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Influence of water content on alkali metal chloride transport in cross-linked Poly(ethylene glycol) Diacrylate.1. Ion sorption

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HIGHLIGHTS

- Interactions between ions and polymer chains influence sorption behavior.
- The relative order of salt sorption does not follow the order of hydrated ion size (i.e., $Li^+ > Na^+ > K^+$).
- Polymer water content influences ion activity coefficients in the membrane.
- Flory-Rehner theory was used to predict water volume fraction in the polymer equilibrated with salt solutions.

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ABSTRACT

The relationship between ion size and sorption properties in water swollen uncharged polymers was investigated as a model system for understanding ion sorption and transport in more complex systems (i.e., charged polymer networks). Alkali metal chloride (e.g., LiCl, NaCl, and KCl) sorption coefficients in a series of cross-linked poly (ethylene glycol) diacrylate (XLPEGDA) polymer membranes were measured as a function of external salt concentrations ranging from 0.01 to 1.0 M. The relative order of salt sorption coefficients was: KCl > LiCl > NaCl. This order does not correspond to the order of ion hydration size (i.e., $Li^+ > Na^+ > K^+$). The alkali metal chloride sorption behavior in XLPEGDA polymers is influenced by both ion hydration and polymer-ion specific interactions. XLPEGDA polymers having three different equilibrium water uptake values were prepared to investigate the effect of water content on salt sorption in these polymers. Generally, ion sorption coefficients increase as polymer water content increases. Salt activity coefficients in the polymers were quantified to better understand the thermodynamic non-ideality of ions in polymer networks. Flory-Rehner theory was used to predict water volume fraction in the polymers equilibrated with salt solution based on salt sorption measurements.

1. Introduction

Polymer membrane-based technologies have been successfully utilized for a variety of desalination applications including reverse osmosis (RO) [1,2], forward osmosis (FO), electrodialysis (ED) [3–5], and others [6–9]. In these applications, separation of water and ions is possible because of differences in their transport rates through the membrane. The solution-diffusion model is used to describe ion transport in dense polymers [10,11]. In this model, penetrants molecularly sorb into the membrane, diffuse through the membrane, and subsequently desorb into the downstream solution [10–13]. Ion transport is, therefore, sensitive to ion sorption (or partitioning) and diffusion in polymers. This study focuses on ion sorption into hydrated uncharged polymers as a model system and baseline for understanding ion sorption and transport in more complex systems, such as charged polymers. Polymer water content and interactions between ions and polymer segments are key factors affecting ion sorption in polymers. Designing and optimizing polymer membranes for water/ion separations requires fundamental understanding of the influence of polymer structure on these factors.

Hydrophilic polymers can be broadly classified as uncharged or charged. Uncharged polymers contain hydrophilic functional groups

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(e.g., ethylene oxide or amide linkages), whereas charged polymers contain ionic groups covalently bound to the polymer backbone (e.g. sulfonic acid, quaternary ammonium, etc.). Ion sorption characteristics in charged polymers can depend strongly on Donnan exclusion (i.e., electrostatic interactions between ions and fixed charge groups), but this effect is absent in uncharged materials [14–16]. Ion sorption in uncharged polymers is often considered to follow a simple partitioning mechanism, where the ion sorption coefficient is effectively independent of external salt concentration [10,17]. However, several studies showed that salt sorption in uncharged polymers does depend to some extent on external salt concentration [13,14]. Also, the effect of ion-specific interactions between ions and polymer chains on ion sorption in uncharged polymers is not well understood [10,13,18,19].

A large majority of salt sorption studies in polymer membranes focused on sodium chloride since it is the most abundant salt in nature, accounting for more than 80% of the ions in seawater [20]. Sodium chloride sorption in polymers, however, is not necessarily representative of sorption of other ions, since charge density and hydration size of ions significantly varies depending on their chemical nature [21–23]. Several studies demonstrated that specific interactions between different ions and polymer segments vary with ion charge density, which influences an ion's hydration tendency and interactions with the polymer [24–26]. Knowledge of specific interactions between ions and polymers in aqueous solution can be used to shed light on ion sorption in dense, hydrophilic membranes due to the similarity of these two phenomena.

Cross-linked poly(ethylene glycol) diacrylate (XLPEGDA) was chosen for this study because the membrane water content can be controlled without significantly altering its chemical structure [27]. A series of XLPEGDA membranes was prepared by varying the pre-polymerization water content, resulting in films having different cross-linking densities and, therefore, different equilibrium water uptake values. Alkali metal chlorides (e.g., LiCl, NaCl, and KCl) were chosen to investigate the effect of ion charge density and hydration size on ion sorption. The interactions between polymer and ions, as well as the interactions between polymer and water, in the membranes result in non-ideal ion behavior in the membrane. Quantitative description of sorption characteristics of alkali metal chlorides in terms of activity coefficients further helps improve understanding of ion sorption in polymers. Furthermore, a classical thermodynamic theory (i.e., Flory-Rehner theory) was used to predict water volume fraction in polymers equilibrated with salt solution and compared to values obtained experimentally.

