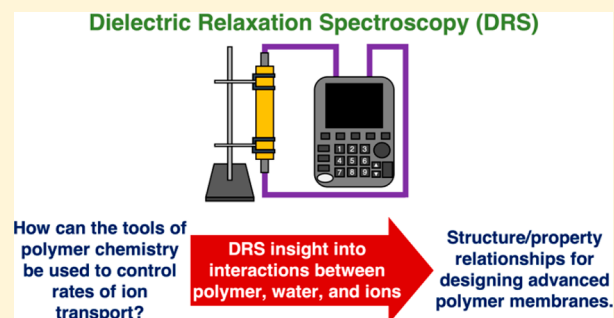


Dielectric Permittivity Properties of Hydrated Polymers: Measurement and Connection to Ion Transport Properties

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ABSTRACT: Polymer membranes are important for a range of aqueous solution-based technologies that require controlled rates of ion transport. Advanced membranes will need to be engineered at the molecular level to control interactions among the polymer, sorbed water, and ions that come into contact with the membrane. Currently, little is known about the nature of these interactions, and broadband microwave dielectric relaxation spectroscopy (DRS) is a tool that could provide critical dielectric permittivity property information to facilitate modeling and understanding of the ion sorption and transport properties of hydrated polymer membranes. A handful of microwave DRS studies on hydrated polymers are reported in the literature, and these studies represent a critical first step toward using DRS to unlock important structure–property relationships. This review discusses microwave DRS and research focused on understanding the influence of polymer chemistry and water content on relative permittivity and ion transport properties of hydrated polymer membranes.



1. INTRODUCTION AND BACKGROUND

Polymeric membranes are currently used in a variety of applications that address the global need for clean water and energy, and the role of membranes in addressing critical challenges related to water and energy is expected to grow in the future.^{1–11} Membranes either currently do or could play important roles in a wide range of applications, including desalination,^{1,4,5,11–13} recovery of valuable compounds (e.g., nutrients^{14–17} and rare Earth elements^{18–21}), batteries,^{22–26} sensors,²⁷ and biological²⁸ applications. In all of these applications, controlling rates of small molecule (e.g., water, ions, and organics) transport is critical for the performance of the membrane and the effectiveness and efficiency of the technology.²⁸

Permeability (flux normalized by membrane thickness and the driving force for transport) is often used to describe rates of transport and includes both the thermodynamic (i.e., sorption) and kinetic (i.e., diffusion) components of transport.^{28–30} The selectivity of a membrane, critical for most membrane applications,¹² can be defined as the ratio of the permeability of the desired compounds relative to that of the undesired compounds. For example, in desalination applications, selectivity typically is defined as the ratio of the water permeability to that of salt (i.e., effective desalination membranes permeate water faster than hydrated ions).^{4,5,31,32} This water/salt permeability selectivity, combined with information about the applied pressure and osmotic pressure differences across the membrane, is directly related to the salt rejection of the membrane, which is critical for desalination processes.^{5,28}

Many of the membrane applications described above require controlled rates of ion transport. Ion permeability is governed by both the thermodynamic partitioning or sorption of ions into the membrane and the rate of ion diffusion through the membrane.^{4,5,29,30} Ion diffusion properties in the membrane are often governed primarily by the water content of the polymer, the size of the ion, intermolecular interactions within the hydrated polymer, or all three,^{5,33–37} and these properties are outside the scope of this review. Ion sorption properties in the membrane primarily are sensitive to electric-potential-based interactions that arise in the system as a result of the charges that are present.³¹

The free energy change that accompanies the movement of an ion from aqueous solution into the hydrated membrane phase, in the simplest case, is due to electrostatic forces that can be described by the Born model.^{31,38,39} This continuum model approach considers the free energy change associated with moving an ion from one dielectric continuum (i.e., aqueous solution) into a different dielectric continuum (i.e., the hydrated membrane). Often, this free energy change is positive, and ions are excluded to some extent from partitioning into the hydrated polymer.^{31,40}

In this simple example (considering only electrostatic forces), ion exclusion is driven by differences in the dielectric

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constant (i.e., static relative permittivity) between the external solution and the hydrated polymer membrane and by the charge density (i.e., size and charge number) of the ion.^{31,41} The dielectric constant or static relative permittivity is the value of the relative permittivity in the limit of low frequency (as discussed in more detail in Section 3.1). The dielectric constant of the hydrated membrane is the key membrane parameter that contributes to electrostatic ion exclusion. The relative permittivity properties of only a handful of hydrated membrane polymers have been reported, and this lack of structure–property relationship knowledge frustrates efforts to model or understand ion sorption properties of hydrated membranes even in the simplest electrostatic exclusion case.

A few studies of relative permittivity as a function of water content in Nafion (a perfluorosulfonic acid polymer that has been widely considered for fuel cell applications)⁴² suggest that the dielectric constant increases linearly with increases in the volume fraction of water sorbed in the polymer. Furthermore, this linear relationship appears to be bound on either end of the compositional space by the dielectric constant of the dry polymer (i.e., zero water volume fraction) and that of pure bulk water (i.e., a water volume fraction of unity).^{31,41,43,44} This relationship suggests that water content may solely dictate hydrated polymer relative permittivity properties.³¹ More recent results, however, demonstrate that polymer chemistry is also an important factor in determining the functional relationship between hydrated polymer relative permittivity and the water content of the polymer.^{36,41,45}

The simplest case electrostatic analysis, described above, oversimplifies the ion sorption process in many practical materials (presumably largely because of a breakdown of the dielectric continuum assumption⁴⁶). The approach, however, does describe the frontier of an observed trade-off relationship between water/salt sorption selectivity and water content in membranes considered for desalination applications.³¹ Additionally, other theories used to describe ion sorption or partitioning in polymers are often based on electrostatic theory.^{47–50} Thus, electrostatic theory analysis is often useful, at least to a first approximation, in efforts to model ion sorption.

It is likely that other secondary interactions (e.g., dispersion forces^{34,49–53} and complexation interactions³⁴) are important for fully describing ion sorption processes over a range of materials and a range of ions.³⁴ Developing a comprehensive fundamental understanding of these interactions will require knowledge about how polymer chemistry influences dielectric permittivity properties, which affect the underlying electrostatic theory. Little is known about how the specific chemistry of a hydrated polymer membrane influences relative permittivity properties, and one focus of this review is to summarize reports that begin to elaborate on how polymer chemistry impacts the relative permittivity of hydrated polymers.

The presence of sorbed water in a hydrated membrane adds additional complexity when compared with dry polymers, which are the subject of a rich dielectric relaxation spectroscopy literature.⁵⁴ In general, most dry polymers have relatively low dielectric constants compared with that of water, so water sorption in polymers generally results in an increase in the relative permittivity of the hydrated polymer as the water content of the polymer increases.^{31,41} Questions remain, however, about how polymer chemistry affects the functional

form of this increase in relative permittivity with increasing water content.

