Supporting Information: Diffusivity of Mono- and Divalent Salts and Water in Desalination Membranes

*Dipak Aryal, Venkat Ganesan**

Department of Chemical Engineering, University of Texas at Austin, Austin, TX 78712, USA

E-mail: venkat@che.utexas.edu

Phone: 512-471-4856

S1. Supplementary Results for Polymer Membranes in KCl and $MgCl_2$ solutions

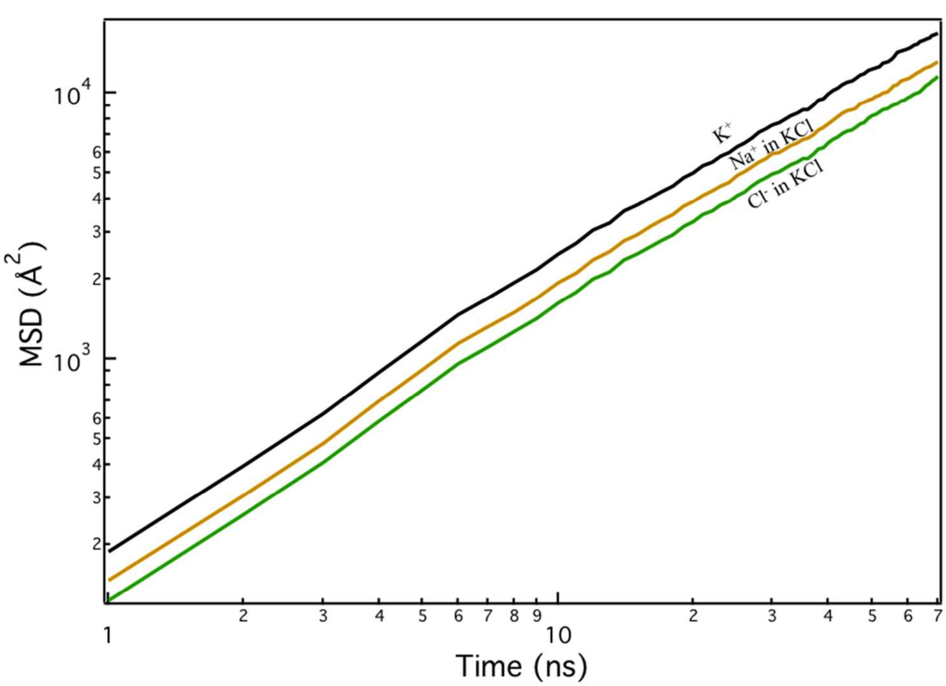

Figure S1. Mean Square displacement of K^+, Na^+, Cl^- ions from polymer membrane at 1 M KCl concentration as a function of time.