2. Experimental methods

2.1. Materials

The structure and physical properties of the polymers used in this study are presented in Table 1. XLPEGDA free standing films were prepared via UV photo-polymerization according to procedures described elsewhere [27]. Poly(ethylene glycol) diacrylate (average M_n = 700 g/mol) and 1-hydroxycyclohexyl phenyl ketone (HCPK, photoinitiator) were purchased from Sigma-Aldrich (St. Louis, MO). Three types of XLPEGDA films, each having a different equilibrium water uptake, were prepared. For XL-0, a prepolymerization mixture containing no added water was prepared by mixing PEGDA and HCPK photoinitiator. De-ionized (DI) water was added to the prepolymerization mixture at 20 wt% based on PEGDA (i.e., 0.2 g water/(g water + PEGDA)) to prepare XL-20 films and 40 wt% was added for XL-40. The HCPK concentration was 0.1 wt% based on PEGDA for all prepolymer mixtures.

The prepolymerization reaction mixture was placed between two quartz plates separated by 400 μm metal spacers and cured in a Fisher Scientific UV chamber (Model FB-UVXL-1000) under 312 nm UV irradiation for 90 s at 3.0 mW/cm^2 to obtain a solid, transparent film. The membranes were soaked and equilibrated in DI water for at least 3 days. Water was replaced several times during the soaking period to remove any unreacted components or material not bound to the polymer network. The weight of the resulting cross-linked networks (i.e., gels) was measured after drying fully washed polymers, and in all cases, approximately 99% of the weight of PEGDA before polymerization was present in the final polymers. Sodium chloride, potassium chloride, and lithium chloride were purchased from Sigma-Aldrich, and salt solutions of desired concentrations were prepared with DI water. Ultrapure DI water was generated by a Millipore RiOs and A10 water purification system (Billerica, MA). DI water generated from the Millipore system has electrical conductivity and total organic carbon (TOC) values of less than 0.055 μS/cm and 5.4 ppb, respectively. All chemicals were used as received unless noted otherwise.

2.2. Differential scanning calorimetry (DSC)

DSC measurements were performed using a TA instruments (New Castle, DE) Q1000 differential scanning calorimeter. The glass transition temperature of fully dried polymers was determined as the midpoint of the heat capacity step change, and the results are recorded in Table 1. To determine the state of water in hydrated XLPEGDA, the surface water on a fully hydrated sample was removed using paper tissue (Kimwipes), and the sample was quickly sealed in an aluminum pan. Sample weights were in the range of 5–10 mg. DSC data were collected during the first scan at a heating rate of 20 °C/min from −90 to 35 °C under a dry N_2 purge at a flow rate of 50 mL/min for both dried and hydrated samples.

2.3. Water uptake measurement

A general liquid sorption measurement method was used for pure water uptake and salt solution water uptake [13,28]. Polymer samples were cut into circular disks and immersed in either DI water or salt solutions of known concentration for at least 24 h. For salt solution water uptake measurements, the solution was changed at least 3 times to ensure that equilibrium was attained. After removing surface water with paper tissue, the wet mass of the sample, m_{wet}, was measured. Then, the polymer film was dried under vacuum at ambient temperature. The fully dried sample mass, m_{dry}, was then measured, and water uptake was calculated as follows:

$$w_u = \frac{m_{wet} - m_{dry}}{m_{dry}} \tag{1}$$

The dry polymer density and water density in swollen polymer were determined using a density kit (Part # 238490, Mettler Toledo, OH, USA) and an analytical balance (Model AG 204, Mettler Toledo, OH, USA) at 25 °C. Heptane was used as the auxiliary solvent since poly (ethylene oxide) does not have an affinity for alkanes [18]. Dried polymer density, ρ_p, was calculated as follows:

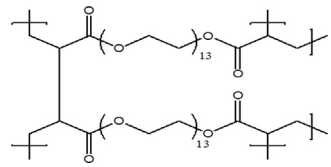
$$\rho_p = \frac{w_{air}}{w_{air} - w_{sol}}\rho_0 \tag{2}$$

where ρ_0 is the auxiliary solvent density, and w_{air} and w_{sol} are mass of the sample in air and in the auxiliary solvent, respectively. The equilibrium volume fraction of water in the hydrated polymer was estimated based on volume additivity of water and polymer as follows [29]:

$$\varphi_w = \frac{w_u}{w_u + \rho_w/\rho_p} \tag{3}$$

where ρ_w is the density of water (1.0 g/cm^3). Polymer samples prepared with different levels of prepolymerization water content have effectively the same dry polymer density, as shown in Table 1 [30].

