



Steady state analysis of water vapor transport in ionomers

N.S. Schneider*, D. Rivin

Natick Soldier Research Development and Engineering Center, Kansas Street, Natick, MA 01760 0520, USA

ARTICLE INFO

Article history:

Received 17 September 2009

Received in revised form

4 December 2009

Accepted 5 December 2009

Available online 16 December 2009

Keywords:

Nafion

Sulfonated triblock ionomers

Steady state analysis of transport properties

ABSTRACT

Diffusion coefficients for water in high permeability ionomers are determined from steady state permeation measurements, corrected for boundary layer resistance and change in vapor concentration along sample length, to circumvent problems due to heat of condensation and structural relaxation. Values for water in the perfluoroionomer, Nafion, converted to solvent self-diffusion coefficients, D_1 , are consistent with the NMR based free volume (f_v) relation for Nafion at high concentrations. At low concentrations D_1 decreases more rapidly than f_v values, an effect attributed to ion hydration involving up to 6 water molecules per sulfonate group. The reduction in D_1 due to concentration averaging in permeation, estimated using the f_v relation, is about 23%. Water vapor sorption isotherms and steady state values of D_1 , for two different types of styrene hydrogenated butadiene triblock ionomers and Nafion can be superimposed using morphology dependent vertical scaling factors. The simple correspondence between results for the hydrocarbon ionomers and Nafion, is attributed to a common transport mechanism based on the restriction of water to ionic pathways. There are a number of claims in the literature that water uptake by highly permeability polymers is greater from the liquid phase than from saturated vapor at unit activity. This paper demonstrates that the disparity, known as Schroeder's paradox, does not occur in sorption under equilibrium conditions or in permeability measurements, if proper corrections for boundary layer resistance and vapor concentration profile are applied.

Published by Elsevier Ltd.

1. Introduction

Ionomers, such as Nafion®, are of interest in a variety of applications [1], where high water vapor permeability or favorable proton conductivity are important, including fuel cell membranes, pervaporative separation of water from liquid mixtures [2] and trace water removal from solvent streams [3]. Work in this laboratory has focused on ionomers as permselective barriers for protective clothing, based on the exceptionally high water vapor transport in combination with potential resistance to hazardous organic chemicals. Full characterization of the transport process requires determination of the sorption isotherm and diffusion coefficients as a function of water vapor concentration at one or more temperatures, depending on the application. However, the proper characterization of water transport behavior is not always a straightforward matter. It has been shown in several studies that sorption kinetics for water in Nafion do not obey Fickian kinetics: weight uptake against square-root of time frequently exhibits initial “S” type curvature [4], rather than being linear through the origin for more than 60% of the steady state concentration. Also

sorption kinetics for membranes of different thickness fail to superimpose when plotted as fractional weight gain against square-root of time reduced by thickness, as shown recently in the work of Satterfeld and Benziger [5]. They carried out an examination of sorption and desorption kinetics of Nafion films over a range of temperatures in a sealed chamber at near saturation concentrations, conditions which exacerbate the complications. Explicit analytical treatments were developed for the contributions of limiting interfacial mass transfer and polymer relaxation dynamics. An additional factor that requires consideration is the temperature change that results from the heat of condensation [6,7]. This has the effect of slowing the sorption and desorption kinetics, which are coupled with return of temperature to the isothermal condition.

To circumvent the various complications in the analysis of water vapor sorption kinetics, we use a method for the determination of diffusion coefficients based on the combination of steady state permeation and equilibrium sorption measurements [4]. Corrections are applied to the vapor concentration, to account for boundary layer resistance and concentration changes along the length of the sample. The diffusion coefficient is obtained as the ratio of the steady state flux to the resulting average membrane concentration. This procedure was summarized in the previously cited study [4] of the transport of water and several alcohols in Nafion and was applied in a later publication [8]. Although some

* Corresponding author. Tel.: +1 508 233 5362; fax: +1 508 233 4331.

E-mail address: nathan.schneider1@us.army.mil (N.S. Schneider).

sorption kinetic studies indicate that diffusion coefficients for water in Nafion go through a maximum as a function of vapor concentration [9,10]. Diffusion coefficients from the steady state analysis increase continuously with vapor concentration and are consistent with the result obtained for liquid water. Despite the apparent effectiveness of the steady state analysis, there has not been a critical test of the reliability of the resulting diffusion coefficients. The present publication provides a detailed summary of the steady state procedure. Steady state diffusion coefficients for water in Nafion are tested by comparison with published results for NMR determined self-diffusion coefficients [11]. Results for two sulfonated triblock ionomers, which represents a different morphology from that of Nafion, are also treated and compared with the Nafion values. It is concluded that differences between the water transport of these two phases segregated ionomers and Nafion can be accommodated simply in terms of vertical scaling factors.

2. Experimental

2.1. Materials

Nafion112, 127 μ and Nafion 117, 178 μ thickness were obtained from CG Processing and were used without further treatment. Based on the 1100 g equivalent weight the ion exchange capacity (IEC) of Nafion is 0.91 meq/g or, 1.82 meq/cc for a density 2.0 g/cc. The triblock polymer, polystyrene-block(polyethylene-ran-butylene)-block-polystyrene, which was converted to the ionomer (SEBS), was purchased from Aldrich. It is described as having an $M_w = 118,000$ and 30 wt% styrene. Sulfonation was carried out with acetyl sulfate in solution following the procedure of Elabd et al. [12]. Degree of sulfonation determined by elemental analysis was 54 mol percent, which is equal to an IEC of 1.65 meq/cc for a density of 1.1 g/cc. Films were cast from a 3 wt% solution in tetrahydrofuran with addition of 20 wt% 1-butanol to facilitate dissolution. The Teflon casting dishes were enclosed in a plexiglass box to slow evaporation in the air flow of a hood. Film formation occurred in about two days but drying proceeded for at least five days. The films were then oven dried at 70 °C for 30 min and allowed to stand open to the air for a week before use. A second triblock polymer is based on a Kraton precursor of similar composition but with styrene incorporated in the mid-block along with hydrogenated butadiene at 50–50 wt% and with total styrene content of 64 wt%. The ionomer (DA64) with 38% sulfonation, IEC 2.2 meq/cc, was provided by DAIS Analytic in the form of films which had been crosslinked with trimethylsilane through residual midblock unsaturation. Additional details are provided in an earlier publication [8].

