SORPTION IN PROTON EXCHANGE MEMBRANES: AN EXPLANATION OF SCHROEDER’S PARADOX

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Introduction

Fuel cells based on the proton-exchange membranes (PEMs) are of great potential as efficient and largely pollution-free power generators for mobile and stationary applications. The PFSA membranes typically consist of a polytetrafluoroethylene (PTFE) backbone with side-chains terminating in SO3H groups. They possess little porosity in the dry state. However, in the presence of water or other polar solvents, the membrane swells and the sulfonic acid groups ionize protonating the sorbed solvent molecules that are responsible for conducting the protons. The conductivity of Nafion® is highly dependent upon hydration level being essentially an insulator below a threshold and rising through several orders of magnitude to about 0.07 ~ 0.1 Siemens/cm at 80 °C when it is fully hydrated.

The water uptake in Nafion® expressed in terms of λ, the number of moles of water per equivalent of polymer, upon contact with liquid or its saturated vapor as reported in the literature. There is an unexplained discrepancy in the water uptake in Nafion® from pure liquid (λw ≈ 22~23) versus that from its saturated vapor (λp ≈ 13.5~14.0), even though both possess unit activity. In fact, when a liquid water-equilibrated membrane was removed and exposed to saturated water vapor, λ dropped from 22 to 14, thus indicating that the two states are thermodynamically stable. The phenomena, known as Schroeder’s paradox, is apparently not uncommon in polymer systems, but has not so far been satisfactorily explained although many different explanations have been advanced.

A sorption model of water in Nation® is proposed here based on that the sorption isotherm is controlled by the swelling pressure determined by the matrix and surface forces of the polymer membrane and sorbed solvent.

Model Description

When the ion exchange membrane, e.g., Nafion®, is in equilibrium with a solvent, e.g., water, some of the sorbed solvent molecules are in a physicochemical state that is different from the bulk solvent molecules depending upon their interaction with surroundings. The model developed here simply assumes that the sorbed solvent molecules are of two types; i) those that are strongly, or chemically, bound to the acid sites, akin to chemisorption, and ii) others that are physically equilibrated between the fluid and the membrane phases, akin to physisorption. It is further assumed that as the membrane swells due to solvent uptake, the solvent molecules meet increasing resistance from the hydrophobic backbone as well as the stretched polymer chains resulting in a swelling pressure on the pore liquid. The model, thus, involves a balance of forces. Equilibrium is achieved when the elastic forces of the polymer matrix counterbalance the increased pressure within the pore liquid in an effort of solvent molecules to equalize the chemical potential of the fluid inside and outside of the pore. The spring constant κ of the spring is assumed to depend upon the temperature (e.g., proximity to the glass-transition temperature, Tg) and pretreatment procedures.

Liquid-Membrane Phase Equilibria

For equilibration between a liquid and membrane phases for an uncharged species \( i \)

\[
\ln \frac{a_{i,m}^F}{a_{i}^F} = \left( \frac{V_i}{RT} \right) \Pi_M
\]

(1)

where the membrane swelling, or osmotic pressure, \( \Pi_M = P_M - P_L \), is the pressure rise within the membrane exerted by the membrane polymer matrix due to stretching to accommodate the imbibed pore liquid. The activity of species \( i \) within the membrane \( a_{i,m}^F \) corresponds to the ‘free’, or non-chemically bound, molecules of \( i \), as denoted by the superscript ‘F’.

Vapor-Membrane Phase Equilibria.

When the membrane equilibrates with a vapor phase, assuming that the pressure changes within the condensed phase in the pore is caused both due to the stretching of the polymer chains upon solvent uptake, \( \Pi_M \), as well as that exerted by the curved vapor-liquid interface within the pores, \( \Pi_s \),

\[
\ln \frac{a_{i,m}^F}{a_{i}^F} = \left( \frac{V_i}{RT} \right) \left( \Pi_M + \Pi_s \right)
\]

(2)

where the vapor phase activity \( a_{i}^F = P_i/P_i^{sat} \) and \( \Pi_s \) is provided by the equation of Young and Laplace

\[
\Pi_s = -\frac{2\alpha \cos \theta}{r_p}
\]

(3)

where \( \theta \) is the liquid-membrane contact angle and \( r_p \) is the mean pore radius of liquid-filled pores. For the case of saturated vapor, \( P_i = P_i^{sat} \), then Eq. (2) gives

\[
\ln a_{i,m}^F = \left( \frac{V_i}{RT} \right) \left( \Pi_M + \Pi_s \right)
\]

(4)

whereas for the case of pure liquid solvent \( i \), from Eq. (1)

\[
\ln a_{i,m}^F = \left( \frac{V_i}{RT} \right) \Pi_M
\]

(5)

It is then clear from the Eq. (4) and (5) that, in general, the amount sorbed from a saturated vapor would be different from that sorbed from a pure liquid, both possessing unit activity. This simple result, thus, provides a reasonable explanation for the Schroeder’s paradox for the sorption in polymers.