Table 1
Properties of the materials used in this study.

	XL-0	XL-20	XL-40
Chemical name	Cross-linked poly(ethylene glycol diacrylate) [XLPEGDA] (M_n = 700)		
Structure			
Prepolymerization water content [wt.%]	0	20	40
Water uptake in de-ionized water [g(water)/g(dry polymer)]	0.500±0.008	0.674± 0.010	0.928± 0.011
Volume fraction of water in fully hydrated film	0.372± 0.004	0.441± 0.004	0.524± 0.003
Dry polymer density [g/cm^3]	1.186± 0.005	1.186± 0.005	1.186± 0.005
Dry polymer T_g [^{o}C]	−42	−42	−41
E′ [MPa]	22.7 ± 0.5	13.6 ± 0.2	8.7 ± 0.3
Crosslink density, υ_e [mmol/cm^3]	3.05	1.83	1.17
	0.839	0.770	0.703

2.4. Dynamic mechanical analysis (DMA)

DMA was performed by Q800 (TA Instruments, New Castle, DE). The polymer films were dried under vacuum at room temperature prior to measurement. Then, the dried sample was cut into rectangular shape with a dimension of approximately 6 × 20 mm. The elastic storage modulus (E') of the sample was recorded at a heating rate of 1 °C/min from −90 to 30 °C at a test frequency of 1 Hz under inert (N_2) atmosphere.

2.5. Determination of cross-link density

The elastic storage modulus (E') of the dried XLPEGDAs at the rubbery plateau from DMA was used to estimate cross-link density. The following relationship from Flory's rubber elasticity theory was used [31]:

$$\upsilon_e = \frac{E'}{3RT} \tag{4}$$

where υ_e is a cross-link density in units of mmol/cm^3, E' is the elastic storage modulus in units of Pa, R is the gas constant, and T is the temperature at which E' is determined (room temperature in this study).

2.6. Ion sorption measurement

The concentrations of ions sorbed in the polymer films were measured using a previously established technique [14]. Polymer samples equilibrated with DI water were cut into circular disks using a 35 mm diameter cutting die. Then, the polymer disks were immersed in aqueous salt solutions of desired concentration, ranging from 0.01 to 1.0 M. This concentration range is relevant for many practical applications [32]. Salt solutions were changed 2 times during the equilibration process, and the soaking time between each change was 10 times a conservative estimate of the timescale of salt sorption by the polymer (i.e., L^2/P_s, where L is the film thickness, and P_s is the salt permeability of the film) [14]. This step ensures that the samples are fully equilibrated with salt solutions of desired concentration.

Following the equilibration step, the thickness and diameter of the film was measured to determine the geometric volume of the sample, V_p. Then, surface salt solution was carefully removed with paper tissue before placing the membrane in a known volume of DI water, V_d, to desorb the salt from the film. Sufficient time was given for the desorption process, based on L^2/P_s, to reach equilibrium, which was always within 24 h for the materials considered in this study. Then, the ion concentration of the desorption solution, c_d, was determined using ion chromatography (IC, ICS-2100, Dionex Corp., Sunnyvale, CA) for anions or flame atomic absorption (flame AA) spectrophotometry (Varian AA240, Clayton South, Victoria, Australia) for cations. Chloride concentrations from IC were mainly used to calculate the salt sorption coefficients reported in this study. Since electro-neutrality must be maintained in these uncharged polymers, either cations or anions can be measured to infer the concentration of all ions in a polymer sample [14]. Flame AA was used to confirm that the cation concentration of the desorption solution was equal to the anion concentration, as it must be for the univalent salts under study. Finally, the salt sorption coefficient was calculated as [14]:

$$K_s = \frac{c_d V_d}{C_s^s V_p} = \frac{C_s^{m,p}}{C_s^s} \tag{5}$$

where $C_s^{m,p}$ is the salt concentration in the film expressed as moles of salt per liter of swollen polymer (i.e., polymer + water + salt), and C_s^s is the salt concentration in solution (moles of salt per liter of solution).