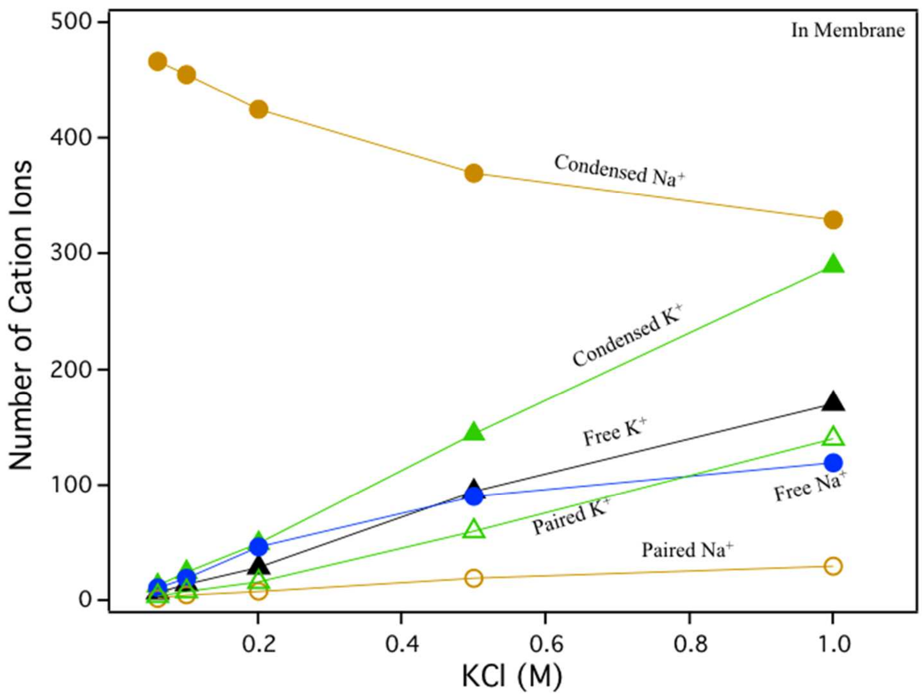

Figure S2. The number of condensed, paired, and free of K^+ and Na^+ ions respectively as a function KCl concentration in the membranes.

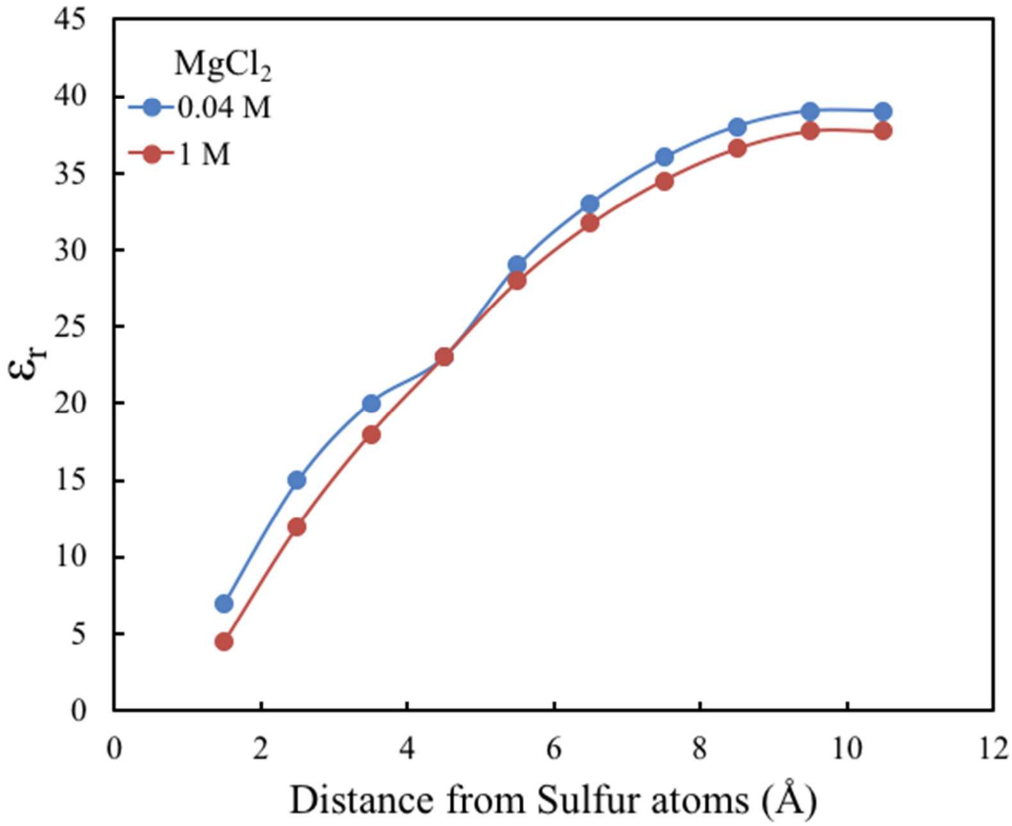

Figure S3. Local dielectric constant of water molecules as a function of distance from sulfur for polymer backbone at 0.04 and 1 M $MgCl_2$ concentration. The lines represent a guide to the eye.

