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Counterion Condensation in Nafion

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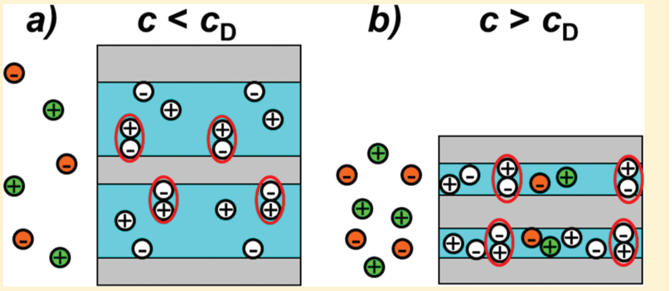
ABSTRACT: Nafion(117) membranes in contact with acidic solutions were characterized by small-angle X-ray scattering and by acid solution uptake measurements. The principle of Donnan equilibrium was used to obtain independent estimates of the extent of counterion condensation in the membranes from the three experiments. The surprising conclusion of our study is that a large fraction of the protons in Nafion are in the condensed form when the membrane is immersed in pure water. Estimates of the fraction of condensed protons range from 72 to 98%.



INTRODUCTION

Polymers that conduct protons are currently a subject of considerable interest due to their relevance in a variety of traditional applications such as chlor-alkali cells[1,2] and the development of clean energy devices such as hydrogen fuel cells[3,4] and photoelectrochemical cells.[5−7] The most widely studied proton conducting membrane is Nafion, a copolymer with hydrophilic perfluorosulfonic acid moieties located randomly along a hydrophobic backbone.[1,2] The ion exchange, electrochemical, and morphological properties of Nafion have been extensively studied.[4,8−18] The moles of sulfonic acid sites per gram of polymer is commonly reported as the ion exchange capacity (IEC). It is generally assumed, either explicitly or implicitly, that proton transport is enabled by the dissociation of all of the acidic protons in the membrane, based on the value of the IEC.[19−22] To our knowledge, there are two prior studies that have addressed the possibility of counterion condensation in Nafion, i.e, the possibility that some of the protons in hydrated Nafion are not dissociated: (1) Sondheimer et al.,[23] who studied the catalytic activity of Nafion, and (2) Rollet et al.,[24] who used small-angle neutron scattering to determine the locations of the dissociated counterions. No quantitative estimate of the extent of counterion condensation was provided in these papers.

The polymer chains in a Nafion membrane exhibit complex conformations due to their self-assembly into hydrophilic and hydrophobic domains.[4,13−16,20] A much simpler situation arises when a linear polyelectrolyte chain such as polystyrenesulfonate (PSS) with randomly located sulfonic acid groups is dissolved in excess water. Incomplete dissociation of these chains, even in the limit of infinite dilution, is obtained due to counterion condensation.[25] The free energy of a completely dissociated chain is higher than that of a partially dissociated chain due to the Coulombic repulsion of closely spaced negative charges that are confined to the polymer backbone.[25,26] The extent of counterion condensation in hydrated dense PSS brushes is higher than that in individual chains due to intra- and interchain Coulombic repulsion of negative charges confined to the brush.[27,28] The purpose of this paper is to extend a technique derived from the work of Balastre et al. on counterion condensation in polyelectrolyte brushes[28] to evaluate the extent of counterion condensation in Nafion. Our efforts to determine the extent of counterion condensation in Nafion is motivated by the possibility that the mobility of condensed counterions is lower than that of that of dissociated counterions. This in turn could have serious implications on membrane performance.

The present study is based on a hypothesis that combines the Donnan equilibrium principle with the self-assembly of copolymers shown schematically in Figure 1, where we show a polymer electrolyte membrane in contact with an aqueous ionic solution. The polymer is microphase separated into hydrophilic and hydrophobic domains. The hydrophilic domains are hydrated due to diffusion of water into the membrane. We assume that a fraction of the positive counterions in the membrane are condensed while the remaining counterions are dissociated, as shown in Figure 1. When the chemical potential of the ions in solution is lower than that of the dissociated ions in the membrane, there is no driving force for ions from the solution to enter the membrane as indicated in Figure 1a. As the concentration of ions in the solution is increased, the chemical potential of the ions outside will exceed that of the dissociated ions within the membrane and the solution will enter the membrane as indicated in Figure 1b. We use the symbol c_D to denote the solution concentration at which the ions begin to crossover and enter the