2.2. Permeation and sorption methods

Permeation measurements were carried out with carrier and sweep flow rates of 1000 cc/min on Nafion samples clamped in a cell with exposed sample area of 6.0E-04 m² (0.75 × 1.25 in). Water vapor was generated at activities, set by the ratio of flows of saturated vapor from a bubbler and a nitrogen dilution stream, which were controlled by electronic mass flow controllers (MKS). Both permeation cell and bubbler were housed in an air thermostat controlled at 32 °C. Permeant concentrations were determined with an auto-sampling, micro gas chromatograph, equipped with a thermal conductivity detector (Agilent). The nitrogen carrier and water peaks are separated by passage through the column and the water concentration is determined as the integrated peak area. Sorption isotherms were determined with a Cahn 2000D micro-balance, using an interface that recorded weight changes and proceeded through a preset series of vapor concentrations (Hidden Analytical). The sample was suspended within a water jacketed

chamber housed in a temperature controlled cabinet. Bubbler temperature was controlled by immersion in a circulating refrigeration bath set to 32 °C. Vapor at set concentrations was delivered at a flow rate of 500 cc/min.

Permeation measurements on the sulfonated triblock ionomer films were carried out similarly to Nafion, but in a modified cell with a raised edge, 76 μ (30 mil) height, 0.64 cm (0.25 in) width, which defined an exposed surface area of 6.0E-04 m². Channels in the cell block were machined at an angle of 30° so that flow impinged on the membrane to improve sweep of the membrane surface in the cavity formed by the raised edge. Measurements were carried out at a flow rate of 500 cc/min, with cell and double-chamber bubbler housed in the same air thermostat at 35 °C, using the previously described instrumentation to determine permeant concentration. Sorption measurements were carried out at 35 °C in a vacuum sorption system (Hidden Analytical), which provided full automated operation through a preset series of vapor concentrations generated by computer-controlled admittance from a small heated liquid source. The change from the earlier 32 to 35 °C was made to facilitate comparison with other data.

3. Steady state data reduction

3.1. Nominal diffusion coefficients

For a membrane of thickness h (cm) the diffusion constant D (cm²/s) can be determined from the integrated form of Fick's first law for a constant diffusion coefficient, as the ratio of the flux J (g/cm²-s) to the concentration gradient (g/cc-cm) at a set vapor activity [13]:

$$J = \frac{(C_1 - C_2)}{h} D \quad (1)$$

If the diffusion coefficient is concentration-dependent, equation (1) takes the form:

$$J = \frac{1}{h} \int_{C_2}^{C_1} D(C) dC \quad (2)$$

At steady state this relation is exact and circumvents complications that arise from relaxation of the phase segregated structure of many ionomers, and from the non-isothermal condition due to the heat of condensation of water or organic vapors [7]. D_{nom} refers to the result of equation (1) without a correction to the flux for the boundary layer resistance. With high moisture-permeable membranes the boundary layer resistance can amount to an appreciable fraction of the total resistance governing the flux across the membrane [4]. The total resistance R , can be expressed as the ratio of the gas phase concentration difference across the membrane, g/m³, and flux, g/m²-s:

$$R = \frac{(C_{2g} - C_{1g})}{J} \quad (3)$$

In the present experimental arrangement, the gas phase boundary layer (BL) resistances were minimized by equal, high flow rates of 500 or 1000 cc/min, on the feed and sweep side of the membrane. The BL resistance was determined as the zero-thickness intercept of a plot of resistance versus total film thickness, at a set vapor concentration, for multiple layers of a highly permeable film. In earlier work with a microporous Teflon membrane (Gore-Tex), it was necessary to balance pressure across the membrane to avoid convective flow and the delicate nature of the thin membrane made it difficult to handle. In this work multiple layers 51 μ Nafion

film were employed, since Nafion is more robust and not subject to convective flow. However, it takes more time to arrive at the steady state, especially with multilayer films. Examples of measurements with Nafion at $P/P_o = 0.39$ and 0.70 , with flow rate of 500 cc/min are shown in Fig. 1. The intercept, is a measure of the gas phase resistance on both sides of the membrane and is unaffected by interfacial resistance at the membrane surface.

A correction for the boundary layer resistance can be made by treating the gas phase and membrane as series resistances. The membrane resistance is obtained by subtracting the boundary layer resistance from the total resistance and is converted to the corrected steady state flux by application of equation (3). The diffusion coefficient follows by application of equation (1), when the concentration difference across the membrane, ΔC , is known. An example of the effect of the boundary layer correction is indicated by data for 178μ Nafion, at $P/P_o = 0.8$, corresponding to a membrane concentration difference of 0.25 g/cc. At carrier and sweep flow rates of 1000 cc/min, the total resistance was 300 s/m of which the boundary layer resistance contributed 97 s/m. The nominal diffusion coefficient of $1.7E-06$ cm²/s is almost 1.5 times the value for the uncorrected flux.