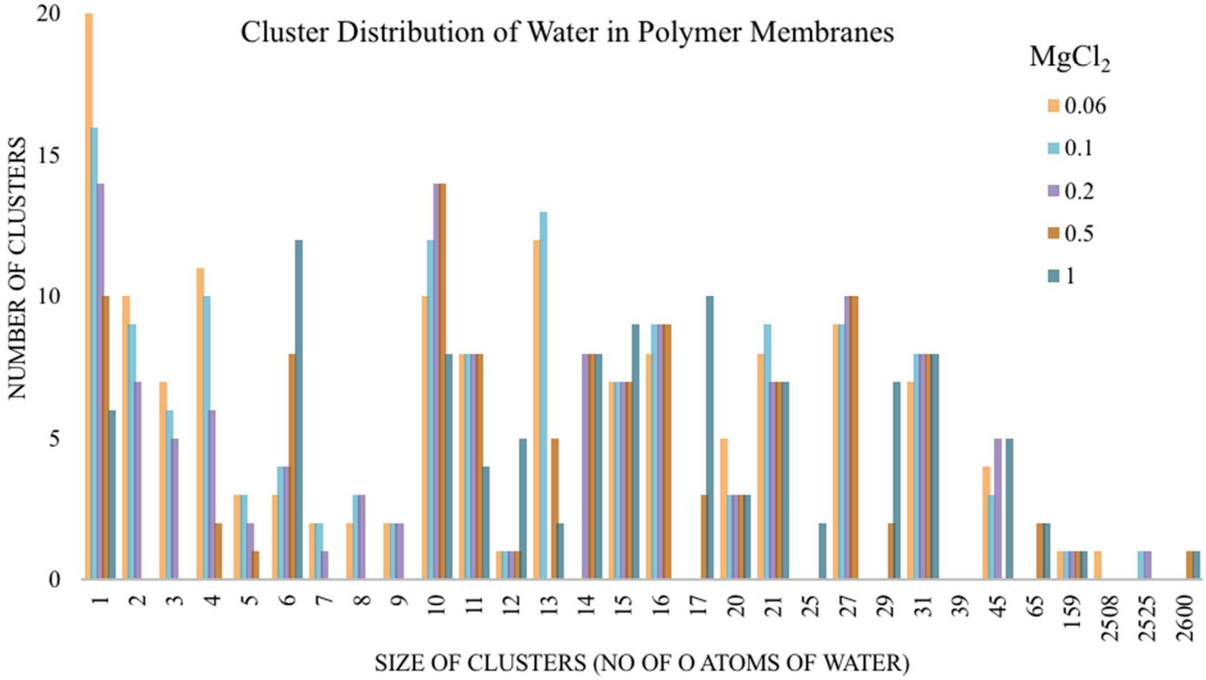

Figure S4. Cluster distribution of water molecules in polymer electrolyte membrane as a function of $MgCl_2$ concentration.

S2. Diffusion coefficients of Mg^{++}, Na^{+}, and Cl^{-} Ions in the 1:1 Mixture of NaCl and $MgCl_2$