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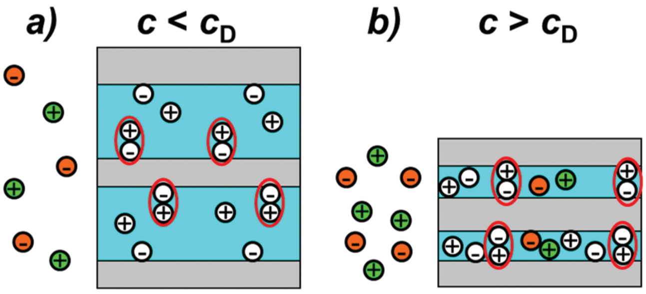

Figure 1. Schematic of a periodically structured polymer electrolyte membrane in contact with an external electrolyte solution. The hydrophilic microphase (colored blue) contains the ionic species while the hydrophobic microphase (colored gray) is free of ions. (a) When the external electrolyte concentration, c, is below the Donnan concentration, c_D, the external ions cannot enter the membrane because their chemical potential is lower than that of the ions in the membrane. (b) When c is greater than c_D, the external ions enter the membrane because their chemical potential exceeds that of the ions in the membrane, resulting in a decrease in the length scale of the periodic structure and a decrease in the concentration of water in the membrane.

membrane (Donnan concentration). The presence of additional ions in the membrane will result in increased screening of the charges inside the membrane when the solution concentration exceeds c_D. The size of polymer chains in free solution decreases as screening increases.[29] One thus expects a shrinking of the hydrophilic channels when the solution concentration, c, is greater than c_D, as shown in in Figure 1b. It is logical to expect a decrease in the acid solution uptake of the membrane when c becomes greater than c_D. Measurements of the domain size and acid solution uptake as a function of c can thus be used to estimate c_D.

The depiction of ion dissociation in Figure 1 is clearly an oversimplification. Our coarse-grained approach is based on two states (Figure 1): a condensed state wherein the counterion is close to the fixed charge (i.e., the distance between the positive and negative ions is much less than the Bjerrum length) and a dissociated state wherein the counterion is far away from the fixed charge (i.e., the distance between the positive and negative ions is much greater than the Bjerrum length). In reality, there will be a distribution of distances between the fixed charges and the counterions. Additional complexities arise due to the different kinds of solvation shells surrounding the dissociated counterions.[30] Our approach does not account for these effects.

EXPERIMENTAL METHODS

Sample Preparation. Nafion 117 membranes (178 μm reported thickness) with a reported IEC of 0.91 mmol/g were purchased from Sigma-Aldrich. Samples were cut and boiled in 10 wt % nitric acid solution for 1 h. The samples were then soaked in deionized water, with the external solution frequently replaced until the pH was neutral. The samples were then boiled in 10 wt % hydrogen peroxide for 1 h and washed and soaked in deionized water, followed by drying at room temperature under vacuum for 3 days.

Small-Angle X-ray Scattering (SAXS). The Nafion samples described above were placed in solutions of HCl inside SAXS cells with Kapton windows as shown schematically in Figure 2 (inset). The cells contained Teflon washers for sealing the contents. The samples were equilibrated in the HCl solutions for a minimum of 24 h before measurements were made. The equilibration time was determined from the time required for the acid solution uptake of the membranes to reach time-independent values (∼1 h). The presence of the HCl solution in the path of the X-ray beam does not affect the angular dependence of the SAXS profiles. SAXS experiments were conducted at beamline 1-4 at Stanford Synchrotron Radiation Lightsource (SSRL). The resulting two-dimensional scattering data were averaged azimuthally to obtain intensity versus magnitude of the scattering wave vector q ($q = 4\pi \sin(\theta/2)/\lambda$, where λ is the wavelength of the X-rays and θ is the scattering angle). The scattering data were corrected for the detector dark current and the scattering from air and Kapton windows.