The final expression for the liquid-phase sorption in the proton exchange membrane is obtained as

\[
\left\{ \frac{\lambda_{i,m} K_i a_{i,m} \left[ 1 - (1-a_{i,m})^{1-K_i-1} \right]}{(1-a_{i,m})^{1+(K_i-1)a_{i,m}^{-1}}} \right\}^{1/2}
\]

\[
\lambda_{i,m} \left[ \frac{\kappa}{\kappa + \frac{\lambda_{i,m} V_i}{V_M}} \right]^{1/2} < 1
\]

(6)

where \( \lambda_{i,m} \) is the monolayer coverage being bound, \( K_i \) is the equilibrium constant of water molecules with ion exchange site of the polymer and \( V \) is the number of equilibrium steps chemical equilibrium between the ion exchange site and each water molecules.
For the vapor-phase sorption, surface energy term is included in the isotherm expression as

\[
\lambda_{i,V} = \left( \frac{1}{\lambda_{i,V}(a_\nu,\nu)} \right)^{-1} \left[ \frac{1-(\nu+1)(a_\nu,\nu)\nu+(a_\nu,\nu)^{\nu+1}}{1+(K_1^{-1})a_\nu-1} \right]
\]

Further, it is then clear from the Eq. (6) and (7) that the solvent loading in liquid sorption, \( \lambda_{i,l} \), would be different from the solvent loading from the vapor sorption \( \lambda_{i,V} \).

**Results and Discussion**

In order to apply this model into water sorption in Nafion\textsuperscript{®}, the parameters of the equations, \( K_1 \), \( \lambda_{i,m} \), and \( \nu \), are obtained based on the following considerations. The equilibrium constant \( K_1 \) between water and the side chain of SO\textsubscript{3}H ion is approximated by that of sulfuric acid in water for the first ionization. The solvent loading parameter, \( \lambda_{i,m} \), is taken as a monolayer coverage being bound in the proton exchange membrane. The number of equilibrium steps, \( \nu \), for hydration of the ions is related to the number of solvent molecules in the hydration shell. For sulfonated styrene-type ion exchanger, six hydration number for SO\textsubscript{3}H group is reported experimentally and recent molecular modeling studies also results in 5 to 6 hydration number for SO\textsubscript{3}H. The activity of water in Nafion\textsuperscript{®}, which is osmotically active, is limited to the water molecules that are outside of the first hydration shell.\textsuperscript{7} In the dry or low humidity conditions, a few water molecules are in the hydration shell and are not enough to shield the ions and as the humidity of the membrane increases, more water molecules are involved in the shielding of sulfonic acid and hydronium ion.

Figure 1 shows the predicted isotherm of water in Nafion\textsuperscript{®} by Eq. (7), the solid line, as well as the experimental data. The model represents the sorption of water in Nafion\textsuperscript{®} and predicts quite precisely all the features of the isotherm throughout the entire range of vapor phase activity; it predicts the high initial slope, gradual increase of the slope after the sorption of the first a few molecules and high slope at high activities after about \( a_{i,V} = 0.7 \sim 0.8 \).

In order to explain the Schroeder's paradox for the sorption of water in Nafion\textsuperscript{®}, Eq. (6) and (7) can be further modified for the sorption of pure liquid, \( a_{i,l} = 1.0 \). The model predicts the loading of water in water solution \( \lambda_{i,l} = 22 \sim 23 \) and \( \lambda_{i,V} = 15 \sim 16 \) for saturated vapor condition. There is a clear difference in solvent loading between liquid and saturated vapor sorption; that is, the solvent loading of vapor phase sorption is less than that of liquid phase, in this case the difference is about seven. This means that seven water molecules per acid site on average are less sorbed in Nafion\textsuperscript{®} when the molecules are sorbed from the vapor compared with the liquid molecules contacting the membrane. The reason for this difference is that the surface energy of the sorption phase affects the chemical potential of the sorption phase in different extents in the liquid and saturated vapor sorption.

The simplified model presented here predicts the isotherms, the solvent loadings from the vapor and liquid phase sorption, and explains the Schroeder’s paradox for the water sorption in Nafion\textsuperscript{®} satisfactorily. It is based on the difference in the states, which are stable in thermodynamic means, of the sorption phases where the sorption phases interact with different environments of the bulk liquid and its saturated vapor phases.

**Conclusions**

A theoretical model is developed for the sorption of solvent in proton exchange membrane. This model predicts isotherm of water in Nation\textsuperscript{®} quite precisely and provides insight into the sorption phenomena in the ion exchange polymer. The sorption isotherm is a result of equilibrium conditions that are established between the elastic forces of the polymer matrix and swelling pressure in the membrane. The swelling pressure is derived from the solvent activity inside of the polymer membrane and the dissociation characteristics of the solvent in the presence of the acid exchange site.

The isotherm equations clearly show the difference in the sorption amount from liquid and its saturated vapor, which is known as Schroeder’s paradox. The paradox could well be explained in terms of surface energy that leads different energy states of sorption molecules for the liquid immersion and saturated vapor conditions.

**Figure 1.** Isotherm of water vapor in Nafion: experimental reports (symbols) from four different groups with model prediction (solid line).

**References**