This review discusses a body of research focused on understanding the influence of polymer chemistry and water content on the relative permittivity properties of hydrated polymer membranes and the implications of relative permittivity properties for ion transport properties. Measurement methods and techniques are discussed first, followed by a review of the relative permittivity properties of both uncharged and charged hydrated polymers. Understanding the influence of polymer chemistry and water content on these properties is critical for developing structure–property relationships to guide future engineering of polymers for membrane applications to address global water and energy challenges.

2. CONNECTING RELATIVE PERMITTIVITY AND ION TRANSPORT PROPERTIES

The relative permittivity properties of hydrated polymers are linked to ion transport properties. The basis for these relationships are established using theory, and experimental studies are beginning to provide important information about the interplay of polymer chemistry, water content, relative permittivity, and ion transport properties. This section reviews the theoretical framework used to connect relative permittivity to ion transport properties, with a specific focus on ion sorption properties.

Electrostatic theory provides, arguably, the simplest connection between relative permittivity and ion transport properties in polymers.^{31,38,39,55} In this approach, the membrane is considered to be a homogeneous dielectric medium, and the free energy change associated with movement of an ion from aqueous solution into the membrane phase can be taken as the solvation energy barrier, ΔW_i , which can be written using the Born model:

$$\Delta W_i = \frac{z_i^2 e^2}{8\pi\epsilon_0 a_i} \left(\frac{1}{\epsilon_m} - \frac{1}{\epsilon_s} \right) \quad (1)$$

where z_i is the charge number of ion i ; a_i is the bare radius of ion i ; e is the elementary charge; and ϵ_j is the permittivity of free space ($j = 0$), the dielectric constant (or static relative permittivity) of the membrane ($j = m$), or the dielectric constant of the solution ($j = s$).⁴⁰ If the solvation energy barrier is representative of the thermodynamic barrier to ion sorption in the membrane, then the ion sorption coefficient, K_i , can be written as

$$K_i \equiv \frac{c_i^m}{c_i^s} = \exp \left[-\frac{\Delta W_i}{kT} \right] = \exp \left[-\frac{z_i^2 e^2}{8\pi k T \epsilon_0 a_i} \left(\frac{1}{\epsilon_m} - \frac{1}{\epsilon_s} \right) \right] \quad (2)$$

where c_i^m and c_i^s are the ion concentrations in the membrane and solution phases, respectively; k is Boltzmann's constant; and T is absolute temperature.^{31,40}

This form of the Born model (eq 2) provides important qualitative insight into how factors such as dielectric constants, ion size, and temperature affect dielectric ion exclusion from membranes. In general, ion sorption is suppressed when the relative permittivity of the membrane is low and when the charge density of the ion is high (i.e., when the ion is small). The influence of these factors on the ion sorption coefficient (a measure of the partitioning of ions from solution into the membrane) is illustrated in Figure 1.

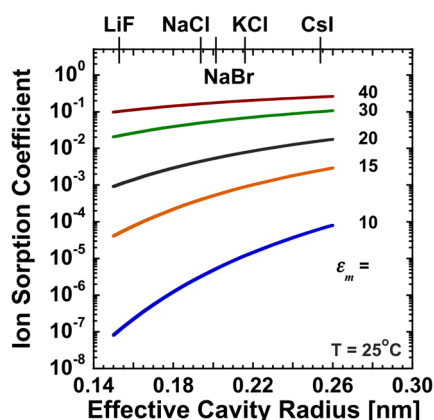


Figure 1. Ion sorption coefficient described using the Born model approach (eq 2) for several values of the membrane dielectric constant and of the effective cavity radius^{51,56} (a measure of the size of the ion). Small (charge dense) ions are excluded to a greater extent (i.e., their ion sorption coefficient is lower) than larger ions, and low dielectric constant membranes are expected to exclude ions to a greater extent than high dielectric constant membranes.

Temperature is not expected to have a significant impact on dielectric ion exclusion so long as the membrane water content does not change significantly with temperature. This situation results from a balance of the temperature dependence of the relative permittivity and the explicit temperature dependence shown in eq 2. Generally, the relative permittivity decreases as temperature increases because of the reduction in the amount of energy that can be stored in polarized dipoles at higher temperatures.⁵⁷ This theoretical prediction of little to no change in the dielectric ion exclusion properties of membranes over modest ranges of temperature is supported by experimental data.^{39,58}

The Born model often predicts ion sorption coefficients that are significantly smaller than experimentally measured values.^{31,40} For example, the experimentally measured solvation energy barrier values for a series of model membranes were found to be over an order of magnitude larger than those values predicted by the Born model.⁴¹ This quantitative disagreement is generally considered to result from the dielectric continuum assumption and the representation of the ion size.^{38,51,55,56} As discussed subsequently, different approaches have been taken to address these sources of disagreement between the model and experimental data.

The original formulation of the Born model uses the bare ion radius (as discussed in regard to eq 1).⁴⁰ Ions hydrate in water, however, suggesting that the use of the bare ion radius may underrepresent the ion size and lead to predicted salt sorption coefficients that are much lower than experimentally measured values. As such, some researchers have used hydrated or Stokes radii in eqs 1 and 2 to account for the effects of ion hydration. A more recent approach, however, suggests using a cavity radius in the Born model in place of the bare ion radius to more effectively capture ion size effects when modeling the ion solvation energy barrier.^{51,56} This cavity radius approach was used in the model that effectively described the frontier of a trade-off relationship between water/salt sorption selectivity and water content in membranes considered for desalination applications.³¹

Models based on specific geometric morphology or structure have been suggested to address the breakdown of the dielectric

continuum approach.^{38,39,55} These models aim to address length scale issues associated with describing a molecular process using a continuum approach.^{38,39,55} One disadvantage of these models is that they are often based on an oversimplified representation of molecular structure in amorphous polymer materials, which are often used in membrane applications. These issues related to connecting molecular-structure- (angstrom or nanometer length scale) and continuum-based theories are still largely unresolved.

Electrostatic theory provides at least qualitative insight into how factors such as ion size and relative permittivity (including effects of water content changes that affect relative permittivity) affect ion exclusion, but other factors contribute to ion exclusion in practical membrane materials. The electrostatic environment of the hydrated polymer can influence the effective charge of the electrolytes via ion pairing.⁵⁵ Additionally, many membrane polymers contain ionizable fixed charges that result in Donnan exclusion of ions (as discussed subsequently).^{4,59} These factors, important for understanding ion sorption in polymers, generally depend on the hydrated polymer relative permittivity.