3. Results and discussion

3.1. Ion hydration and interaction with polymer chain

Ion charge density and hydration are reviewed first since these properties help explain the influence of ion-polymer interactions on ion sorption in polymers [25,33,34]. In aqueous electrolyte solutions, water molecules form hydration shells around ions by aligning their dipole moments either towards or away from the ion, depending on its charge [35]. Alkali metal ions (e.g., Li^+, Na^+, and K^+) and water molecules form coordinate bonds, where the oxygen atoms of water molecules orient toward the hydrated cation, and the hydrogen atoms orient away from the ions (cf. Fig. 1) [36,37]. For anions (e.g., F^-, Cl^-, and Br^-), the situation is reversed, with water molecules closest to the anion orienting such that one hydrogen atom is directed towards the ion and the other away from the ion [36,37]. The electrostatic influence of an ion on surrounding water molecules increases as charge density increases, resulting in stronger ion hydration. In the alkali metal ion series, where ionic charge is constant, ion charge density increases as ion crystal radius decreases (i.e., the ion charge density order is: $K^+ < Na^+ < Li^+$, cf. Table 2). Therefore, the hydrated radii of ions correlate with their charge density.

Li^+ and Na^+ are high charge density cations that bind water molecules strongly [38]. However, K^+ ions disrupt water structure adjacent to the ion and do not bind water molecules as effectively as Li^+ and Na^+ due to the lower charge density of K^+ [38]. Neutron and X-ray diffraction of alkali cations (e.g., Li^+, Na^+, and K^+) in water suggest that the distance between the ion and the oxygen on water molecules closest to the ion increases as the surface charge density of the ion

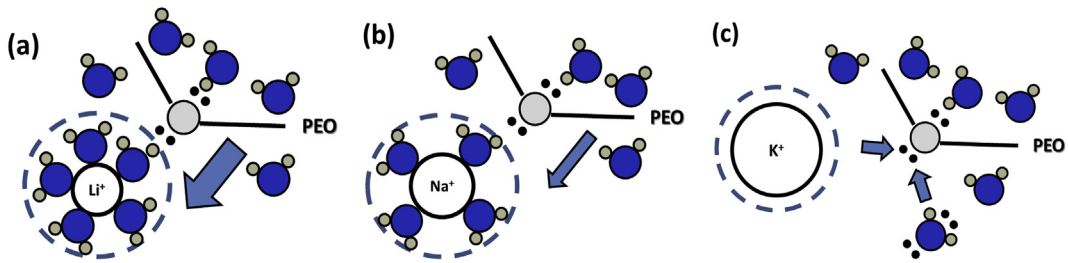


Fig. 1. Schematic of the interactions of the three alkali metal ions with water and ether groups of XLPEGDA [26,41–43]. The number of water molecules in the dashed-line circles surrounding the ions represents relative hydration number and hydrated radii of the ions. (a) Li^+ ion (strong hydration): the arrow indicates a net positive charge of a hydrated Li^+ complex attracted to polymer dipoles. (b) Na^+ ion (intermediate hydration): the arrow indicates relatively weak attraction toward polymer dipoles. (c) K^+ ion (weak hydration containing no tightly bound water): the arrow indicates direct binding to dipole moment of ether oxygen group, and competition with water molecules for binding sites.

Table 2
Properties of ions considered in this study.

Properties	Li^+	Na^+	K^+	Cl^-
Crystal Radius, r [Å] [40]	0.60	0.95	1.33	1.81
Surface area of spherical ion [Å^2] $O = 4\pi r^2$	4.52	11.3	22.2	41.2
Surface charge density [mC/cm^2] q/O[a]	0.354	0.141	0.072	0.039
Hydrated Radius [Å] [40]	3.82	3.58	3.31	3.32
Distance between ion and oxygen on nearest H_2O molecule[b] [Å] [38]	1.87	2.40	3.09	–
Electrostriction pressure [GPa] [39]	0.9	0.11	0.06	–

[a] q is the elementary charge (1.6×10^{-19} C).
[b] Oxygen-oxygen distance in bulk water is 2.82 Å [38].

decreases [36]. The strong hydration of Li^+ is indicated by a shorter Li^+-oxygen distance (1.87 Å) than that of oxygen-oxygen in bulk water. The weaker hydration of K^+ is indicated by a longer K^+-oxygen distance (3.09 Å) than that of oxygen-oxygen in bulk water (2.82 Å) [36,38]. Na^+ hydration is considered to be intermediate, where the Na^+-oxygen distance (2.40 Å) is longer than that of Li^+-oxygen but shorter than the oxygen-oxygen distance in bulk water (cf. Table 2) [36,38]. These observations are supported by reports of electrostriction pressure values (cf. Table 2), which characterizes the degree of rearrangement of water molecules towards the center of a hydrated ion due to the electrostatic force that the ion exerts on surrounding water molecules. The higher electrostriction pressure of Li^+ suggests stronger hydration of Li^+ relative to that of Na^+ or K^+ [39].