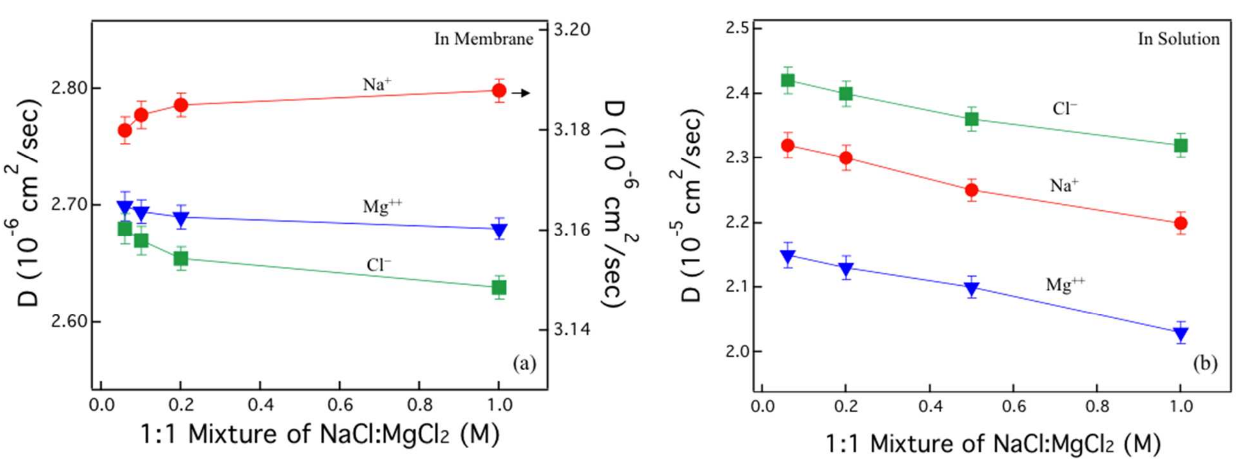

Figure S5. Diffusion coefficients of Mg^{++}, Na^{+}, and Cl^{-} both (a) in membrane, and (b) in pure as a function of 1:1 mixture of NaCl and $MgCl_2$ concentration. The lines represent a guide to the eye.

In Figure S5, we present the results for the diffusion coefficients of Mg^{++}, Na^{+} and Cl^{-} ions in the membrane as a function of mixture concentration. In general, we observe trends similar to those seen in $MgCl_2$ solutions: (a) The diffusion coefficients of both Mg^{++} and Cl^{-} ions decrease slightly with increasing mixture concentration; (b) The diffusivities of Na^{+} ions are seen to increase with increasing mixture concentration.

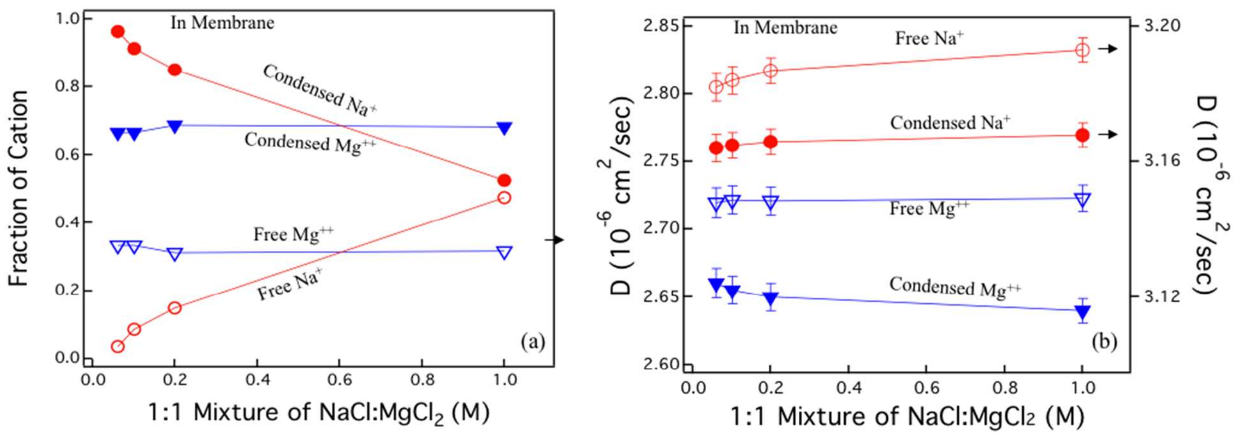

Figure S6. (a) The fraction of condensed (closed symbols) and free (open symbols) Mg^{++} and Na^{+}ions; (b) Diffusivity of condensed and free Mg^{++} , and Na^{+} ions in membranes as a function 1:1 mixture of NaCl and $MgCl_2$ concentration. The lines represent a guide to the eye.

We again categorized the condensed and free ions and their diffusivities as a function of mixture concentration and display the results in Figure S6. Overall, the trends seen mirror those discussed in the context of Figure 8 of the main article. The differences are seen to arise in the fraction of condensed/free Mg^{++} ions which are seen to remain almost constant over the entire mixture concentration. In contrast, the fraction of condensed Na^{+} ions decreases while the free Na^{+} ions increase with increasing mixture concentration. At low salt concentrations, the fraction of condensed Mg^{++} is seen to be lower than that of the condensed Na^{+}, however, with increasing salt concentration the *number* of condensed Mg^{++} ions increases and eventually exceeds that of the condensed Na^{+} ions. These results can be straightforwardly understood based on the preferential interactions between the sulfonate groups and Mg^{++} ions relative to the Na^{+} ions.

