Explicit Proton Transport in Hydrated Nafion

Matt K. Petersen

Center for Biophysical Modeling and Simulation and Department of Chemistry

University of Utah, Salt Lake City

Multi-State Empirical Valence Bond Model (MS-EVB)

The definition of the protonated species can change during the dynamical process.

Schmitt and Voth, J. Phys. Chem. B 102, 5547 (1998) Schmitt and Voth, J. Chem. Phys. 111, 9361 (1999) Day et al, J. Chem. Phys. 117, 5839 (2002)

$$\begin{split} H_{ii} &= V_{H_{3}0^{+}}^{intra} + \sum_{k}^{nH_{2}0} V_{(H_{2}0)_{k}}^{intra} + \sum_{k}^{nH_{2}0} V_{(H_{2}0)_{k},H_{3}0^{+}}^{inter} + \sum_{k < k'}^{nH_{2}0} V_{(H_{2}0)_{k},k'}^{inter} \\ V_{ij} &= (V_{const.} + V_{ex.}) \bullet A(R_{00}, R_{0H}) \\ E_{0} &= \sum_{ij} c_{i}^{0} c_{j}^{0} H_{ij}(x) \qquad F_{k}(x) = -\sum_{ij} c_{i}^{0} c_{j}^{0} \frac{\partial}{\partial X_{k}} H_{ij}(x) \qquad H = \begin{bmatrix} H_{11} & V_{12} & V_{13} & V_{14} \\ V_{21} & H_{22} & V_{23} & V_{24} \\ V_{31} & V_{32} & H_{33} & V_{34} \\ V_{41} & V_{42} & V_{43} & H_{44} \end{bmatrix} \end{split}$$

MS-EVB v. non-Dissociable Classical Potential

MS-EVB

Ion pair radial distributions for both the MS-EVB hydronium and classical non-dissociable hydronium ions.

Note the distinctive peak in the classical curve about $\sim 3\text{\AA}$.

Classical

Hydronium Oxygen/Sulfonic Oxygen Radial Distribution



The anomalous peak in the classical curves is a consequence of the nondissociable limitation of the classical field.

Petersen et al, J. Phys. Chem. B 109, 3727 (2005)

Self-Consistent Iterative MS-EVB

A multi proton extension to the MS-EVB method has been developed wherein the computational cost scales linearly with respect to the number of excess protons.

In the SCI-MS-EVB method a single MS-EVB problem is solved iteratively for each 'EVB-complex' within the effective field of all other complexes./

Wang and Voth, J. Chem. Phys. 122, 144105 (2005)

$$q_{s} = \sum_{i}^{states} c_{B_{i}}^{2} q_{s}^{H_{3}O^{+}} + \sum_{j\neq i}^{states} c_{B_{j}}^{2} q_{s}^{H_{2}O} + \sum_{i,j,i\neq j}^{states} c_{B_{i}}^{2} c_{B_{j}}^{2} q_{ex,ij}^{A} A(R_{OO}, R_{OH})$$

in general;

$$\alpha = \sum_{i}^{\text{states}} c_{B_{i}}^{2} \alpha_{s}^{H_{3}O^{+}} + \sum_{j \neq i}^{\text{states}} c_{B_{j}}^{2} \alpha_{s}^{H_{2}O}$$

Free Energy of Ion Pair Dissociation

The potential of mean force for the SCI-MS-EVB hydronium (black) and SCI-MS-EVB (red) CEC.

Î CEC atoms

 $(H_{3}O^{+})$

atoms (H₃O⁺

 $\overline{q}_{j;i} \overline{r}_{j;i}$



Solvation Structures



Characterization of Ion Pair Dissociation



Grotthuss v. Vehicular Diffusion



The trajectory of the state with the largest amplitude can be decomposed into discrete and continuous components.



Mean Squared Displacement

Grotthuss Shuttling in Nafion



$$\langle \vec{r}_{CEC_1} \bullet \vec{r}_{CEC_1} \rangle = \langle \vec{r}_c \bullet \vec{r}_c \rangle + \langle \vec{r}_d \bullet \vec{r}_d \rangle + 2 \langle \vec{r}_c \bullet \vec{r}_d \rangle.$$

The same treatment in bulk water displays negligible negative correlation

The total MSD is not only less than the sum of the components but less than either component.

As water diffuses away from some mean position the amplitudes shift restoring the position of the CEC.

The Sulfonate counter ion acts as a proton 'sink'.



Conclusions

A dissociable model is critical in understanding the dynamical process of proton diffusion in hydrated Nafion.

Grotthuss shuttling is an important part of proton transport in the PEM. Intuitively, one might suppose that shuttling would increase the total charge diffusion, however this is not the case.

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Greg Voth

(University of Utah, Dept. Of Chemistry)

Feng Wang

(Boston University, Dept. of Chemistry)



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