Interactions between ions and polar groups on a polymer chain depend on the ion charge density as well. Based on literature data, a schematic diagram of interactions between hydrated alkali metal ions and ether oxygen groups in XLPEGDA polymers is shown in Fig. 1 [26,41–43]. Small, high charge density ions (e.g., Li^+ and Na^+) tightly bind water molecules in their hydration shell, interacting with the polar groups of polymers via perturbation of hydrogen bonding, as shown in Fig. 1(a)–(b) [41–43]. The net positive charge of these ions is maintained after forming hydration complexes, so the ions are attracted to lone pair electrons on the ether oxygen of the polymer chain [26,43]. Large ions with low charge density, such as K^+ in this study, do not have strongly bound hydration layers, enabling them to interact directly with polar groups on the polymer chain (cf. Fig. 1(c)) [26,38]. Due to these direct interactions, ions with low charge density may compete with water molecules for binding sites on polymer chains [26]. These interactions of ions with uncharged polymers in aqueous solutions have been observed via NMR [44,45]. Experimental observations, such as water uptake and ion sorption in alkali metal chloride solutions in this study, will be discussed based on this proposed interaction mechanism.

3.2. State of water in XLPEGDA polymers

Properties of XLPEGDA polymers containing different water uptake values are shown in Table 1. As prepolymerization water content varies from 0 to 20 and 40, pure water uptake increases from 0.50 to 0.67 and 0.93, respectively. DSC measurements of the polymers equilibrated with water provide information regarding the interaction of the polymer with water and the state of water in the polymers [46,47]. The intermolecular interactions between water molecules can be disturbed by interactions with polymer chains. Water molecules that tightly bind to a polymer chain cannot undergo a transition to the solid state, and, as a result, do not release a heat of fusion. Water molecules that are not associated with the polymer chain exhibit a sharp melting peak at 0 °C, which is analogous to bulk water. Between tightly bound water and free water in hydrated polymers, loosely bound water exists, interacting with non-freezing water. These water molecules can exhibit a relatively broad endothermic peak near 0 °C [46,48].

Fig. 2 shows DSC curves of a series of XLPEGDA polymers equilibrated with water. XL-0 exhibits no peak around 0 °C, indicating that water molecules in this polymer are tightly bound to the polymer chains [46]. XL-20 displays a broad endothermic peak slightly below 0 °C, which indicates the presence of loosely bound water [46,47]. The combination of a sharp peak near 0 °C and a broad peak below 0 °C is observed for XL-40, suggesting co-existence of free and loosely bound water in this polymer [46,47]. These results show how water clusters in hydrated polymers develop as cross-link density decreases. In XL-0, polymer hydration presumably occurs primarily on hydrophilic functional groups, such as the ether oxygen in these polymers. Loosely bound water in XL-20 is associated with non-freezing water and interacts weakly with the ether oxygen. Additionally, a hydrogen bonded complex between water molecules, similar to that in bulk water, is observed in XL-40.

Previous studies suggest that the ethylene oxide (EO) units are the loci of hydration in PEG [49,50]. Therefore, the number of water molecules associated with each EO unit in a series of XLPEGDA polymers can be calculated based on pure water uptake measurement. In the polymers considered in this study, the number of water molecules per EO unit decreases from 2.8 to 2.0 to 1.5 as polymer cross-link density increases. In the cases of XL-0 and XL-20, water molecules are mostly bound to the polymer chains, and free water is only observed in XL-40.

3.3. Salt water uptake in XLPEGDA polymers

Fig. 3(a) presents equilibrium water uptake as a function of alkali chloride concentration in the external solution for the materials considered here. Water uptake generally decreases as external salt concentration increases. This result can be explained by the effect of salt on the activity of water in the external solution. Water activity in aqueous alkali metal chloride solutions was calculated using the Pitzer model [51,52]. As shown in Fig. 3(b), the thermodynamic activity of water