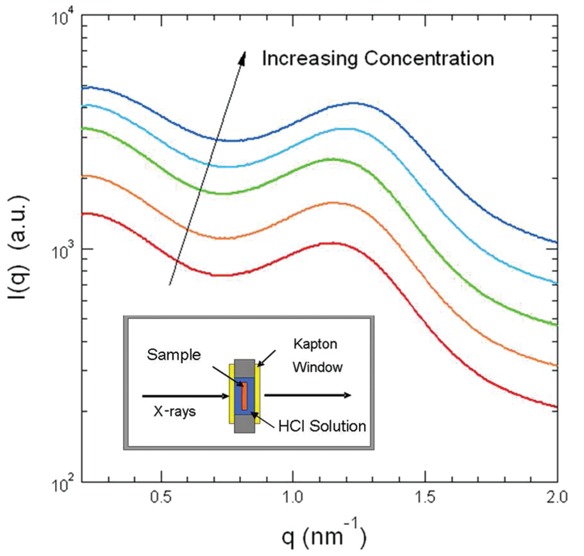

Figure 2. Plots of SAXS intensity, I, versus scattering vector, q, of Nafion in contact with HCl solutions of varying concentration. Curves are shifted vertically for clarity. Increasing concentrations are shown in ascending order: 0 M (red), 0.01 M (orange), 0.1 M (light green), 0.4 M (light blue), 1 M (blue). The inset illustrates schematic of SAXS cell used to ensure contact between Nafion and the acidic solution.

Acid Solution Uptake Experiments. Dry Nafion 117 samples were removed from vacuum and weighed using a mass balance. Samples were then placed in HCl solution vials of known concentration and sealed to prevent evaporation. Membranes were removed for measurement using Teflon tweezers and placed on a Kimwipe to blot off excess liquid. Samples were then weighed on a mass balance and returned to the solution vials. Acid solution uptake, SU, is defined as the ratio of the weights of the sample after acid solution uptake to that of the dry film weight, as shown in eq 1.

$$\mathrm{SU} = \frac{\text{hydrated film weight} - \text{dry film weight}}{\text{dry film weight}} \qquad (1)$$

It is important to note that SU is a measure of the uptake of both acid and water molecules.

Acid Release Experiments. The objective of this experiment is to determine the concentration of dissociated negative ions inside the membrane, c_{m-}, when it is equilibrated in an external acid solution with molar concentration, c. It is obvious that c_{m-} is related to the moles of free acid molecules in the membrane. Nafion membranes were equilibrated in a vial containing HCl solutions as described above, removed from solution, and blotted dry to remove solution on the surface of the films. The membranes were then placed in a second vial consisting of 7−10 mL of deionized water and allowed to equilibrate for 24 h. The membranes were then removed, and the resulting pH of the solution was measured. Samples were placed in a third vial, and the pH of this solution was also measured to ensure complete removal of the absorbed electrolyte. The amount of Nafion used in each experiment was chosen such that the measured pH in the second vial was measurably lower than the pH of deionized water. Control measurements were also performed using polystyrene films to ensure that residual acid residing on the surface of the films after our blotting protocol did not affect our measurements. The value of c_{m-} is determined from the number of moles of acid removed from the Nafion film and SU.

■ RESULTS

SAXS intensity, I, from Nafion equilibrated with HCl solutions with varying concentrations, c, is plotted as a function of the scattering vector, q, in Figure 2. The SAXS profiles contain a single broad peak at $q = q_{\mathrm{peak}}$ in the vicinity of 1.2 nm^{-1}. This feature, which is consistent with previous SAXS studies on Nafion, indicates the presence of a periodic structure with a length scale $d = 2\pi/\ q_{\mathrm{peak}}$ in the vicinity of 5 nm. In Figure 3a we show the dependence of d on c. It is evident that d is nearly independent of c when $c < 0.01$ M. When $c > 0.03$ M, d decreases rapidly with increasing c. The lines in Figure 3a are error-weighted least-squares fits through the low and high concentration data sets. The intersection of these lines, which occurs at $c = c_D = 0.07 \pm 0.07$ M, provides one estimate of the Donnan solution concentration, based on the hypothesis presented in Figure 1.

The dependence of acid solution uptake, SU, of the Nafion membranes on c is shown in Figure 3b. It is evident that SU is nearly independent of c when $c < 0.01$ M. When $c > 0.03$ M, SU decreases rapidly with increasing c. The low concentration data in Figure 3b are in agreement with a large body of literature on water-equilibrated Nafion.[31] The lines in Figure 3b are error-weighted least-squares fits through the low and high concentration data sets. The intersection of these lines, which occurs at $c = c_D = 0.06 \pm 0.04$ M, provides a second estimate of the Donnan solution concentration, based on the hypothesis presented in Figure 1.

The macroscopic deswelling of the membrane shown in Figure 3b and the microscopic deswelling of the hydrophilic domains seen in Figure 3a are remarkably similar. Consequently, it is not surprising that the values of c_D determined from the two experiments are similar. For simplicity, we use the values of c_D based on the acid solution uptake experiments in the discussion that follows.