3.2. Effective diffusion coefficients

The previous treatment neglects two additional factors that influence the effective concentration gradient across the membrane: the change in vapor concentration across the boundary layer resistance and depletion of the feed stream plus accumulation in the sweep stream along the sample length. Measurements are preferably made in countercurrent flows, wherein feed and sweep stream are set to the same flow rate and enter at opposite ends of the cell to minimize change in the trans-membrane concentration gradient. Corrected membrane concentrations are calculated at four locations, i.e. the entrance and exit of carrier and sweep streams, to obtain an average effective driving force. With equal carrier and sweep flow rates the BL resistance on each side of the membrane is one-half that obtained by the procedure described earlier. The change in vapor concentration across the boundary layer resistance, R_b , is calculated by application of equation (3), and subtracted from the entering gas phase concentration to obtain the vapor concentration at the membrane surface. In addition, the vapor concentration is corrected for depletion in the feed stream and for accumulation in the sweep stream with flow between cell entrance and exit. The four gas phase concentrations are converted to corresponding membrane concentrations using an analytical representation of the sorption isotherm, concentration (g/cc)

against vapor activity (P/P_o). The membrane concentration difference at sweep inlet, ΔC_{in} and sweep outlet, ΔC_{out} , are combined to obtain a ln-normal concentration gradient:

$$\Delta C_{eff} = \frac{(\Delta C_{in} - \Delta C_{out})}{\ln(\Delta C_{in} - \Delta C_{out})} \quad (4)$$

The largest difference between ΔC_{in} and ΔC_{out} occurs with vapor at unit activity, 0.211 and 0.132 g/cc, respectively. For the concentration range in the current studies, ln-normal concentrations proved to be indistinguishable from the arithmetic average concentration differences. An effective diffusion coefficient, D , is obtained as the ratio of the measured flux to the concentration gradient, $\Delta C_{eff}/h$, equation (1). A correction for swelling is applied equal to one-half the concentration difference across the membrane and assuming that the increase is restricted to the thickness direction. It is assumed that the increase is equal to one-half the upper surface concentration and limited to the thickness direction. If the lower surface membrane concentration is nearly zero or small compared to the upper surface concentration, then, D will only be a function of the upper surface concentration. An example of the corrections for the 178μ Nafion sample at $P/P_o = 0.8$ is as follows: carrier inlet and outlet membrane concentrations 0.18 and 0.15 g/cc; sweep inlet and outlet concentrations 0.043 and 0.062 g/cc; ln-normal concentration difference 0.113 g/cc. The calculated diffusion coefficient is $2.5 E-06$ cm²/s at a concentration equal to 0.165 g/cc. Compared with the nominal diffusion coefficient of the earlier example, this result is nearly 50 percent higher and is shifted to a one-third lower concentration at the same activity.

One of the main limitations inherent in the determination of diffusion coefficients from steady state data, is that the average vapor concentration at the membrane surface is much lower than the delivered vapor concentration, due to the gradient across the boundary layer resistance and change in vapor concentration with permeation. This has the effect of substantially reducing the range of concentrations that can be studied. The concentration range can be extended by increasing the flow rate to reduce the boundary layer resistance. However, this approach is limited by the difficulty of delivering a controlled vapor concentration at flow rates above 1000 cc/min and the reduced sensitivity of the boundary layer resistance to further decrease at high flow rates. The more useful approach is to increase the membrane thickness, most readily by using multiple layers. The disadvantage is that time to steady state increases as the square of the thickness. Another limitation, inherent to permeability measurements, is that the apparent diffusion coefficient is an average over the concentration distribution in the membrane. Despite these problems the steady state procedure is capable of yielding consistent diffusion coefficients as shown previously for water in Nafion of different thicknesses [4].

4. Experimental results

4.1. Nafion results

A detailed study of water vapor transport in Nafion, together with experimental data and results from comparable steady state measurements for a number of alcohols was published earlier [4]. The final results of the steady state analysis were estimates of effective binary diffusion coefficients, D , rather than solvent self-diffusion coefficients. The present goal is to provide a test of this steady state analysis, by conversion to solvent self-diffusion coefficients for comparison with a free volume relation representing NMR pulse gradient self-diffusion measurements [11]. Previously cited steady state measurements for water in Nafion [4] provide

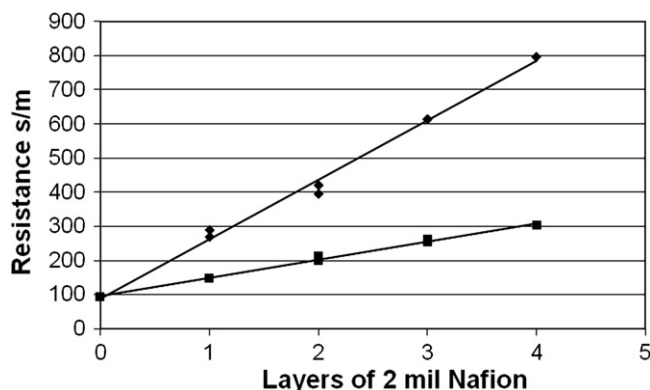


Fig. 1. Resistance for water vapor versus number of layers of two mil Nafion film. Upper line, filled diamonds at $P/P_o = 0.7$, lower line, filled squares at $P/P_o = 0.385$.

a useful starting point with some minor changes. Whereas, earlier the concentration at the sweep inlet was set to zero, a concentration difference across the boundary layer resistance, is included in the present treatment. This produces a small non-zero membrane concentration at the sweep inlet. In addition, the earlier definition of the upper membrane concentration as the sum of the ln-normal concentration plus one-half the lower surface concentration, is replaced by the ln-normal average of inlet and exit upper membrane concentrations. The two changes result in a net increase of about two percent in the magnitude of D , and in the concentration but will have no effect on the comparisons of interest.

The diffusion coefficient, D , determined at steady state, requires no frame of reference correction and approximates the mutual diffusion coefficient, since there is no moving boundary and a fixed concentration gradient. The following expression was proposed for the relation of the solvent self-diffusion coefficient D_1 to the mutual diffusion coefficient [14], (ϕ_1 is the volume fraction of solvent in the membrane, α_1 is the solvent activity):

$$D_1 = \frac{D}{\phi_2} \frac{\delta \ln \phi_1}{\delta \ln a_1} = \frac{D}{\phi_2 Q} \quad (5)$$