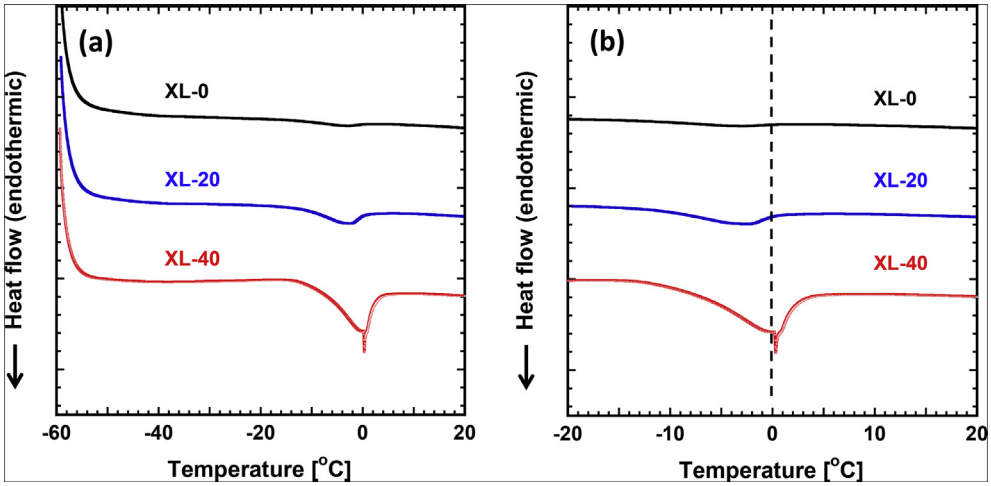


Fig. 2. First scan differential scanning calorimetry thermograms of hydrated XLPEGDA polymers: (a) in the entire temperature range between −60 °C and 20 °C and (b) between −20 °C and 20 °C. The scan rate was 20 °C/min.

decreases as salt concentration increases over the ranges considered in this study. Consequently, the membranes sorb less water as water activity in the external solution decreases (cf. Fig. 3(c)). This phenomenon is often called osmotic de-swelling [15].

The extent of osmotic de-swelling depends on the polymer cross-link density. As shown in Fig. 3(a), the magnitude of osmotic de-swelling increases as prepolymerization water content increases. The increased amount of water in the prepolymer mixture increases the probability of forming wasted cross-links (i.e., cross-link loops), which, in turn, reduces the effective cross-link density of the polymer (cf. Table 1) [27]. Therefore, XL-40 has a lower cross-link density than XL-20 and XL-0, resulting in a higher degree of osmotic de-swelling at higher salt concentrations. For example, the water uptake difference between 0.01 and 1.0 M NaCl solution for XL-0 is 0.06 g water/g dry polymer, whereas that for XL-40 is 0.12 g water/g dry polymer.

At low salt concentrations (i.e., 0.01–0.1 M), only slight differences are observed in the amount of water sorbed by the polymer depending on the type of salt solution. Ion specific swelling becomes apparent at higher concentrations (i.e., 0.3–1.0 M). The order of water uptake in this series of XLPEGDA polymers is: LiCl > NaCl ≥ KCl. Since the alkali metal chloride solutions have a common anion (i.e., Cl^-), any water uptake differences among these solutions can be attributed to the cations. The charge density of the cations considered in this study follows the order: Li^+ > Na^+ > K^+ [35]. A correlation between polymer swelling in aqueous salt solutions and ion charge density in the solution is widely reported in the literature [25,26,42,53]. Ions with higher charge density (e.g., Li^+) bring more water molecules into the polymer matrix, whereas ions with lower charge density (e.g., K^+) carry fewer water molecules, which results in varying polymer water uptake in different salt solutions. Similarly, salt water uptake correlates with ion charge density at higher external salt solution concentrations.

3.4. Ion sorption in XLPEGDA polymers

LiCl, NaCl, and KCl concentrations in a series of XLPEGDA polymers were measured using the desorption technique described previously. Because these polymers do not contain fixed charges, cation and anion concentrations are equal in the membrane due to electro-neutrality. Also, all ions sorbed into the membrane can be extracted into initially deionized water by the desorption procedure [14]. The molar concentrations of cations and anions in a series of XLPEGDA polymers were effectively equal to each other, and the detailed data are presented in the Supplementary Material. Therefore, the desorption solution can be analyzed for either cations or anions to determine the sorbed salt concentration in the membrane.

LiCl, NaCl, and KCl sorption coefficient isotherms in XLPEGDA polymers are presented in Fig. 4. Interestingly, the order of the salt sorption coefficients changes as polymer water uptake increases. For example, the location of the LiCl sorption coefficients relative to those of NaCl and KCl changes significantly with water uptake. In XL-0, which has the lowest water content among the polymers considered here (i.e., 0.50 g water/g dry polymer, Fig. 4(a)), the order of salt sorption is: KCl > LiCl > NaCl. In XL-20 (cf. Fig. 4(b)), whose water uptake is 0.67 g water/g dry polymer, the LiCl sorption coefficient is lower than that of KCl at < 0.5 M external salt concentrations. But this order is reversed at 0.7 M or higher external salt concentrations. In XL-40