Donnan exclusion in charged polymer membranes occurs as a result of the presence of fixed charges attached to the polymer backbone.^{4,59,60} These fixed charge groups must be balanced by oppositely charged counterions and create a thermodynamic situation whereby ions of the same charge as the fixed charge groups (and their associated counterions) are excluded from the membrane phase. The key result of Donnan exclusion is that so-called mobile salt is excluded from the membrane, which is desirable for desalination applications.⁴

Donnan exclusion can be modeled by combining a charge balance, which accounts for the fixed charges on the polymer backbone, with thermodynamic information about the hydrated and ion-containing polymer matrix.⁴ Although modeling Donnan exclusion is not new, recent efforts have demonstrated that previously reported disagreements between Donnan theory and experimental data result from improper treatment of the fixed charge concentration and thermodynamics of the system.^{61,62} This approach uses the Manning counterion condensation model⁴⁷ to account for ion pairing between fixed charges and corresponding counterions. The model treats the remaining electrolyte sorbed in the membrane using the Debye–Hückel approximation,⁴⁷ and both this aspect of the model and the evaluation of the ion pairing process rely on electrostatic theory and, thus, knowledge of the hydrated polymer relative permittivity.

As discussed in this section, effective modeling of ion sorption in membranes relies on knowledge of hydrated polymer relative permittivity. Therefore, it is critical to understand the complex interplay between polymer chemistry and water content factors that influence relative permittivity. Techniques for measuring the relative permittivity properties of membranes are available, and these techniques can be used to further investigate structure–property relationships that affect ion sorption in hydrated polymer membranes.

3. MEASUREMENT TECHNIQUES

The dielectric permittivity properties of a material can result from a variety of physical phenomena or dielectric relaxation mechanisms (e.g., ionic conduction, dipole relaxation, atomic polarization, and electronic polarization), and these different mechanisms generally are observed at different frequencies.^{63–65} Polymer backbone and side chain relaxations can

be probed using dielectric relaxation spectroscopy (DRS), typically at frequencies below the order of 10 MHz. Alternatively, dipole relaxations attributed to the permanent dipoles of water^{64–66} sorbed in hydrated membranes are probed using DRS in the microwave frequency range.^{41,43,67,68} This section discusses the measurement and analysis of these relaxations.

As will be discussed in more detail in this section, relative permittivity is frequency dependent, and the dielectric constant is generally defined in the low frequency limit.^{64,68} In hydrated polymers, measurement artifacts are often observed at low frequency because of ionic conductivity.^{43,68,69} As a result, in hydrated systems, the dielectric constant is determined at high (typically microwave) frequencies. For example, the dielectric constant of pure bulk water can be measured at and below 1 GHz.⁶⁷ By analogy, researchers have bridged the gap between conventional low frequency DRS measurements of the dielectric constant and microwave DRS measurements of the dielectric constant by taking the hydrated polymer dielectric constant (i.e., the value of ϵ_m discussed in Section 2) as the relative permittivity of the sample in the microwave frequency range.^{36,41,43,45,67,68,70}

3.1. Dipole Relaxation Processes. Dipoles can polarize in the presence of an electric field, and the molecular environment experienced by the dipole affects the rate at which the dipole can orient or relax.^{54,64} Broadband DRS subjects dipoles to an oscillating field over a range of frequencies to probe the extent and time scale of the dipole relaxation processes that occur in the material.^{54,64} In the simplest case, dipole relaxation processes are described by a single Debye relaxation model:^{68,71,72}

$$\epsilon^* = \epsilon_\infty + \frac{\epsilon_s - \epsilon_\infty}{1 + i\omega\tau} = \epsilon_\infty + \frac{\Delta\epsilon}{1 + i\omega\tau} \quad (3)$$

where ϵ^* is the relative complex dielectric permittivity, ϵ_∞ is the high frequency relative permittivity limit, ϵ_s is the low frequency relative permittivity limit (or dielectric constant), ω is the angular frequency of the applied field ($\omega = 2\pi f$, where f is frequency), and τ is the relaxation time constant for the process ($\tau = 1/(2\pi f_{\max\text{-loss}})$, where $f_{\max\text{-loss}}$ is the frequency where the maximum dielectric loss occurs).^{68,72} Additionally, the difference $\epsilon_s - \epsilon_\infty$ is often referred to as the dielectric strength, $\Delta\epsilon$, which is related to the relative concentration of dipoles that participate in the relaxation process (i.e., a system containing more dipoles that participate in the relaxation process would have a higher dielectric strength than a system containing fewer dipoles).⁴⁴

This single Debye relaxation model works well in situations where there is a population of dipoles that relax with a single relaxation time constant (e.g., liquid water^{41,67}). The real, ϵ' , and imaginary, ϵ'' , parts of complex dielectric permittivity, ϵ^* , can be expressed using the Debye dispersion formulas for a single Debye relaxation process:⁶⁸

$$\epsilon' = \epsilon_\infty + \frac{\epsilon_s - \epsilon_\infty}{1 + (\omega\tau)^2} = \epsilon_\infty + \frac{\Delta\epsilon}{1 + (\omega\tau)^2} \quad (4)$$

$$\epsilon'' = \frac{(\epsilon_s - \epsilon_\infty)\omega\tau}{1 + (\omega\tau)^2} = \frac{\Delta\epsilon\omega\tau}{1 + (\omega\tau)^2} \quad (5)$$

The real, ϵ' , and imaginary, ϵ'' , parts of the complex dielectric permittivity are typically referred to as the relative permittivity and dielectric loss, respectively.⁵⁴ Measured complex dielectric

permittivity data, measured as a function of frequency, can be deconvoluted into ϵ' and ϵ'' and fit to eqs 4 and 5 to determine the dielectric constant, the high frequency relative permittivity, and the relaxation time constant.

The physical picture of the single dipole relaxation process (described by eqs 4 and 5) is that at sufficiently low frequencies, the field oscillations are slow enough that the dipoles remain in phase with the field.⁶⁴ At these frequencies, energy is stored in the aligned dipoles, and a low frequency plateau is observed in the real part of the complex dielectric permittivity data (Figure 2).⁶⁴ The magnitude of this ϵ' plateau

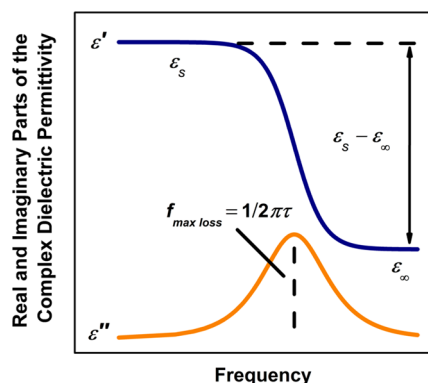


Figure 2. Real, ϵ' , and imaginary, ϵ'' , parts of the complex dielectric permittivity versus frequency for a single Debye relaxation process described by eqs 4 and 5. The real part of the complex dielectric permittivity (i.e., the relative permittivity) plateaus at low frequency to a value that is generally taken to be the dielectric constant, ϵ_s .⁶⁴ As frequency increases, the relative permittivity decreases as the imaginary part of the complex dielectric permittivity (i.e., the dielectric loss) peaks at a frequency that can be related to a characteristic relaxation time of the dipoles.⁶⁴

is typically taken as the dielectric constant.⁶⁴ As frequency increases, the field oscillations become faster and exceed the rate at which the dipoles can align.⁶⁴ Thus, energy begins to dissipate and a relaxation peak in the dielectric loss (ϵ'') data is observed (Figure 2).^{64,65} A simultaneous decrease in the relative permittivity is observed as a result of a reduction in the ability of the dipoles to store energy, and at frequencies greater than that of the relaxation, the relative permittivity plateaus to ϵ_∞ .