In early applications, equation (5) was considered useful over a wide concentration range but, later comparisons revealed that it holds only at low concentrations since predicted values become increasingly too high with increasing concentration. The following modification [15], accurately predicted D_1 over the full concentration range in a test with data for two aromatic solvents in two hydrocarbon polymers:

$$D_1 = \frac{D(\alpha \phi_1 + (1 - \phi_1)(1 + 2\phi_1))}{Q} \quad (6)$$

The term alpha is dependent on the ratio of the molecular weight of solvent to polymer, among other factors. In the present study with phase segregated ionomers, it was assumed to be small and was nominally set to 0.05. Values of Q were calculated from the algorithm fitted to the sorption isotherm at activities that correspond to each of the set of upper membrane concentrations. Fig. 2 illustrates the behavior of $Q = d(\ln a_1)/d(\ln \phi_1)$ determined from the slope of the sorption isotherm together with the older and newer versions of the thermodynamic factor. The oscillation in Q at low concentrations is due to the combined effect of a minimum in $d(a_1)/d(\phi_1)$ at 0.08 g/cc and a maximum in ϕ_1/a_1 at 0.12 g/cc. The two versions of the thermodynamic factor are identical at low concentrations but beyond the minimum at about 0.085 g/cc are

distinguished by a steeper continuing increase of the earlier version with increasing concentration. Fig. 3 shows the transformation of steady state diffusion coefficients, D , for water in Nafion to solvent self-diffusion coefficients, D_1 , which follows from application of the thermodynamic factor. There is a cross-over from self-diffusion coefficients, D_1 , which are lower than the SS values to those increasingly higher than SS values above 0.13 g/cc.

A definitive NMR pulse gradient diffusion study [11], demonstrated that the solvent self-diffusion coefficients for water in Nafion could be represented accurately by the following modified Fujita free volume (fv) relation over a wide range of concentrations and temperatures:

$$\ln \left(\frac{D_1}{D_1(0)} \right) = \frac{\left(\left(\frac{f_s}{B_d} \right) - \left(\frac{f_p}{B_d} \right) \right) \phi_s}{\left(\frac{f_p}{B_d} \right)^2 + \left(\left(\frac{f_p}{B_d} \right) \left(\left(\frac{f_s}{B_d} \right) - \left(\frac{f_p}{B_d} \right) \right) (\phi_s) \right)} \quad (7)$$

The parameters f_p and f_s are defined as the fractional free volume of polymer and solvent, B_d is the minimum hole size needed for solvent molecule displacement, ϕ_s is the volume fraction of solvent, and $D_1(0)$ is the zero concentration solvent self-diffusion coefficient. Values of the parameters at 32 °C, were extracted from the set of parameters in Table 2 of ref. [17] which were based on measurements at seven temperatures in the range 298–357 K. The data for 25–56 °C was chosen since, the values of $f_p/B_d = 0.091$ and $f_s/B_d = 0.222$ are stable within this range. However, there is considerable random error in $D_1(0)$ which was fitted with a least squares line, shown in Fig. 4, to obtain the values of $D_1(0) = 6.023\text{E-}08$ at 32 °C and $D_1(0) = 6.872\text{E-}08$ at 35 °C. Inclusion of data at successively higher temperatures would affect values of all parameters, but $D_1(0)$ most strongly.

To account for the fact that 70 wt% of Nafion consists of impermeable fluorocarbon phase, an adjustment was made in calculating the volume fraction concentration of water [11]. It was assumed that water is only associated with the fluoroether fraction, which represents only 30% of Nafion and was assigned a density of two. This leads to the following relation for the volume fraction water:

$$\phi_1 = \frac{V_{\text{solvent}}}{(V_{\text{solvent}} + V_{\text{pendant}})} = \frac{V_{\text{solvent}}}{V_{\text{solvent}} + \frac{0.3}{2}} \quad (8)$$

where V_{solvent} is the volume of water per gram of Nafion and V_{pendant} is the volume of the fluoroether fraction. However, it will be shown that it is unnecessary to correct for the impermeable fraction by comparisons where the NMR parameters are used to

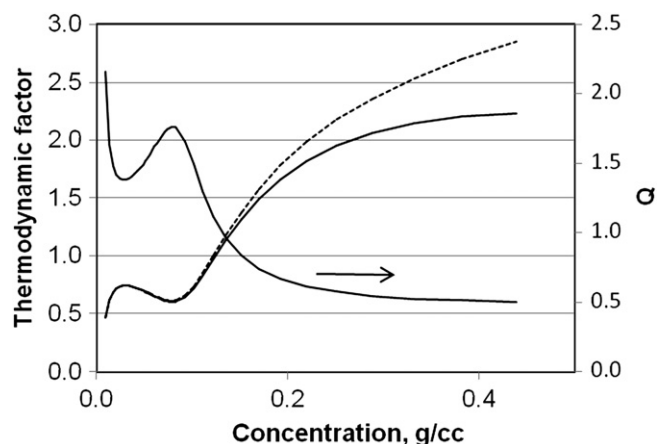


Fig. 2. Thermodynamic factors. Upper curve, right hand axis is $Q = d(\ln a_1)/d(\ln \phi_1)$. Dotted line is thermo factor $1/(Q\phi_2)$, solid line is thermo factor $f(\phi_1)/Q$.

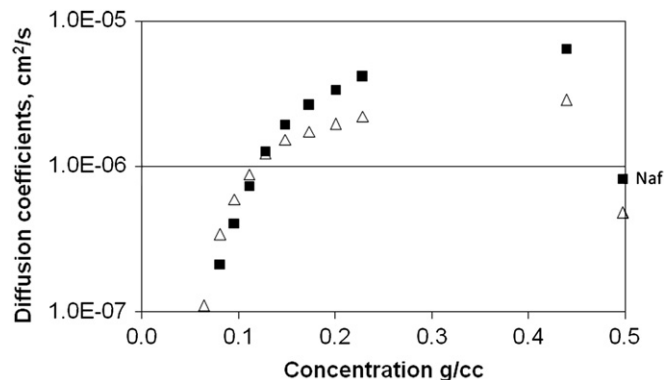


Fig. 3. Comparison of experimental Nafion steady state diffusion coefficients, D , open triangles, and self-diffusion coefficients, D_1 , solid squares.