Figure S6 b displays the individual mobilities of condensed and free Mg^{++} and Na^{+} ions in the membrane as a function mixture concentration. Therein, it can be seen that with an increase in the salt concentration, the diffusivity of condensed Mg^{++} ions slightly decreases, whereas the mobility of free Mg^{++} ions remains relatively insensitive to the salt concentration. Interestingly, we observe that diffusivities of both condensed and free Mg^{++} and Na^{+} ions in the mixture are higher than those seen in $MgCl_2$ (Figure 7a) solutions. This can be explained by noting that, in the mixture of salts, there are a fewer number of Mg^{++} ions (as compared to the pure $MgCl_2$ solutions) in the systems. Whence, the number of condensed Mg^{++} ions is lower at a specified salt concentration compared to the pure solution. Moreover, there is also expected to be the competition with sulfonate groups of newly added Na+ ions from salt.

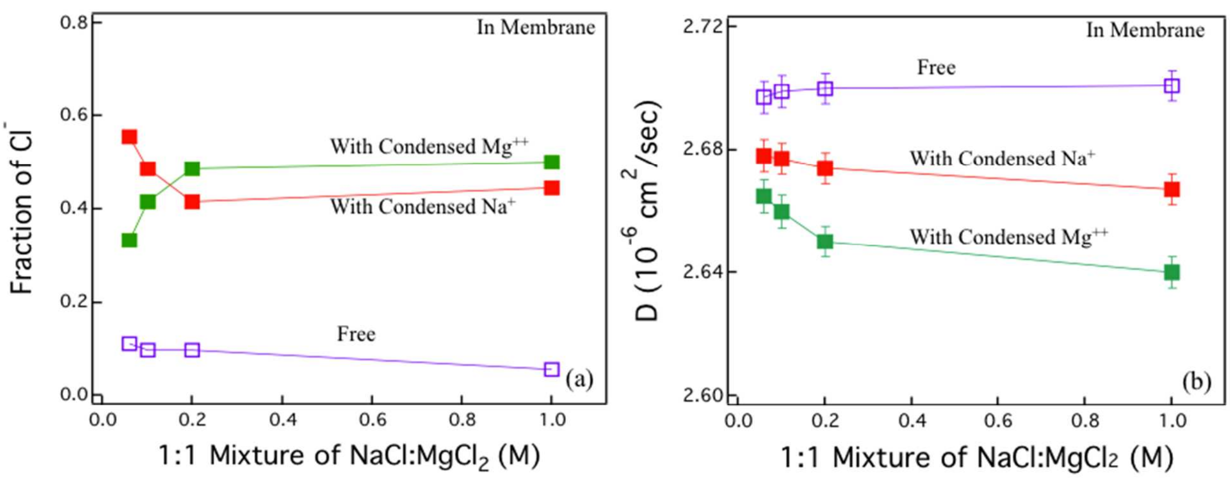

Figure S7. (a) The fraction of Cl^{-} ions that associated with condensed Mg^{++} and Na^{+} ions, and free Cl^{-} ions. (b) Diffusion coefficients of Cl^{-} ions that associated with condensed Mg^{++} and Na^{+} ions, and free Cl^{-} in membrane as a function of 1:1 mixture of NaCl and $MgCl_2$ concentration. The lines represent a guide to the eye.

