$	FTIR – $\beta_{\text{HF},\Lambda}$ (cm ⁻¹)
FTIR	1059 [†]	_	_
$\Lambda = 0$	1031.93*	_	27
$\Lambda = 3$	1049.15*	+17.22	10
$\Lambda = 4$	1049.85*	+0.70	9
$\Lambda = 5$	1049.92*	+0.07	9
$\Lambda = 6$	1050.79*	+0.87	8
$\Lambda = 7$	1051.02*	+0.23	8
$\Lambda = 8$	1052.03*	+1.01	7
$\Lambda = 9$	1052.14*	+0.11	7
$\Lambda = 10$	1052.95*	+0.81	6
$\Lambda = 11$	1053.19*	+0.24	6
$\Lambda = 12$	1053.07*	-0.12	6
$\Lambda = 13$	1050.79*	-2.28	8
$\Lambda = 14$	1053.48*	+2.69	6
$\Lambda = 15$	1052.94*	-0.54	6

Table S1-2. QM-calculated β_{HF} frequencies versus observed β_{HF} band center from fully hydrated N212 (value obtained with permission from Loupe et al.² Copyright 2020 American Chemical Society). The average and standard deviation for $\Lambda = 3-15$, are $\overline{\beta_{HF}}$ and $\sigma_{\beta_{HF}}$, respectively (bottom).

Between $\Lambda = 3$ to 15: $\overline{\beta_{HF}} = 1051.64 \text{ cm}^{-1}$; $\sigma_{\beta_{HF}} = \pm 1.47 \text{ cm}^{-1}$ *DFT calculated frequencies (PBE0-D3/LACV3P**++) †Value obtained from Loupe et al. (**Ref. 13**)

Hydrated 1-mer-CF₃ Model Construction

The dry α -form (i.e., α_0) 1-mer-CF₃ *initial* structure was constructed to closely resemble the geometryoptimized dry Nafion monomer from our prior work.¹³ Paddison and Elliot noted the challenges to determining the global minimum structure and obtaining a smooth potential energy surface for an Aquivion model, as it requires systematic optimizations over all degrees of freedom for the entire structure.²² We did not search for the global minimum energy structure because the calculated 1-mer-CF₃ IR frequencies are in good agreement with observed FTIR bands at extreme states of hydration (**Table S1-1**).



CIP: contact ion-pair. SSIP: solvent-separated ion-pair.

Figure S1-6. Geometry optimized 1-mer-CF₃ complexes for $\Lambda = 0-15$. Not all outer sphere atoms (purple) are shown. Color code: Hydrogen (white), carbon (grey), non-hydronium and non-Zundel oxygen (red), hydronium oxygen (blue), Zundel oxygen (green), fluorine (light green), sulfur (yellow), hydrogen bonds (dashed green lines).

Fifteen hydrated 1-mer-CF₃ model structures were prepared by sequentially adding water to the *optimized* α_0 model. Upon each addition, the resulting hydration complex was geometry-optimized, without inclusion of an external dielectric medium^{7,12} or implicit solvent (e.g., continuum solvation model)^{23–26}. Water molecules were manually placed to maximize hydrogen bonding interactions with the exchange site and adjacent waters. All discussion of 1-mer-CF₃ complexes hereafter pertain to geometry-optimized structures, unless indicated otherwise.

<u>1-mer-CF₃ Hydration Structure</u>

Each optimized 1-mer-CF₃ complex has a unique arrangement of water (**Fig. S1-6**). **Table S1-3** lists Λ -dependent interatomic distances for each complex. The geometries of the α_1 , α_2 , and β_3 hydration complexes are nearly identical to those reported by others.^{27–30} Structural analysis of the $\Lambda = 0.5$ complexes are listed below.

 α_0 : The 0.97 Å SO-H bond length is identical to SO-H bond lengths reported for $\Lambda = 0$ RSO₃H structures.^{7,10,13,27,30}

 a_1 : The SO-H bond is polarized and weakened by the nearby water molecule, leading to a slight bond elongation (1.01 Å). The proximity of the water is reflected in the 2.59 Å SOH…OH₂ inter-oxygen distance. The water serves as both a hydrogen bond acceptor and donor to the -SO₃H site, resulting in a small 'ring-like' hydrogen bond network.^{27,30}

 α_2 : The SO-H bond is further elongated (1.06 Å) and the 2.47 Å SOH····OH₂ distance is shorter than that of the α_1 complex. The α_2 complex features a ring-like hydrogen bond network, where both waters interact with each other and the -SO₃H site.

Table S1-3. 1-mer-CF₃ interatomic distances (Å) versus Λ .