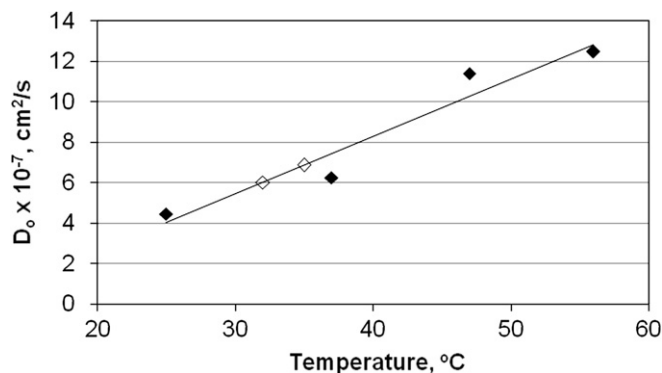


Fig. 4. Interpolation of free volume parameter D_0 at 32 °C, $6.023\text{E-}07$, and at 35 °C, $6.87\text{E-}07$, open diamonds, from least squares fit to NMR determined values, filled diamonds [11].

calculate a reference free volume curve using unadjusted concentrations. In further discussion the NMR solvent self-diffusion coefficients will be designated as D_1^* to distinguish from the steady state experimental values.

A comparison of SS D_1 results for 178 μ films and for multilayer 51 μ films with the NMR fv curve appears in Fig. 5, where the 178 μ results have been multiplied by 0.85 and 51 μ results multiplied by 1.1, representing a difference of 30 percent. The effectiveness of the SS analysis can be appreciated by the contrast with values for D_{nom} , which is 2.3 times greater for the 178 μ than for the 2-layer 51 μ film at vapor activity, $P/P_0 = 0.7$. In the comparison with the fv curve, shown in Fig. 5, adjusted SS values of D_1 fit on the free volume curve for a concentration of 0.15 g/cc, corresponding to vapor activity, $P/P_0 = 0.7$, and for higher vapor activities. The value of D_1 for liquid water is 30 percent below the fv curve. This is probably a consequence of a decrease in temperature at the lower membrane surface, resulting from the heat of vaporization. In vapor permeability measurements, the temperature decrease that would result at the lower membrane surface is offset by the heat of condensation at the upper membrane surface. Heat transfer calculations in permeation from a static liquid source indicate a temperature drop of about 4 °C at the lower membrane surface. At concentrations progressively lower than 0.15 g/cc, D_1 falls below the fv curve to an increasing degree. This disparity is unrelated to the effect of any approximations in the SS analysis and in the conversion from D to D_1 , which should become diminishingly small as the concentration decreases. It is possible that increasing restrictions to diffusion at

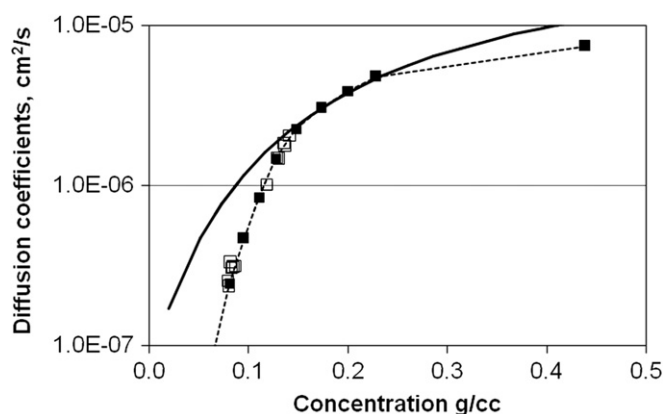


Fig. 5. Comparison of experimental Nafion self-diffusion coefficients, D_1 multiplied by 0.85, filled squares, with free volume representation of NMR determined solvent self-diffusion coefficients at 32 °C, solid line. Open squares are values of D_1 for multilayer 2 mil Nafion films multiplied by 1.1.

limited swelling levels, due to the impermeable fluorocarbon fraction in Nafion, contribute to the rapid decrease in D_1 . The structural impedance would not affect NMR values, if the NMR diffusion length scale is small compared to structural dimensions. In fact there was no evidence of tortuosity in the NMR measurements [11]. However, it will be shown in the later section that diffusion results for the two triblock ionomers are difficult to reconcile with this explanation.

4.2. Concentration averaging of the diffusion coefficient

The close correspondence of SS Nafion D_1 values with NMR solvent self-diffusion coefficients, D_1^* is unexpected since the SS values should be lower as a result of averaging across the concentration distribution in the membrane (equation (2)). In order to examine the effects of concentration averaging it is necessary to have values of the solvent self-diffusion coefficient which are unaffected by the possibility of increasing structural interference with diffusion at low concentration. An evaluation of the effect of concentration averaging can be made by use of the fv relation and by including the effect of the thermodynamic factor in the conversion from SS values of D to self-diffusion coefficients, D_1 . To implement this approach, the concentration interval represented by the difference between upper and lower experimental membrane concentrations, was divided into 100 or more equal increments. Free volume values of D_1^* at each concentration increment were converted to SS D_1 values, by reverse application of the thermodynamic factor. The set of values was integrated over the concentration range to obtain a simulated value of the experimental SS diffusion coefficient D . This value was converted to an average solvent self-diffusion coefficient, $D_{1\text{avg}}$, by applying the thermodynamic factor. Concentration averaged self-diffusion coefficients were calculated by this procedure for each of the experimentally determined Nafion membrane concentrations.