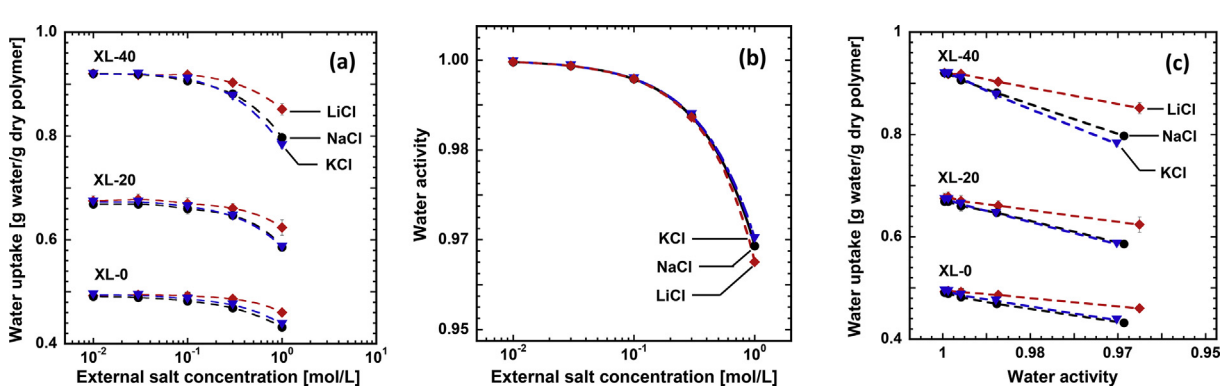


Fig. 3. (a) Influence of external salt concentration on water uptake in a series of XLPEGDA polymers. (b) Water activity in aqueous alkali metal chloride solutions. (c) Water uptake as a function of water activity. The dashed lines are drawn to guide the eyes.

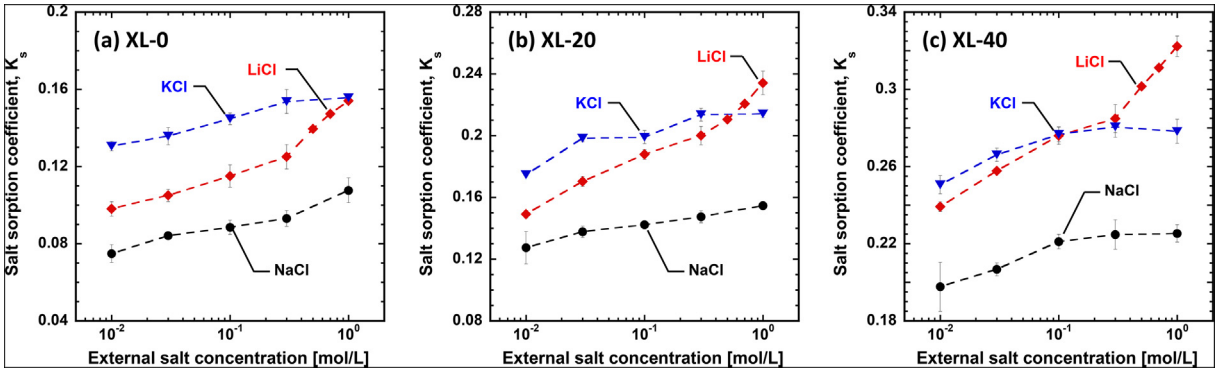


Fig. 4. Salt sorption coefficient, K_s, of alkali metal chlorides as a function of external salt concentration in: (a) XL-0, (b) XL-20, and (c) XL-40. K_s is defined as $C_s^{m,p}/C_s^s$, where $C_s^{m,p}$ is moles of sorbed salt in the polymer per liter of swollen polymer and C_s^s is moles of salt per liter of solution. The dashed lines were drawn to guide the eye. Experimental uncertainties are reported as the standard deviations of at least six measurements.

(0.93 g water/g dry polymer, Fig. 4(c)), the LiCl sorption coefficient is slightly lower than that of KCl at < 0.1 M external salt concentration. This order is reversed at > 0.3 M external salt concentration.

Simply relating the size of the hydrated cation to the magnitude of salt sorption is unable to provide a proper explanation for the order of salt sorption coefficients observed in this study. Yasuda et al. suggested that a polymer's ability to sorb salt is highly limited in the absence of water [13]. Yasuda's model assumes that all salt in the membrane phase is solvated by the water in the membrane phase. According to this model, direct interactions between polymer chains and ions are limited in membranes with higher water uptake since water molecules form cluster at or near polymer chains. As the membrane water content decreases, however, increasing polymer/water and polymer/ion interactions may induce highly non-ideal behavior of ions in the membrane, which, in turn, affect ion sorption. Lobo et al. and others reported changes in the order of sorption of different salts as polymer water content varied [54–57]. Among the polymers considered in this study, only XL-40 contains free water. XL-20 and XL-0 contain bound and/or non-freezing water. Thus, these polymers are considered to have low or moderate water contents, where polymer/ion and polymer/water interactions presumably affect the sorption of different salts.