Λ	SO…H	$SO(H) \cdots OH_n^{(+)}$				
0	0.97	_				
1	1.01	2.59 $(n = 2)$				
2	1.06	2.47 ↓				
<u>3†</u>	<u>1.55</u>	2.54 (n = 3)				
4	1.70	2.63				
<u>5</u> ‡	<u>3.26</u>	<u>3.78</u>				
6	3.25	3.76				
7	3.31	3.85				
8	3.29	3.85				
9	3.44	4.06				
10	3.46	4.01				
11	3.54	4.21				
12	3.46	4.02				
13	3.43	3.97				
14	2.97	3.34				
15	2.90	3.34				
[†] SO–H covalent bond breakage						

[†]SO-H covalent bond breakage. [‡]H₃O⁺ separation from SO₃⁻.

 β_3 (contact ion-pair): The proton is dissociated from the exchange site resulting in a hydronium ion. The distance between the hydronium proton and its nearest sulfonate oxygen (i.e., SO···H₃O⁺) is 1.55 Å. The hydronium and sulfonate ions are arranged as a contact ion-pair, with a 2.54 Å SO···OH₃⁺ interoxygen distance, comparable to the SOH···OH₂ distances of the α_1 and α_2 complexes.

 β_4 (contact ion-pair): The hydronium ion donates three hydrogen bonds (~1.02 Å each): two to separate waters and one to the -SO₃⁻ site. The hydronium-sulfonate ion-pair exhibits slightly greater separation (SO···OH₃⁺ is 2.63 Å) than the β_3 ion-pair. Additionally, the SO···H₃O⁺ distance (1.70 Å) is slightly longer than in the β_3 complex.

 β_5 (solvent-separated ion-pair): The sulfonate and hydronium ions are arranged as a solvent-separated ion-pair. The ions are bridged by a water to which they are hydrogen bonded to. The ion-pair exhibits significantly longer SO····H₃O⁺ and SO····OH₃⁺ distances (3.26 Å and 3.78 Å, respectively), compared to the β_3 and β_4 contact ion-pairs.

The exchange site remains β beyond $\Lambda = 5$, with the hydronium and sulfonate ions consistently bridged by one water (i.e., solvent-separated ion-pair). The SO···OH₃⁺ distance fluctuates between 3.34 Å and 4.06 Å.

1-mer-CF3 Conformational Analysis

Figure S1-7 shows the initial and optimized geometries of the α_0 1-mer-CF₃ model, as well as N_{np} values and dihedral angles of the monomer backbone and sidechain. The N_{np} values are governed by the distance between the sulfur atom and its nearest backbone terminal carbon (S···CF₃).

Initial α_0 **Model** (Fig. S1-7a): The backbone is elongated with carbon atoms arranged primarily *anti*³¹ to one another and fluorine atoms mostly staggered across adjacent carbons (i.e., fluorocarbon backbone is in a *trans*^{18,22,31–33} or 'staggered *trans*' conformation^{22,33}). One end of the chain is partially folded (or 'kinked'^{22,33}) toward the -SO₃H site, with a *gauche*^{18,22,32,33} F₃C-C-C-C dihedral angle (φ_{BB}) of 138°. The sidechain is almost fully extended, with a CF₂-CF(CF₃)-O-CF₂ dihedral (φ_{SC}) of 187°.

Optimized α_0 **Model** (Fig. S1-7b): The backbone is bent closer towards the -SO₃H site ($\phi_{BB} = 97^\circ$), yet the sidechain remains nearly the same ($\phi_{SC} = 189^\circ$). The resultant N_{np} value is 13 and S…CF₃ is 8.65 Å.

From $\Lambda = 0$ to $\Lambda = 4$, φ_{SC} varies by approximately 100°, while φ_{BB} changes by only ~10°. This supports reports of hydration-induced PFSA sidechain flexibility, with water acting as a plasticizer.^{34,35} The PTFE backbone stiffness is attributed to high torsional energy barriers between CF₂-CF₂ units.^{22,36} Force field torsional potentials for CMD simulations of Nafion oligomers have been investigated by Vishnyakov and Neimark.^{32,37,38}

From $\Lambda = 1$ to $\Lambda = 4$, S…CF₃ decreases by 4.24 Å, enabling backbone atoms to penetrate the innersphere (N_{np} increases by 6). The largest increase in N_{np} between consecutive Λ , between $\Lambda = 1$ and $\Lambda = 2$ (N_{np} increases by 4), coincides with the largest decreases in S…CF₃ (decreases by 2.95 Å). The φ_{SC} angle decreases the most (by 56°) between $\Lambda = 3$ and $\Lambda = 4$.

From $\Lambda = 4$ to $\Lambda = 15$ the overall conformation and N_{np} remain largely unchanged, reflected by relatively constant S···CF₃ and ϕ_{SC} values.



Figure S1-7. 1-mer-CF₃ conformational analysis. (a) Initial α_0 structure (b) Table of interatomic distances (Å) and dihedral angles versus Λ for optimized 1-mer-CF₃ models. All outer-sphere fluorine atoms are hidden from full monomer illustrations for visual clarity.