The results in Fig. 6 show that values of $D_{1\text{avg}}$, multiplied by a factor of 1.3, superimpose on the fv curve at higher concentrations above 0.13 g/cc but fall below the fv curve for a range of lower concentrations before turning upward to approach the fv curve. Note that the liquid values, indicated by the arrow, have been moved from a concentration of 0.439 to 0.290 g/cc. The factor which renders agreement with fv diffusion coefficients at higher concentrations represents a 23% reduction in fv values due to concentration averaging. Fig. 6 also includes a comparison with SS D_1 adjusted by the factor of 0.85 to bring the data in to register with the fv curve. In comparison to $D_{1\text{avg}}$, the SS D_1 values are high by

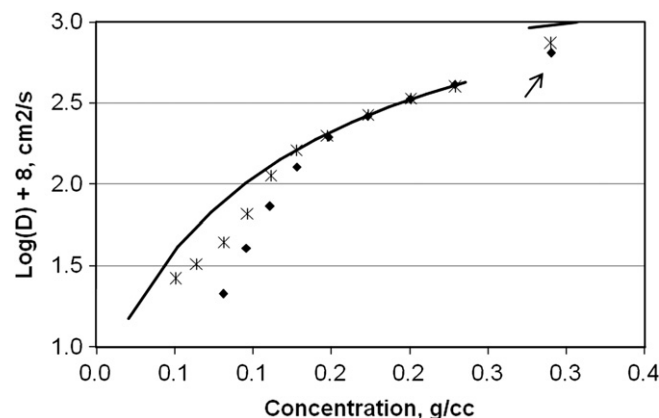


Fig. 6. Comparison of concentration averaged self-diffusion coefficients, $D_{1\text{avg}}$ multiplied by 1.3, double crosses, with the free volume curve, and with SS self-diffusion coefficients multiplied by 0.85, filled diamonds. Value for liquid moved from concentration 0.439 to 0.290 g/cc, indicated by arrow.

a factor of 1.5. The cause of the higher values was not examined but, it might be noted that a uniform 15% reduction in flux is sufficient to lower D_1 by 40% without disturbing the comparisons in Fig. 6. The concentration averaged values, $D_{1\text{avg}}$, and adjusted SS D_1 values agree quite well at higher concentrations, but the two sets of data begin to separate as the concentration falls below 0.15 g/cc. Concentration averaged values of the SS solvent self-diffusion coefficients should converge to the NMR zero concentration value, $6.0\text{E-}08\text{ cm}^2/\text{s}$, but the continuing downward trend in Fig. 6 extrapolates to $8\text{E-}10\text{ cm}^2/\text{s}$, nearly two orders of magnitude lower than the fv value. The experimental lower limit is determined by the percolation threshold, which is reported to be close to 4 wt% (0.08 g/cc) [16]. By coincidence the present results at this concentration correspond to a diffusion coefficient about $3\text{E-}08\text{ cm}^2/\text{s}$, which is comparable to the fv prediction.

4.3. Sulfonated triblock results

Water solubility in the SEBS and DA64 ionomers is far greater than Nafion, reaching 250 wt% under immersion conditions, compared to 22 wt% for Nafion. This is a consequence of the limited effectiveness of the residual unmodified styrene endblock in restraining swelling. It has been shown previously that sorption isotherms for water in several crosslinked triblock ionomers of varying composition or cation modification can be superimposed with Nafion over an extensive range of activities when rescaled by a factor related to the initial structure, before extensive relaxation of the sulfonate endblocks occurs at high vapor activities or immersion conditions [8]. Fig. 7 compares water concentrations in the two triblock ionomers, multiplied by 0.6 for SEBS and 0.55 for DA64 with the isotherm for Nafion. The rescaled isotherms for the two triblock ionomer isotherms follow the same dependence of concentrations on activity as Nafion, before rising more rapidly above activity 0.8. The magnitude of the scaling factors implies a saturation concentration of 30 wt% for the triblock ionomers, which is well below the measured value, indicating relaxation of the structure in the approach to saturation. Saturation concentrations should be proportional to the IEC, which varies from 1.82 for Nafion to 1.65 for SEBS and 2.2 for DA64. The contrast with the volumetric IEC values indicates that structural differences also play a significant role in the degree of swelling.

Permeabilities for the triblock ionomers and Nafion as a function of concentration in Fig. 8 demonstrate the superior efficiency of Nafion in transporting water. The low permeability of DA64, despite

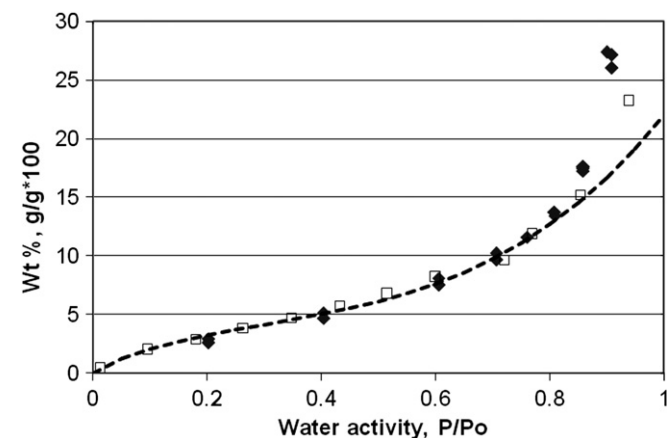


Fig. 7. Comparison of sorption isotherms for SEBS, concentrations rescaled by 0.6, filled diamonds, and for DA64, concentrations rescaled by 0.55, open squares, with Nafion isotherm, dotted line.

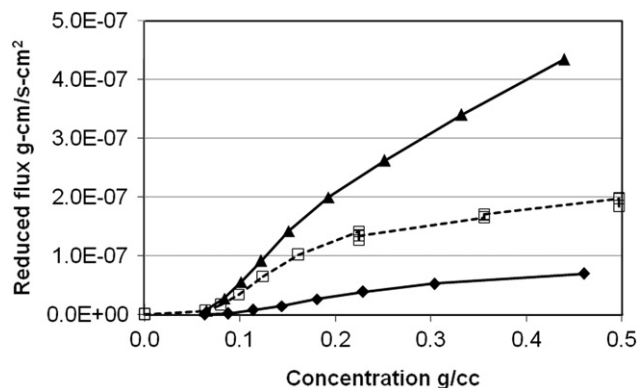


Fig. 8. Steady state flux for Nafion filled triangles; SEBS open squares; DA64, filled diamonds.

having sulfonate anion in the midblock, is unexpected. The midblock comprises 55 wt% of the total styrene content and at 38% sulfonation there is one sulfonate anion for 7.7 repeat units of styrene and hydrogenated butadiene. This contrast with one sulfonate anion for 2.6 repeat units in the endblock. The dilute midblock sulfonate anion combined with steric restrictions could be an obstacle to the formation of extended ionic pathways.