In the dilute limit where ideal mixing is obtained and the activity coefficients can be approximated to be unity, we expect the concentration of dissociated protons inside the hydrophilic channels of the membrane equilibrated with pure water, c_{m0+}, to be equal to the measured value of c_D.[32] On the basis of the IEC and pure water uptake of Nafion, the estimated concentration of protons (both dissociated and undissociated) inside the hydrophilic channels of the membrane, c_{IEC}, is 3.2 M. This value is obtained by dividing the IEC by the liquid water uptake, followed by a unit conversion to volumetric concentration using the density of water. The fraction of free counterions in the hydrated membrane under the ideal mixing approximation is thus $c_D/c_{\mathrm{IEC}} = 0.02 \pm 0.01 (= 0.06\ \mathrm{M}/3.2\ \mathrm{M})$. In other words, $98 \pm 1\%$ of the protons are condensed in Nafion equilibrated with pure water.

The standard analysis of Donnan equilibrium relates the concentration of dissociated negative ions inside the membrane, c_{m-}, to the external ionic concentration, c, ignoring contributions due to effects such as chain stretching due to acid solution uptake, microphase separation, and nonideality of the solutions both inside and outside the membrane. At low values of c, c_{m-} is nearly zero, and positive deviations from zero are expected when c exceeds c_D (Figure 1). The relationship between and c_{m-} and c depends on the concentration of negative charges (fixed charges) bound to the membrane, c_b.[33]

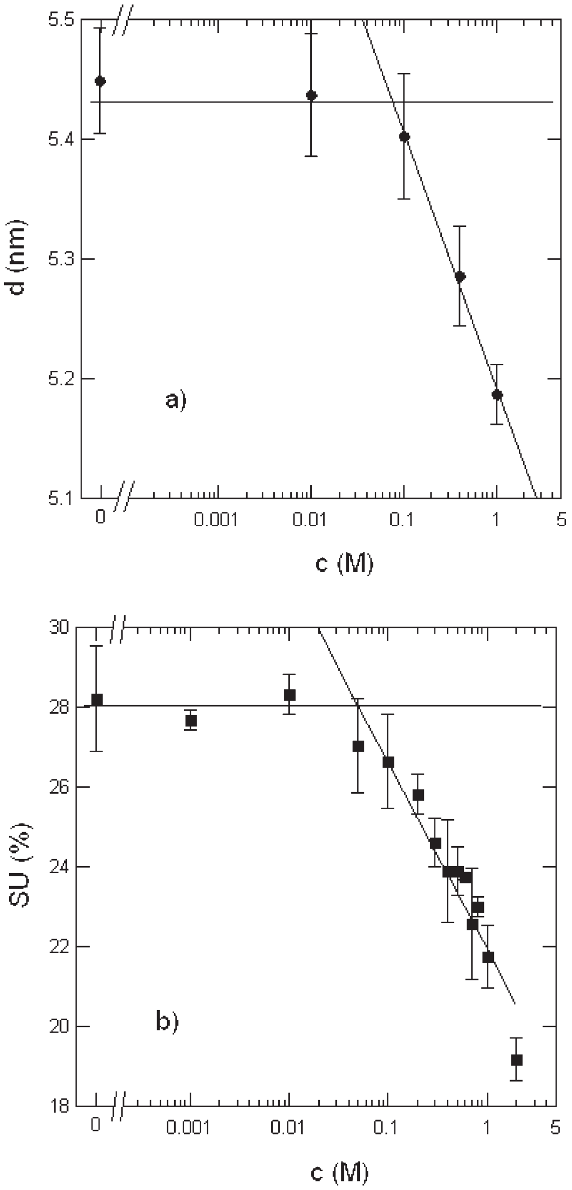

Figure 3. Response of Nafion to changes in external HCl concentration, c, characterized by (a) domain size, d, measured by SAXS and (b) acid solution uptake, SU. Both figures indicate that deswelling occurs at approximately $c = 0.06$ M HCl, which leads to the conclusion that $98 \pm 1\%$ of the protons in Nafion are in the condensed form.

$$c_{m-} = \frac{-c_b + \sqrt{c_b^2 + 4c^2}}{2} \qquad (2)$$

Figure 4 compares the experimentally determined c_{m-} versus c dependence with theoretical predictions with $c_b = c_D = 0.06$ M and $c_b = c_{\mathrm{IEC}} = 3.2$ M, which constitute the two limits of interest. It is clear that the experimental data are not in agreement with either prediction. We also use an error-weighted least-squares fit to determine a fitted value of the bound ion concentration, c_{Fit}. The fitting leads to $c_b = c_{\mathrm{Fit}} = 0.9 \pm 0.3$ M, and this curve is also shown in Figure 4. The value of c_{Fit} indicates that $72 \pm 9\%$ of the