Although the preceding discussion described a single Debye relaxation process, many hydrated polymer systems exhibit multiple (or a distribution of) dipole relaxation processes over a range of frequencies, and the relative permittivity and dielectric loss signatures of these processes superimpose in the dielectric spectra.^{36,41,43,44,70} The approach, described above, can be generalized to account for multiple relaxations. Complex dielectric permittivity data, measured using broadband DRS, can be used to elucidate the relaxation time constants and dielectric strengths of the different relaxation processes.^{36,41,43,44,70}

3.2. Measuring and Characterizing Dipole Relaxations in the Microwave Frequency Range. In hydrated polymers, broadband DRS measurements made in the microwave frequency range are of particular interest because water molecule dipoles often relax in this frequency range.⁶⁸ In addition to dipole relaxations that result from sorbed water in hydrated polymers, dipoles on the polymer side chains, backbone, or both can be probed using DRS.⁵⁴ Although the

physical picture and analysis of these different relaxation processes are similar to those described in the previous section, the dynamics of dipole relaxations associated with the polymer are generally much slower compared with the situation for water molecules, which generally are able to move more freely than polymeric dipoles. As such, polymer side chain and backbone dipole relaxations are often observed to occur at lower frequencies (e.g., less than the order of 10 MHz)^{69,73,74} than water dipole relaxations, which can be observed in the microwave frequency range.

Broadband DRS is conducted in the microwave frequency range of the spectrum using a vector network analyzer (VNA).^{64,75} In general, the VNA generates and measures the oscillating field used in the measurement, and it is used to make swept frequency stimulus–response measurements on the sample.⁶⁴ The VNA subjects the sample to an oscillating field at a particular frequency; measures the incident, reflected, and transmitted signals; separates and detects the signals; and processes the signal measurements to generate a series of scattering parameters (*S*-parameters).⁶⁴ The specific details of this process depend on the specific VNA and the sample holder used in the measurement. For broadband DRS measurements, this process is performed for all frequencies of interest.

3.2.1. Sample Holders. Although the VNA is critical for generating and measuring signals during broadband DRS, an appropriate sample holder is needed to effectively measure the dielectric permittivity properties of a material. The specific technique used to conduct the measurement depends on the chosen sample holder. Examples of broadband techniques for characterizing samples using microwave frequencies include coaxial probe, free space, and transmission line techniques.^{63–65} Each one has advantages and disadvantages that make the technique more amenable to certain types of materials. An overview of these techniques is provided below.

Typically, form factor of material and frequency range are important factors to consider when selecting the most appropriate sample holder and technique. To probe water dipole relaxations in hydrated polymers, for example, the technique must be capable of measuring solid samples, and it must also perform broadband microwave frequency measurements. In the microwave frequency range, wavelengths range from 1 mm to 1 m and, thus, can approach (or exceed) the physical dimensions of the sample.⁵⁷ As such, the sample must be large or thick enough for the microwaves to sample the material effectively, and this constraint can often limit the range of frequencies used to make the measurement. These requirements inherently require sample holders that are different from the conventional parallel plate (or capacitor-type) sample holders that are generally used to conduct DRS on samples at lower frequencies (e.g., frequencies at or below the order of 10 MHz).⁶⁴

An open-ended coaxial probe can be used to measure microwave signals that reflect from a sample.⁶⁴ Similar to listening to a heartbeat through a stethoscope, the probe is pressed onto or into the sample, and it is critical that the probe be in intimate contact with the sample. Because of this constraint, the technique is most convenient for liquids, semisolids, or solids that have a very flat surface.⁶⁴ The technique can be used over a broad frequency range (i.e., 0.2 to 50 GHz), but the sample must be sufficiently thick (with respect to the wavelength of the microwave radiation) to be effectively a semi-infinite medium.⁶⁴ Additionally, only

reflected signals are measured using this method. This approach is often not appropriate for thin polymer films, as sample thicknesses generally need to be larger than 1 cm to effectively make the measurement.⁶⁵

In situations where it is not practical to bring a coaxial probe into contact with the sample or in situations where it is desirable to measure both the reflected and transmitted signals, the sample can be placed between two antennas, which are used to make the measurement. This so-called free space technique can be used to make measurements up to 325 GHz.⁶⁴ It can be ideal for solid slabs, powders, and liquids, and it is also ideal for high temperature measurements, because the sample can be housed in an environmentally controlled chamber during the measurement.⁶⁴ To characterize solid samples at low frequencies (<50 GHz), however, the technique requires thick samples (because of the wavelength issue described above) that have flat parallel faces.⁶⁵ As such, this technique is often not particularly useful for relatively thin polymer films.

Perhaps the most effective sample holder for characterizing the dielectric permittivity properties of hydrated polymer films in the microwave frequency range is a transmission line.^{41,44,64,67} Using a coaxial waveguide as a transmission line sample holder enables broadband dielectric permittivity measurements to be made in the microwave frequency range.^{36,41,67} A significant advantage of this approach is that thin film samples can be wrapped around the center conductor of the coaxial waveguide, and this approach can be used to increase the effective sample thickness (now determined by the width of the sample wrapped around the conductor, Figure 3)

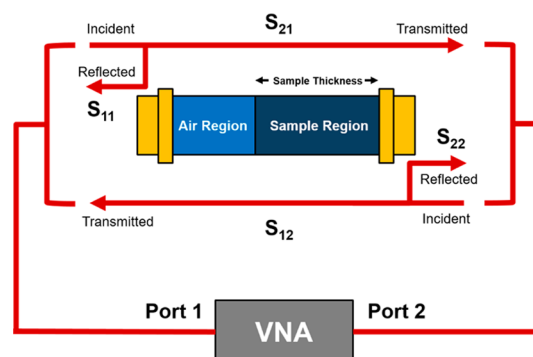


Figure 3. Two-port VNA measuring four *S*-parameters (S_{11} and S_{22} are based on reflected signals and S_{12} and S_{21} are based on transmitted signals).^{41,75} In this transmission line example, the sample is loaded into the transmission line with a fixed sample thickness (i.e., the dimension along the axis of the transmission line), and this sample thickness can be varied, depending on the dielectric loss properties of the sample, as a function of frequency and accounted for during data analysis.^{36,67} Adapted with permission from ref 41. Copyright 2019 Elsevier.

to an extent that permits the microwave radiation to effectively sample the material. As such, film samples with thicknesses on the order of micrometers can be measured using microwaves, so long as the films are sufficiently tough enough to be wrapped around the conductor of the transmission line.