Values of D_1 for the triblock ionomers were calculated by application of the thermodynamic factor to SS D values, as described earlier for Nafion with an adjustment in $D_1(0)$ due to the temperature change from 32 to 35 °C. Fig. 9 compares the SS D_1 values for the two triblock ionomers with SS D_1 for Nafion, represented by the dotted line, and with the solid line for the fv curve for Nafion solvent self-diffusion coefficients. The triblock D_1 values are lower than the corresponding Nafion values but can be brought into coincidence with the fv curve at concentrations above 0.14 volume fraction (0.16 g/cc) with a vertical shift, by a factor of 2.1 for SEBS and 8.8 for DA64. As discussed later, the scaling factors are believed to incorporate the effects of structural organization and polymer segmental dynamics on solvent mobility. At lower concentrations triblock ionomer D_1 values track increasingly lower than the fv curve, but superimpose on the dotted curve for SS Nafion D_1 values.

Earlier, it was suggested that the departure from the NMR fv curve at low concentrations might be attributable to the increasing structural impedance to diffusion. The absence of any difference in the course of diffusion coefficients at low concentrations that reflects the differences in the structure of the three ionomers

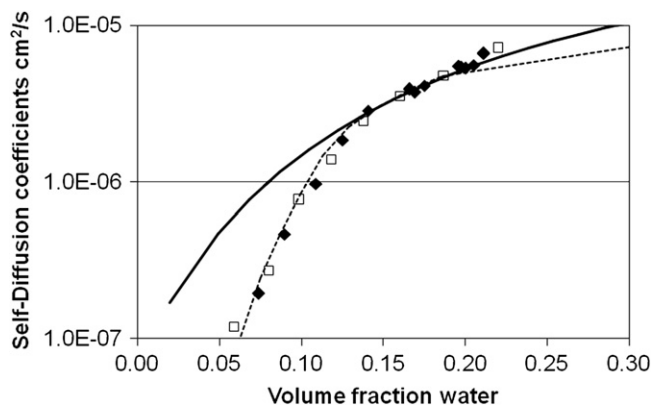


Fig. 9. Self diffusion coefficients for water at 35 °C: SEBS shifted vertically by a factor of 2.1, filled diamonds; DA64 shifted vertically by a factor of 8.8, open boxes; Nafion shifted vertically by a factor of 0.85, dotted curve. Solid line is free volume representation of NMR determined solvent self-diffusion coefficients for water in Nafion.

suggests that the behavior is due to change within the ionic pathways rather than the large scale morphology. Calorimetric measurements, show a rapid increase in heat of sorption, from a value equal to the heat of condensation for water at greater than six water molecules per sulfonate anion (19 wt%), to a nearly two-fold higher heat at one molecule per sulfonate anion (3.2 wt%) [17]. Increasingly strong interactions with the sulfonate anion, rather than structural effects, are a possible cause of the rapid decrease in diffusivity at concentrations approaching the percolation threshold. The departure from the NMR f_v curve with decreasing concentration which occurs at $\phi_1 = 0.14$ to 0.16, is equal to 5 to 6 water molecules per sulfonate for Nafion (IEC = 1.82 meq/cc) and SEBS (IEC = 1.65 meq/cc) and 4 to 5 molecules of water for DA64 (IEC = 2.2 meq/cc). There was no indication of an immobile water fraction in the published NMR study [11]. However, a percolation threshold has been observed both by pulse gradient NMR and by proton conductivity at 4 wt% (0.074 volume fraction) for Nafion and at 12 wt% (0.091 volume fraction) for SEBS (60% sulfonation) [16]. Recent molecular dynamics simulations at 15 wt% water in SEBS, have shown that almost every water molecule neighbors a sulfonate oxygen [18]. It is reported that the inhomogeneous distribution of water hinders water mobility and results in a self-diffusion coefficient of water that is two orders of magnitude lower than that in bulk water. These results are consistent with diffusional limits imposed by strong water sulfonate–anion interactions, which are independent of differences in ionomer morphology.

5. Conclusions

The SS approach was developed to circumvent problems associated with determining diffusion coefficients from sorption kinetics, which is complicated by gas phase mass transfer resistance in a flow cell, by a temperature rise due to the heat of condensation of water and, under certain conditions, by polymer relaxation dynamics. Failure to take proper account of these factors can lead to erroneous conclusions about the concentration dependence of the diffusion coefficient, as noted earlier. The procedure is especially important with water and with high permeability ionomers, such as Nafion and the triblock ionomer, where the boundary layer resistance can approach the membrane resistance at high water vapor activity.

One of the main goals of the present work was to test the reliability of the steady state approach using a Fujita type f_v relation based on NMR determined solvent self-diffusion coefficients D_1^* for water in Nafion. Previously published SS diffusion coefficients, which were converted to solvent self-diffusion coefficients, D_1 , were shown to superimpose on the f_v curve for activities above 0.7 when reduced by a factor of 0.85. An examination of the effect of concentration averaging of the diffusion coefficient in permeation measurements was performed, starting with the f_v expression for the NMR self-diffusion coefficients, to avoid complications due to increasing structural impedance at low concentrations. The analysis indicates that concentration averaging in permeation measurements results in a 23% reduction in values and, by reference to $D_{1,avg}$, that the SS self-diffusion coefficients are high by 50%. Within this level of uncertainty, the comparison of D_1 with the f_v curve and close agreement of Nafion diffusion coefficients for films with large differences in thickness, provide confidence in the quantitative reliability of properly executed SS diffusion coefficients, even for an ionomer of exceptionally high water vapor permeability.