S2: ReaxFF Molecular Dynamics Simulations



Figure S2-1. Geometry-optimized configurations of CF₃SO₃(H) (i..e, triflic acid/triflate ion) using DFT and ReaxFF in the presence of different numbers of water molecules.



Average cell densities over between 1900-2000 ps

Figure S2-2. Nafion MD cell densities during ReaxFF simulation. Top: table of densities averaged over final 100 ps of each simulation; Bottom left: densities versus time over 2 ns. Bottom right: densities versus time over initial 20 ps. All cells have an initial 1.8 g/cm³ initial density.



Figure S2-3. Number of α sites $(N_{S_{\alpha}})$ versus ReaxFF simulation time for each λ .

Table S2-1. Maximum number of exchange site inner-spheres that a water resides in (q) for each Nafion-water cell.

λ	0	1	2	3	5	7	10	15	20
q	_	4	5	5	5	4	4	4	4



Figure S2-4. Two-dimensional conceptual illustration of a $\lambda = 3$ system. Waters are categorized as inner- and outer-sphere. Inner-sphere waters are non-bridge or bridge. Outer-sphere waters are bulk-like or isolated. The histogram number (n_{hist}), number of overcounts (n_{over}), and water count discrepancy (δ) are calculated for the example system.



Figure S2-5. Nanophase evolution with increasing λ . Colored Connolly surfaces (1.4 Å probe radius) are applied to atom groupings according to nanophase.

<u>S3: Solvent Autoprotolysis Calculations</u>

No sulfonic acid autoprotolysis (i.e., self-association or autoionization) was observed in the λ_0 MD cell. However, the expected number of equilibrium autoprotolysis products in a λ_0 volume (V_{λ_0}) packed with a pure protic solvent (HA) can be calculated from the solvent autoprotolysis constant (K_{ap}). Assuming the solvent is monoprotic (or only has one appreciably labile proton), the following equilibrium reaction represents the autoprotolysis of an acid, HA.

$$2HA \rightleftharpoons H_2A^+ + A^-$$
 (Reaction 1)

The autoprotolysis constant is the product of the conjugate acid and base concentrations (Eq. 1).

$$K_{ap} = [H_2 A^+][A^-]$$
 (1)

The conjugate acid and base concentrations are equimolar. It follows that the concentration of either species is the square root of K_{ap} (Eq. 2).

$$[H_2A^+] = \sqrt{K_{ap}} \tag{2}$$

The product of the protonated acid concentration by the volume of the cell is the expected number of the conjugate acid.

 $n_{[H_2A^+]} = [H_2A^+]V_{\lambda_0}N_A$ (3)

Equations 1-3 are demonstrated below with sulfuric acid and water.

Example Calculations

Cell volume: $V_{\lambda_0} = (280 \text{ nm}^3) \left(\frac{1.00 \, l}{10.0^{24} \text{ nm}^3}\right) = 2.81 * 10^{-22} \, l$

Example 1: Sulfuric acid, H₂SO₄ (K_{ap} = $2.4*10^{-4}$ at 25 °C). Dielectric, $\kappa \approx 100.^{40,41}$

$$n_{[H_3SO_4^+],V_{\lambda_0}} = (\sqrt{2.4 * 10^{-4} \text{ mol}^2 l^{-2}})(6.022 * 10^{23} \text{ mol}^{-1})(2.81 * 10^{-2} \ l) = 2.6$$

Example 2: Water, H₂O (K_{ap} = K_w = 10.0⁻¹⁴ at 25 °C) $\kappa \approx 80$.

$$n_{[H_30^+],V_{\lambda_0}} = (\sqrt{10^{-14} \text{ mol}^2 l^{-2}})(6.022 * 10^{23} \text{ mol}^{-1})(2.81 * 10^{-22} l) = 1.69 * 10^{-5} l^{-5}$$

Since no H₃O⁺ ion is expected in a V_{λ_0} cell packed with water at equilibrium, the minimum cell size required to observe a single H₃O⁺ ion is calculated by the division of V_{λ_0} by $n_{[H_3O^+],V_{\lambda_0}}$.

$$V_{cell} = \left(\frac{1.69*10^{-5} \text{ H}_3 \text{O}^+}{V_{\lambda_0}}\right)^{-1} = 5.91*10^4 \text{ V}_{\lambda_0}$$

Summary: At equilibrium, two $H_3SO_4^+$ ions are expected in a V_{λ_0} cell packed with sulfuric acid. However, a cell packed with water requires a volume $\sim 10^5$ times larger than V_{λ_0} , for a single H_3O^+ ion to be observed. Nafion, with a far lower dielectric constant ($\kappa \approx 4$) than water ($\kappa \approx 80$) and relatively low number density of acid sites, must require a volume several orders of magnitude greater than V_{λ_0} for a single $SO_3H_2^+$ ion to be observed.

S4: References

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