To make accurate transmission line measurements, it is critical to ensure that the sample is tightly wrapped around the center conductor in a manner that fills all of the annular space of the transmission line. Air or other fluid gaps introduce measurement artifacts.⁴¹ Additionally, the sample length (i.e.,

width of the sample wrapped around the conductor) must be sufficiently large to be sampled effectively by the field. In hydrated membranes, however, sorbed water can absorb microwave radiation, so samples need to be sufficiently short to ensure transmission of the signal through the sample. Often in water-containing systems, sample length is varied as a function of frequency to mitigate these issues.^{36,67}

3.2.2. Relating Measured Data to Relative Permittivity Properties. Regardless of the sample holder used to make the measurement, the VNA measures scattering parameters (or S-parameters).⁷⁵ A two-port VNA can measure four S-parameters: a transmitted and a reflected S-parameter for each direction of incident radiation (Figure 3). For isotropic materials, these S-parameters are expected to be symmetric (i.e., $S_{ij} = S_{ji}$).^{75,76} The measured S-parameters are mathematically related, nonlinearly, to the relative complex dielectric permittivity, ϵ^* , and the relative complex permeability, μ^* , of the sample.⁷⁶

Several algorithms, including the Nicolson, Ross, and Weir (NRW) method^{77,78} and the Baker–Jarvis⁷⁹ method, have been used to convert the measured S-parameters into ϵ^* , and those approaches are summarized here. When using the NRW method, it is possible to calculate multiple ϵ^* and μ^* values from a single set of S-parameters, and the NRW method breaks down in situations where the sample length is an integer multiple of one-half of the wavelength of the measurement.^{63,76,80} The Baker–Jarvis method can introduce random errors into the data because of electrical noise in the experimental system, and systematic errors, which can only be minimized but not eliminated, can occur because of measurement offset and leakage.^{76,80}

To address these challenges, Lu et al. numerically calculated the complex relative permittivity using the transmission S-parameters (i.e., S_{12} and S_{21} in Figure 3).⁶⁷ They noted that this approach is particularly effective for accurately calculating the complex relative permittivity properties of high loss materials, such as hydrated polymers, which are considered high loss materials because of the tendency of water to absorb microwave radiation (i.e., water has a high dielectric loss compared with those of many organic polymers). Chang et al.⁴¹ used an improved algorithm proposed by Bartley and Begley⁷⁶ to calculate the complex relative permittivity of hydrated polymers. The Bartley and Begley approach smooths out the effects of measurement error due to noise and signal mismatch.⁸⁰ Both methods can be used to calculate the complex relative permittivity properties of hydrated polymers from measured S-parameters.

4. RELATIVE PERMITTIVITY PROPERTIES OF SOLUTIONS AND HYDRATED POLYMERS

Although this review focuses on the dielectric permittivity properties of hydrated polymers, it is instructive to first review the dielectric permittivity properties of miscible binary mixtures, particularly those mixtures composed of water and polar organic solvents. These systems provide a framework for understanding more complicated mixtures of water and polymer. This section begins with a review of dielectric properties of solutions and then transitions to hydrated polymers.

Within the field of hydrated polymers for ion-transport applications, a distinction is often made as to whether the polymer contains fixed charges or not.⁵ In electric-field-driven membrane processes, membranes necessarily have ionizable

fixed charge groups (e.g., sulfonate or quaternary ammonium) that boost the concentration of counterion charge carriers within the membrane phase (important for conductivity).^{3,6,59,81,82} In other membrane processes, such as desalination, fixed charges are not necessarily required, although the presence of fixed charges in the polymer can contribute to Donnan exclusion of co-ions (as discussed in more detail in Section 2), which can help to enhance salt rejection properties in materials for desalination applications.^{4,59}

Hydrated polymers containing fixed charges can have an effective membrane phase ionic strength often on the order of 1 mol/L (sorbed water), which is typically greater than the ionic strength of the aqueous solution surrounding the membrane.^{3,5,48,83} Conversely, uncharged polymers often have an effective membrane phase ionic strength that is lower than that of the aqueous solution surrounding the membrane.⁸³ Because of the very different ionic environments of these two classes of polymers, two subsections are included for hydrated polymers: one focused on uncharged polymers and the other focused on charged polymers.

4.1. Miscible Solutions. Studies performed on binary solution mixtures provide insight into the molecular interactions that affect relative permittivity mixing rules. Because these systems contain only small molecules, as opposed to high molecular weight polymers, they are instructive as a starting point for understanding how polymer water content influences the relative permittivity properties of the polymer/water mixture. Discussion of these solution cases focuses on the dielectric constants of the solutions (i.e., the plateau value of the relative permittivity at sufficiently low frequency).

Perhaps the simplest case scenario for modeling the dielectric constant of a binary mixture would be a situation where the dielectric constant of the mixture varies linearly (as a function of composition) between the static dielectric constants of the two pure liquids. Although this mixing model is highly idealized, mixtures of water/dimethyl sulfoxide (DMSO) exhibit this type of linear behavior (Figure 4).⁸⁴ Both components in this DMSO/water mixture are relatively high dielectric constant materials, unlike most polymer/water systems.

The dielectric constant of a mixture, however, often does not vary linearly with composition between the dielectric constants of the pure components. For example, data measured for

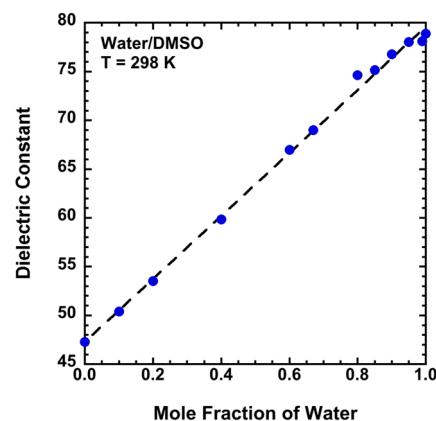


Figure 4. Microwave dielectric relaxation spectroscopy data, measured at 298 K, showing a linear relationship between the dielectric constant of pure water and that of pure DMSO.⁸⁴

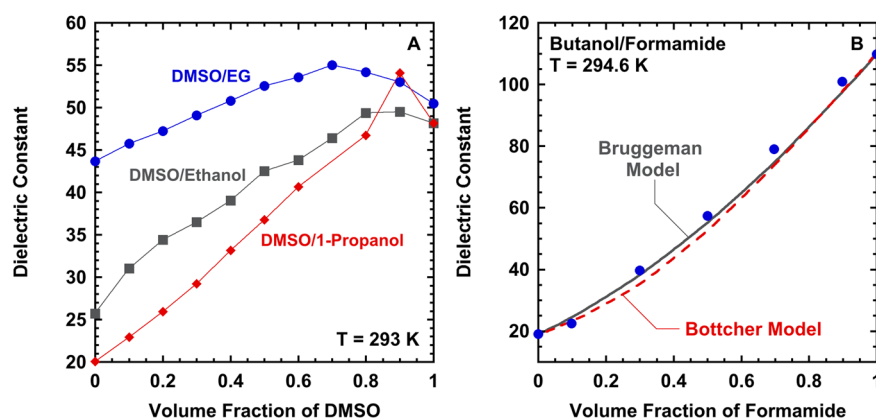


Figure 5. Dielectric constant data (A) measured for binary solutions of DMSO and ethylene glycol (EG), ethanol, or 1-propanol^{85,86} and (B) measured for butanol/formamide solutions.⁸⁷