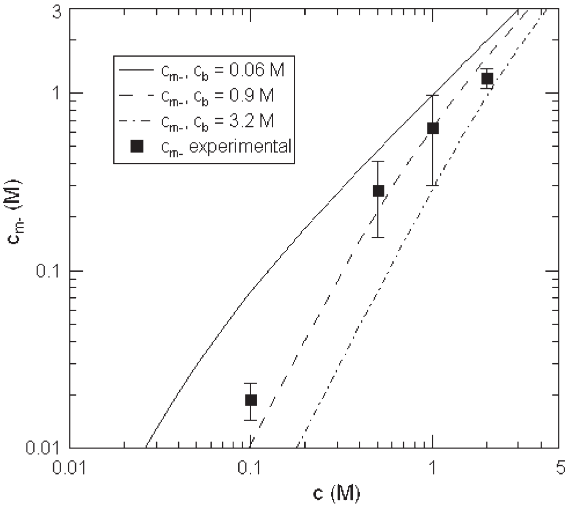

Figure 4. Results of acid release experiments. Squares represent the measured concentration of dissociated negative ions inside the membrane, c_{m-}, as a function of the external acid concentration, c. Curves represent theoretical predictions based on Donnan equilibrium (eq 2) the assumed concentration of negative charges bound to the membrane, c_b, equal to 0.06 M (solid line), 0.9 M (dashed line), and 3.2 M (dashed and dotted line). This leads to the conclusion that 72 ± 9% of the protons in Nafion are in the condensed form.

protons are in the condensed form. We offer no explanation for the difference in counterion condensation estimated using the Donnan theory and that using SAXS and acid solution uptake except to note that many previous studies on acid solution uptake in ion-exchange resins have reported significant discrepancies between the Donnan theory and experiment.[34,35]

Our assumption of ideal mixing is a reasonable approximation for HCl solutions with $c < 0.06$ M.[36] It is conceivable, however, that our assumption of ideal mixing within the membrane is not valid. If all of the protons in the membrane were fully dissociated, then the activity coefficient of the ions in the membrane would have to be 0.02 in order to satisfy the chemical potential equality constraint at $c = c_D$. In other words, large negative deviations from ideality for the ionic solutions inside the membrane are needed if the extent of counterion condensation in the membrane is significantly lower than our estimate. We are not aware of any theoretical justification for large negative deviations from ideality for confined ionic solutions. It is important to note that the activity coefficient of a 3.2 M HCl solution is about 1.3;[36] i.e., unconfined acidic solutions exhibit positive deviations from ideality. While *ab initio* computer simulations of ionically functionalized carbon nanotubes show that the distance between fixed charges has a significant impact upon dissociation,[37] generalizations to other kinds of confined systems have not yet been made. We hope that our results will motivate further studies of the effect of confinement on the thermodynamics of ionic solutions.

We conclude this section by reviewing some of the previous studies on Nafion that are directly related to the work presented here. Two groups have used acid solutions to examine the static properties of Nafion.[20,38] However, neither group used the results to determine the fraction of free ions versus ion pairs. Measurements of the transference number and electro-osmotic drag coefficient of Nafion in contact with acidic solutions presented in refs 39−42 can, in principle, be used to determine counterion condensation, but we are not aware of a framework that enables this determination. Likewise, proton diffusion measurements such as those of Zawodzinski and co-workers[43] may also contain signatures of counterion condensation, but these have not yet been identified. As mentioned in the Introduction, the works of Sondheimer et al.[23] and Rollet et al.[24] represent the only previous studies on the subject of counterion condensation in Nafion.

■ CONCLUSION

In summary, we have conducted SAXS and uptake measurements on Nafion membranes in contact with acidic solutions. The principle of Donnan equilibrium was used to interpret the data. Our experiments indicate that a large fraction of the protons within Nafion in contact with pure water are in the condensed form. Estimates of the fraction of condensed protons range from 72 to 98%; the former value is obtained from the acid release experiments while the latter value is obtained from SAXS and acid solution uptake measurements. Our conclusions are similar to those of Balastre et al.,[28] who also concluded that 80% of the counterions in hydrated polyelectrolyte brushes were condensed. These conclusions are based on the ideal mixing assumption inside the membrane. Further work on determining the chemical potential of ions in confined media and the relationship between dissociation constants and transport properties in polymer electrolyte membranes seems warranted.

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