Similar to the analyses for Cl^{-} ions discussed in the article, in the present case, we again classified the Cl^{-} ions in the polymer membrane into five populations: (I) Those which are associated with the condensed Mg^{++} ions; (II) Those which are associated with condensed Na^{+} ions; (III) Those which are associated with free Mg^{++} ions; (IV) Those which are associated with free Na^{+} ions; and (V) Free Cl^{-} ions as shown in Figure S7 a (data for population III and IV are not shown for clarity). The relative fraction (f) of the different populations exhibit the trend: $f_I > f_{II} > f_{III} > f_V > f_{IV}$. More explicitly, Cl^{-} ions again tend to favor pairing with condensed Mg^{++} (f_I) and Na^{+} (f_{II}) ions. As a consequence, the majority of the Cl^{-} ions resulting from the addition of salt are seen to become associated with the condensed ions. The corresponding the mobility of these categorized ions are displayed in Figure S7b and conform to intuitive expectations and demonstrate that the diffusivities of these populations follow the order $D_V > D_{IV} > D_{III} > D_{II} > D_I$. These results for the diffusivities and the populations of relative fractions, demonstrate that the mobility of Cl^{-} ions in the membrane is influenced by the diffusivities of the population I and II and rationalize the salt concentration dependencies seen in Figure S5.

S3. Impact Salt Concentration on Diffusion of Sulfur atoms of Polymer Backbone

We also studied the influence of salt concentration on the dynamics of the charged groups of polymers. Figure S8a depicts diffusion coefficients of S atoms as a function of mono (KCl) and divalent ($MgCl_2$) concentration. In polymer electrolyte KCl solution, the diffusivities of S atoms are seen to increase with increasing salt concentration. In contrast, the mobility of S atoms in $MgCl_2$ decreases with salt concentration and are seen to be almost two times slower than that in KCl. As we discussed earlier (Figure 4a) with increasing salt concentration, the K^{+} ions are less strongly associated with S atoms than that of Na^{+} ions, whereas in contrast, Mg^{++} ions become more strongly coupled with S atoms (Figure 8a). Being divalent cations, we also expect

Mg^{++} ions to also serve as cross-linkers between ionic groups, resulting in a significant reduction in the mobility of charged polymeric groups. Such expectations are seen to borne in the results displayed in Figure S8b.

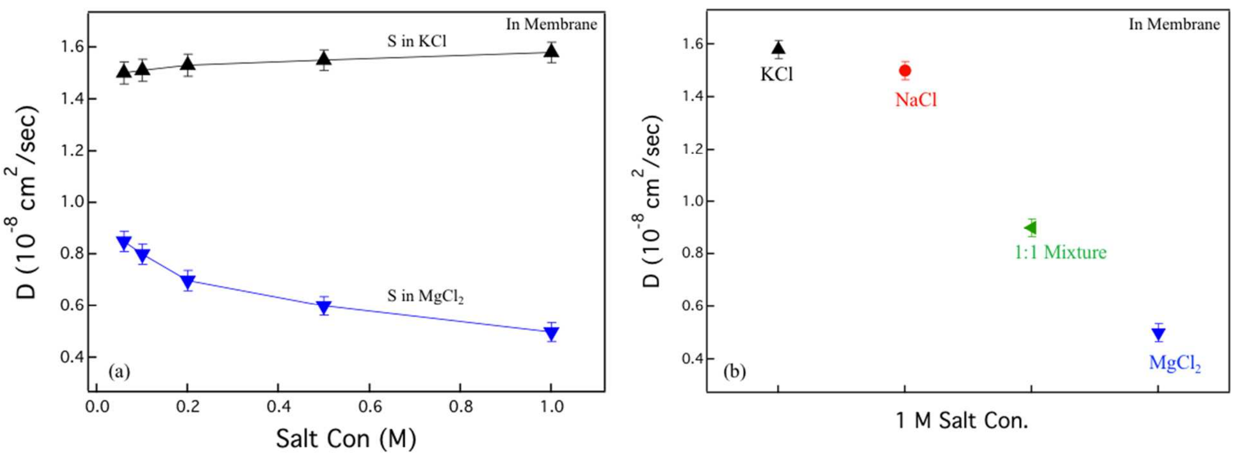

Figure S8. Diffusion coefficients of sulfur atoms (a) in KCl, and in $MgCl_2$ as a function of salt concentration, (b) in KCl, NaCl, $MgCl_2$, and 1:1 mixture of NaCl and $MgCl_2$ at 1 M salt concentration. The lines represent a guide to the eye.