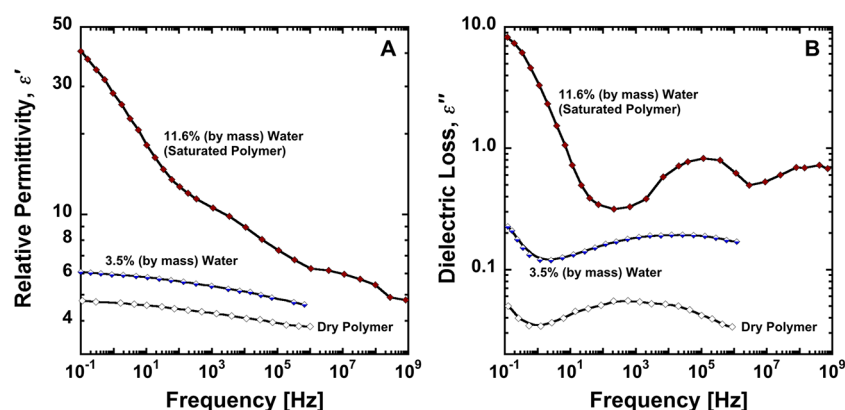


Figure 6. (A) Dielectric relative permittivity and (B) loss data, measured at $-20\text{ }^{\circ}\text{C}$, as functions of frequency for cellulose acetate polymers.⁹³ The cellulose acetate polymer was either dry, fully hydrated with water (11.6% water by mass), or hydrated to an intermediate extent (3.5% water by mass).

mixtures of DMSO with ethylene glycol (EG), ethanol, or 1-propanol exhibit static dielectric constant maxima at compositions that are rich in DMSO (Figure 5A).^{85,86} The nonlinearity of the data in Figure 5 may be attributed to the nature of hydrogen bond complexes that form in these solutions. The Kirkwood equation rationalizes these data in terms of molecular dipole alignment and complex formation.^{85,86} Therefore, the higher dielectric constants observed for the DMSO/EG system compared with those of the DMSO/ethanol and DMSO/1-propanol systems may be due to the more polar nature of the EG molecule (two $-\text{OH}$ groups) compared with ethanol and 2-propanol (each with a single $-\text{OH}$ group).

Other nonlinear behavior has been observed in binary solutions. The formamide/butanol system exhibits a nonlinear dielectric constant dependence on the volume fraction of formamide in the mixture (Figure 5B).⁸⁷ In this system, the Bruggeman^{88,89} and Bottcher⁹⁰ models describe the variation of the static dielectric constant with composition.

Bruggeman's model is based on the assumption that the mixture can be described as having highly dispersed volume fractions (i.e., a well-mixed solution), and the model allows for long-range interactions between components that give rise to nonlinear effects.^{88,89} The Bruggeman model assumes that one component is dispersed in a matrix of the other component, so the model is inherently asymmetric, but the Bottcher model is

a symmetric model that is based on effective medium theory and treats solutions like statistical mixtures.^{91,92}

Dielectric relaxation spectroscopy studies on binary miscible solutions show that the relationship between the dielectric constant and solution composition can be either linear or nonlinear. This behavior is ultimately linked to the nature of the intermolecular interactions between the solvents, and it provides a framework for considering similar issues in hydrated polymers. The remainder of this section reviews data for hydrated polymers with a particular focus on how relative permittivity depends on hydrated polymer water content.

4.2. Uncharged Polymers. The majority of reported dielectric relaxation spectroscopy results for uncharged polymers are data measured at submicrowave frequencies. Segmental relaxation processes in polymers typically occur at the order of 10 MHz or slower frequencies. These low frequency measurements, therefore, can be very effective at characterizing segmental dynamics in a wide range of uncharged (and often dry) polymers.⁵⁴

Few studies have considered hydrated uncharged polymers. This section focuses on those studies that consider hydrated uncharged polymers (i.e., polymers that do not contain fixed charge groups that readily ionize when the polymer hydrates with water). The dielectric spectroscopy studies performed on many of these hydrated materials were performed at relatively low frequencies and low temperatures as an effort to characterize segmental dynamics in the polymers.^{74,93–95} As

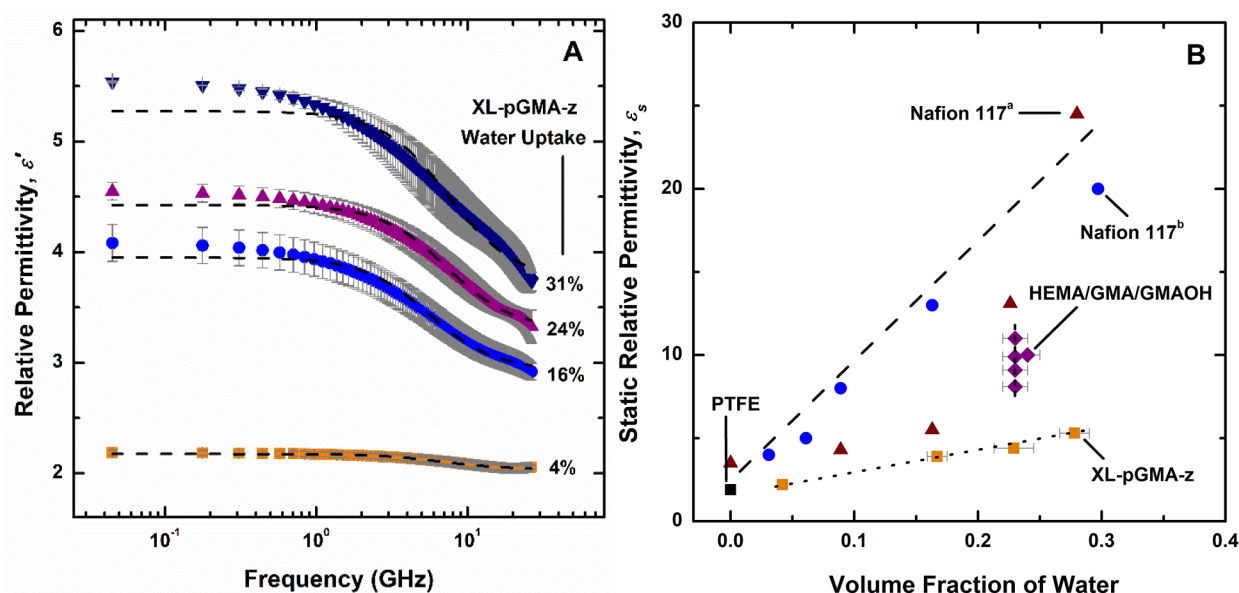


Figure 7. (A) Relative permittivity of a series of model polymers, XL-pGMA-z, plotted as a function of frequency. The dashed curves are fits of the data to a single Debye relaxation. (B) Static relative permittivity (i.e., dielectric constant) data for PTFE,⁴¹ XL-pGMA-z,⁴¹ HEMA/GMA/GMAOH,⁴⁵ Nafion 117^a,⁴⁴ and Nafion 117^b⁷⁰ plotted as a function of the volume fraction of water sorbed in the polymer. The dashed lines illustrate the different functional relationships between the static relative permittivity (i.e., dielectric constant) and volume fraction of water in the polymers. Adapted with permission from ref 41. Copyright 2019 Elsevier.