The second goal was to compare water transport behavior of two triblock ionomers with Nafion. Despite differences in morphology the sorption isotherms of the two triblock ionomers, when shifted by vertical rescaling factors, are superimposable over an extended range of concentration with Nafion. Also diffusion

coefficients as a function of concentration for the two triblock ionomers can be superimposed at concentrations above 0.16 g/cc (0.14 volume fraction) with the Nafion f_v curve, when modified by vertical scaling factors. It is important to recognize that the comparisons are made on the basis of the concentration of water in the total polymer, without correcting for a water impermeable fraction. This outcome suggests that water transport in phase segregated ionomers, is restricted to ionic regions and that there is minimal interaction with the hydrophobic content. That this correspondence holds for all three ionomers, even at low concentrations, indicates that the decreasing values of D_1 are due to changes in anion–water interactions within existing ionic pathways rather than at the level of the phase segregated morphology.

The magnitude of the vertical scaling factors is dependent on two factors which affect permeant diffusion; segmental mobility and morphology. There are distinct differences in both factors between Nafion and the triblock ionomers. In Nafion the sulfonate anion is the terminal group on the mobile fluoroether side chain, whereas in the triblock ionomers the sulfonate anion is a substituent on the aromatic ring of the more rigid polystyrene chain. The triblock ionomer SEBS, preserves features of the long range periodicity of the precursor triblock, with the sulfonated styrene end-blocks dispersed in the dominant hydrophobic phase. In contrast, phase segregated structure in Nafion is not highly organized and the lack of a regular structure probably facilitates the development of ionic pathways. It is not possible to elaborate in detail given the absence of a well defined model for the structural change with sulfonation that leads to water vapor permeability in the initially hydrophobic polymer. It remains to be determined if the simple relations observed for the transport properties of these two triblock ionomers and Nafion will hold in general for other phase segregated ionomers differing in chemical composition or architecture.

Finally, it is appropriate to comment on the relation of this work to some recent publications on Schroeder's paradox, which involves the higher uptake of solvent from liquid compared to vapor at unit activity. Choi and Datta [19], developed an explanation for water in Nafion, based on the difference in free energy for liquid and vapor filling of pores. The model was capable of accounting for a difference between 22 mol water per sulfonate anion (36 wt%) for liquid compared to 13.5 mol water (22 wt%) for vapor at saturation and formed the basis for an accurate Nafion sorption isotherm [17]. However, the vapor sorption isotherm determined in our laboratory [4] is consistent with an immersion uptake of 22 wt%, which was incorrectly referenced by Choi and Datta as an estimate of the saturation vapor concentration. Vapor sorption isotherms reported in the same publication for methanol, ethanol and 1-propanol in Nafion are also consistent with liquid immersion uptake. Behavior associated with Schroeder's paradox has also been observed in a nonporous dimethyl siloxane elastomer [20], but only with 2-propanol among a set of solvents. Differences between vapor and liquid steady state permeability for water in Nafion films [21] have also been attributed to Schroeder's paradox, as the result of assumed differences in saturation concentration for the membrane in contact with water and vapor at unit activity. A dependence of permeability on flow rate was reported, which increased continuously to 1000 cc/min with liquid but exhibited a maximum with increasing flow rate with vapor at fixed activity. We demonstrate in this and previous publications that there is no difference between equilibrium sorption from saturated vapor and liquid, or in permeation measurements provided that the effects of boundary layer resistance and concentration profile are accounted for. The cumulative evidence of our studies of sorption and permeation measurements of vapor and liquid in several ionomers weighs against the existence of any difference that would support Schroeder's paradox, a conclusion also reached in another recent study [22].

References

- [1] Yeager HL, Gronowski AA. Membrane applications part 3. In: Tant MR, Mauritz KA, Wildes GL, editors. Ionomers, synthesis, structure, properties, and applications. London: Blackie, (Chapman and Hall); 1997 [chapter 7].
- [2] Huang RYM, Shao P, Feng X, Anderson WA. Ind Eng Chem Res 2002;41: 2957–65.
- [3] Freger V, Korin E, Wisniak J, Korngold E. J Membr Sci 1997;133:235.
- [4] Rivin D, Kendrick CE, Gibson PW, Schneider NS. Polymer 2001;42:623–35.
- [5] Satterfield MB, Benziger JB. J Phys Chem B 2008;112:3693–704.
- [6] Armstrong Jr AA, Wellons JD, Stannett V. Makromol Chem 1966;95:78–91.
- [7] Wang P, Meldon JH, Sung N. J Appl Polym Sci 1996;59:937–44.
- [8] Schneider NS, Rivin D. Polymer 2006;47:3119–32.
- [9] Morris DE, Sun XJ. J Appl Polym Sci 1993;50:1445–52.
- [10] Legras M, Hirata Y, Nguyen QT, Langevin D, Metayer M. Desalination 2002;147: 351–7.
- [11] Gong X, Bandis A, Tan A, Meresi G, Wang PT, Inglefield AA, et al. Polymer 2001;42:6485–92.
- [12] Elabd YA, Napadensky E. Polymer 2004;45:3037–43.
- [13] Crank J, Park GS. Methods of measurement. In: Crank J, Park GS, editors. Diffusion in polymers. London: Academic Press; 1968 [chapter 1].
- [14] Duda JL, Ni YC, Vrentas JS. Macromolecules 1979;12:459.
- [15] Vrentas JS, Vrentas CM. Macromolecules 1993;26:6129–31.
- [16] Edmondson CA, Fontanella JJ. Solid State Ionics 2002;152–153:355–61.
- [17] Reucroft PJ, Rivin D, Schneider NS. Polymer 2002;43:5157–61.
- [18] Vishnyakov A, Niemark AV. J Phys Chem B 2008;112:14905–10.
- [19] Choi P, Jalani NH, Datta R. J Electrochem Soc 2005;152(3):E84–9.
- [20] Vallieres C, Winkelmann D, Roizard D, Favre E, Scharfer P, Kind M. J Membr Sci 2006;278:357–64.
- [21] Majsztrik PW, Satterfield MB, Bocarsly AB, Benziger JB. J Membr Sci 2007;301: 93–106.
- [22] Onishi LM, Prasnitz JM, Newman J. J Phys Chem B 2007;111:10166–73.