such, these low frequency measurements can be sensitive to glass transition and polymer plasticization phenomena due to water sorption.^{54,96} This situation contrasts the microwave dielectric relaxation spectroscopy studies, discussed elsewhere in this review, that probe water molecule dynamics in hydrated polymers.

In general, water sorption in uncharged polymers leads to an increase in the relative permittivity and the dielectric loss properties of the material. This behavior has been illustrated for a variety of materials, including poly(hydroxyethyl acrylate),⁷⁴ poly(2-hydroxyethyl methacrylate),⁹⁴ and cellulose acetate⁹³ (Figure 6). In general, these observations are consistent with the physical picture of mixing together a low permittivity material (i.e., the dry polymer) with water, which has a much higher dielectric constant than that of a typical dry polymer.

Evidence of electrode polarization can be observed in Figure 6B at low frequency.^{68,93} This polarization artifact results from a capacitive buildup of charge at the electrode–polymer interface in parallel plate sample holder systems.⁶⁸ The polarization intensifies as the water content of the material increases.

Many reported studies on hydrated uncharged polymers have focused on interrogating polymer segmental dynamics, so many of those studies were performed over ranges of temperature. In general, the relative permittivity of hydrated polymers tends to increase with increasing temperature.^{74,94,95} This result generally is due to additional thermally stimulated or facilitated motion of dipoles on the polymer backbone.^{74,94,95} Additionally, polymer plasticization, due to water sorption in the polymer, could facilitate dipole motions on the polymer backbone.⁹⁶ The thermal effects may be particularly pronounced around the glass transition temperature of the polymer.⁵⁴ The temperature dependence, described here, contrasts that discussed previously where, often in small molecules, relative permittivity tends to decrease

as temperature increases as a result of a reduction in the amount of energy that can be stored in polarized dipoles at higher temperatures.⁵⁷ The situation in polymers is different from that of small molecules largely because of differences in molecular size and the influence of temperature on polymer segmental motions.

To probe functional relationships between polymer water content and relative permittivity, Chang et al. measured relative permittivity as a function of water content in a series of model hydrated polymers, XL-pGMA-z.⁴¹ The dielectric constants for the XL-pGMA-z materials were obtained by fitting the data to the single Debye relaxation model (Figure 7A). This approach standardized the process of determining the dielectric constant for the materials, but the single Debye relaxation model describes the data less effectively as the water uptake of the polymer increases. For example, in the highest water content polymer shown in Figure 7A, the offset between the lowest frequency relative permittivity measurement and the single Debye relaxation model is around 4%. The static relative permittivity (i.e., dielectric constant) of the hydrated polymers increased as water content increased, but the slope of this increase was substantially lower than that observed for several charged polymers (Figure 7B).⁴¹

Although the XL-pGMA-z data appear to vary linearly with water content (at least over the range of materials considered), it is important to note that the data were not coincident with a linear relationship between the dielectric constant of the dry polymer and that of bulk water (such as that suggested in Figure 4). This observation suggests that the simple linear mixing model (described in Section 4.1) may not be sufficient to describe the dependence of the dielectric constant on water content for all hydrated polymers. A qualitative relationship between ion sorption and static permittivity was also reported to suggest that the measured static permittivity properties were related to measured ion sorption properties that are critical for membrane applications.⁴¹

The functional relationship between polymer functional group configuration and the static relative permittivity of the material was also explored using another model hydrated polymer, HEMA/GMA/GMAOH.^{36,45} At equivalent water content, a vicinal diol-rich (GMAOH-rich) material had a higher static relative permittivity than a single hydroxyl group-rich (HEMA-rich) material (Figure 7B).^{36,45} The results of this study suggest an opportunity for engineering polymer dielectric permittivity properties by simply adjusting the distribution of hydrophilic functional groups in the material.

4.3. Charged Polymers. Dielectric relaxation spectroscopy has been used to characterize hydrated charged polymers at both low frequency^{69,97,98} and high frequency.^{43,44,67,70} Many of these hydrated proton exchange membranes are of interest for fuel cell applications, and fuel cell performance depends on the ability of the membrane to facilitate proton transport.^{99–105} Water dipole relaxations are coupled to the proton transport properties of the membrane, so dielectric relaxation spectroscopy provides insight into the transport mechanisms that influence how these membranes might perform in a fuel cell application.^{43,70} Few studies, however, have considered the interplay between relative permittivity and ion sorption and transport in hydrated charged polymers for other applications, such as desalination. This section focuses on the use of microwave DRS to probe the relative permittivity of hydrated polymers and on the use of relative permittivity properties to further understand the state of water in hydrated charged polymers.

4.3.1. Relative Permittivity. Paddison et al. reported relative permittivity properties of hydrated Nafion and sulfonated polyaromatic polyether ketone (SPEEK) polymer membranes.^{43,70} Measured in the microwave frequency range (0.045–30 GHz), the relative permittivities of both polymers considered by Paddison et al.^{43,70} increased with increasing water content, similar to the results reported for other polymers.^{36,41,44,84} Additionally, the relative permittivity properties of both polymers considered by Paddison et al. decreased as the frequency used to make the measurement increased.^{43,70} These observations are consistent with Debye relaxation processes and suggest that more energy can be stored in polarized water dipoles in polymers that contain more water.

Furthermore, Paddison et al. compared the relative permittivity of Nafion to that of SPEEK. They observed that SPEEK had lower relative permittivity than Nafion at comparable water content.⁴³ This result reflects the significant difference in the chemistry of the materials (i.e., SPEEK is a hydrocarbon-based aromatic polymer, whereas Nafion is a perfluorinated polymer) and is consistent with a morphological model, proposed by Kreuer,¹⁰⁶ for perfluorinated- and hydrocarbon-based proton exchange membranes.

In Kreuer's model, the sorbed water in SPEEK may be more restricted in narrow transport channels than in the situation in Nafion, where unfavorable interactions between water and the perfluorinated polymer lead to the formation of water clusters.^{42,106,107} More restricted water motion likely drives lower relative permittivity in SPEEK compared with in Nafion, as more restricted water is less able to store energy in polarized dipoles. These results provide further evidence that both polymer chemistry and structure play a role in influencing the relative permittivity, which influences the ion transport properties, of hydrated charged polymers.

The influence of polymer fixed charge group concentration on relative permittivity was explored by Lu et al. using Nafion117 and Flemion SH150.^{44,67} These materials are chemically similar, but they have different concentrations of sulfonate (i.e., fixed charge) groups on the polymer backbone. Typically, these concentrations are represented as the ion exchange capacity (IEC) or equivalent weight (EW) of the polymer. The IEC and EW of Nafion117 are 0.909 mequiv/g_(dry-polymer) and 1100 g/equiv, respectively, and the IEC and EW of Flemion SH150 are 1.1 mequiv/g_(dry-polymer) and 909 g/equiv, respectively.^{44,67} Thus, Flemion SH150 has a higher specific concentration of sulfonate groups than Nafion117.

Using microwave DRS measurements (made over a frequency range of 0.045 to 26 GHz), Lu et al. observed that Flemion SH150 had greater relative permittivity than Nafion117 at conditions where the water content of the two membranes was equivalent.^{44,67} As such, a higher concentration of fixed charge groups in Flemion SH150 promoted greater water mobility and, thus, higher relative permittivity compared with the situation in Nafion117. Given the equivalent water content of the materials considered, the results suggest that additional sulfonate groups in Flemion SH150 promoted water motion instead of potentially immobilizing water molecules via hydrogen bonding interactions with the additional sulfonate groups on the polymer backbone.

Although several of the studies discussed in this section explored the connection between polymer water content, chemistry, and structure and relative permittivity, connections between relative permittivity and ion sorption properties are still needed to further develop structure–property relationships. Bontha and Pintauro proposed a structure/morphology-dependent model for predicting the ion sorption properties of hydrated polymers.^{108,109} Their approach aimed to overcome the quantitative disagreement between the measured ion sorption properties and those properties predicted using electrostatic-continuum-based theories.^{31,40} As discussed in Section 2, this disagreement is recognized to be largely due to the dielectric continuum assumption.^{38,51,55,56}

By assuming a polymer pore structure, ion radius, and solvent physical properties, the Bontha and Pintauro model can be used to compute the relative permittivity profile in the pores of the polymer.¹⁰⁹ Using this profile, ion sorption free energy was calculated as a function of distance from the pore wall. The model accurately predicted the ion sorption free energies for Nafion117.¹⁰⁹ The pore structure assumptions may work well for some materials where structure is highly regular, but these assumptions may oversimplify the molecular situation in some amorphous polymers where free volume space between polymer chains may be less regular in size, shape, or both.¹¹⁰

4.3.2. State of Water. Water–polymer and water–water interactions that occur in hydrated charged polymers result in a distribution of so-called water states, and these states can be sensitive to changes in polymer chemistry, polymer water content, or both.^{106,111–115} Many studies simplify this distribution of water states by considering three discrete water states:^{42,101–103} strongly bound water that interacts strongly with ionic binding sites (e.g., sulfonate groups), weakly bound water that interacts weakly with ionic binding sites, and free/bulk-like water that moves freely and has effectively no interaction with the ionic binding sites.^{116–118}

Typically, the presence of free/bulk-like and weakly bound water facilitate ion sorption and transport in hydrated charged polymers.^{5,41,119} This situation may be linked to a need for ions to be at least partially hydrated in order to transport through the membrane.⁵ Because microwave DRS characterizes water dipole relaxations that are related to the extent and dynamics of water motions in hydrated charged polymers, the technique can be used to probe states of water in hydrated polymers. This section summarizes studies that have used microwave DRS to characterize states of water in hydrated polymers, often to provide insight into ion transport properties.

Lu et al. used microwave DRS to study the state of water in Nafion117 and Flemion SH150.^{44,67} They observed that the weakly bound and free/bulk-like water content increased as the overall polymer water content and relative permittivity increased. The observed increase was more significant in Flemion than in Nafion. These results may be due to higher sulfonate group concentration (i.e., lower EW) in Flemion than in Nafion, which likely leads to enhanced connectivity of water clusters and a higher degree of phase-separation between hydrophilic and hydrophobic domains in Flemion compared with in Nafion.⁶⁷ The high relative permittivity of Flemion may facilitate ion sorption and transport through the membrane.

Paddison et al. observed lower relative permittivity for sulfonated polyaromatic polyether ketone (SPEEK) membranes than for Nafion membranes at comparable water content. This observation was attributed to the presence of less free/bulk-like water in the SPEEK membranes than in Nafion.⁴³ As discussed in Section 4.3.1, this result is consistent with an overall structure/morphology picture of the materials, proposed by Kreuer,¹⁰⁶ suggesting that water in SPEEK may be more restricted compared with that in Nafion. The presence of less free/bulk-like water in SPEEK than in Nafion could result in reduced ion sorption and reduced rates of ion transport.

Chang et al. used microwave DRS to study the influence of hydroxyl functional group configuration on the dielectric permittivity and ion transport properties of a series of water content equivalent HEMA/GMA/GMAOH materials.⁴⁵ The relative permittivity of these materials was manipulated by varying the configuration of the hydroxyl groups within the polymer. The content of freezable free/bulk-like water also was affected by the hydroxyl group configuration. Increases in the free/bulk-like water content of the material correlated with increases in relative permittivity.

The examples discussed in this section illustrate the use of microwave DRS to probe the states of water in hydrated charged polymers. State of water analysis is important for understanding ion sorption properties and the rate of ion transport in hydrated charged polymers. Different states of water can arise in hydrated polymers because of the nature of interactions between water and polymer. Microwave DRS could be a useful technique for learning more about these interactions at a particular temperature of interest, in contrast to thermal analysis techniques that generally must be performed over a range of temperatures to probe states of water.

5. SUMMARY

Relative permittivity properties are important for modeling and understanding ion sorption and transport properties in hydrated polymers, which are important for membrane applications that could address global needs for water and

energy. Although dielectric relaxation spectroscopy (DRS) has been widely used to characterize polymer segmental motions, fewer studies have been performed in the microwave frequency range on hydrated polymers. These microwave DRS measurements could provide critical insight into the relative permittivity and, thus, ion sorption and transport properties of a range of hydrated polymers.

Although general structure–property relationships are beginning to form (e.g., relative permittivity is known to increase as polymer water content increases), these initial studies are only a first step. Polymer chemistry and structure appear to have a significant effect on relative permittivity and its dependence on polymer water content, but currently, detailed structure–property relationships are largely unknown. Furthermore, the interplay of dielectric permittivity properties and other ion exclusion mechanisms (e.g., Donnan exclusion) have been discussed from a theoretical perspective, but little experimental work has been performed to further investigate these issues. Future investigation of these issues facilitated, at least in part, by microwave DRS promises to facilitate structure–property relationship development.

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Notes

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