Hydration of XLPEGDA is presumed to occur mainly near the polar ether oxygen groups. Hydrogen bonds form between the lone-pair electrons on the ether oxygen groups and the protons of water molecules. This hydrogen-bonding hydration is largely influenced by the presence of solutes in solution, such as cations and anions [58]. Given that LiCl, NaCl, and KCl share Cl^-, which is a large, low-charge density ion that binds water molecules weakly, the sorption of alkali chlorides are largely influenced by the cations [35,41,44]. Sorption of Li^+ and Na^+ in XLPEGDA polymers may be explained by an enhancement of electron pair acceptance (EPA) of coordinated water molecules (cf. Fig. 1(a)–(b)) [34,42,58]. The partial transfer of positive charge from the lithium ion to the hydrogen atoms of coordinated water molecules leads to a decrease in net charge at the lithium ion, but results in an increased net positive charge at each of the hydrogen atoms [26,58]. Consequently, hydrogen bonds between Li^+-coordinated water molecules and ether oxygen groups in XLPEGDA chains are stronger than those between hydrogen atoms in bulk water and ether oxygen groups in XLPEGDA [58]. Therefore, for a given external salt concentration, salt sorption coefficients of LiCl are higher than those of NaCl, despite the higher hydrated size of Li^+. The hydrogen atoms coordinating Na^+ are also more prone to accept electron pairs than those in bulk water, but the net positive charge of hydrated Na^+ is smaller than that of hydrated Li^+ [38].

K^+ is a large, relatively low-charge density cation which can directly interact with polar groups in XLPEGDA due to its weak ion hydration (cf. Fig. 1(c)) [26,41]. Water molecules near K^+ ions preferentially form a bulk water-like structure rather than coordinating with K^+ and the polymer, resulting in direct binding between ether oxygen groups in the polymer and K^+ ions (cf. Fig. 1) [26,41]. In a study of alkali chloride binding to poly(ethylene oxide) in aqueous solution, Sartori et al. observed that the binding constant of potassium ions to ethylene oxide is considerably higher than those of sodium and lithium ions [59]. This result supports the observations in the present study, namely that KCl sorption in XLPEGDA is higher than LiCl and NaCl sorption at a given external salt concentration.

3.5. Mean activity coefficients of salt in XLPEGDA polymers

At equilibrium, the electrochemical potential of an ion in a polymer membrane and in the contiguous external solution must be equal [60]. The ion electrochemical potential consists of activity, electrical potential, and hydrostatic pressure terms. Assuming the electrical potential of a phase is constant and the hydrostatic pressures in membrane and solution phases are equal, the electrochemical potential of an ion can be expressed by ion activities in the membrane and in the external solution. The detailed derivation can be found elsewhere [61]. For an uncharged membrane equilibrated with alkali metal chlorides (i.e., the valences of cations and anions are +1 and − 1, respectively), this relation can be expressed as follows:

$$a_+^m a_-^m = a_+^s a_-^s \tag{6}$$

where a represents activity, subscripts "+" and "–" represent cations (i.e., Li^+, Na^+, and K^+) and anions (i.e., Cl^-), respectively, and superscripts "m" and "s" represent membrane phase and solution phase, respectively. Activity is, by definition, the product of an activity coefficient and concentration, which converts Eqn. (6) to the following expression [60]:

$$(\gamma_+^m C_+^m)(\gamma_-^m C_-^m) = (\gamma_+^s C_+^s)(\gamma_-^s C_-^s) = (\gamma_\pm^s)^2 (C_s^s)^2 \tag{7}$$

where γ represents activity coefficient, C represent concentration, and subscript "±" represents the mean value of cations and anions. For an uncharged polymer, the concentration of cations is equal to the concentration of anions in the membrane phase, so $C_s^m = C_+^m = C_-^m$. The mean activity coefficient of a monovalent electrolyte in the membrane phase is defined as $\gamma_\pm^m = \sqrt{\gamma_+^m \gamma_-^m}$ [62]. Rearranging Eqn. (7) yields:

$$\gamma_\pm^m = \gamma_\pm^s \frac{C_s^s}{C_s^m} \tag{8}$$

The salt concentration in the membrane phase, C_s^m was determined from salt sorption experiments. The mean activity coefficient of the electrolyte in solution, $\gamma_\pm^s$, was determined from the Pitzer model [51,52].

Fig. 5(a) shows activity coefficients for the three salts used in this study as a function of concentration up to the point beyond which the Pitzer model is not valid (5.3 M for LiCl) or up to the solubility limit

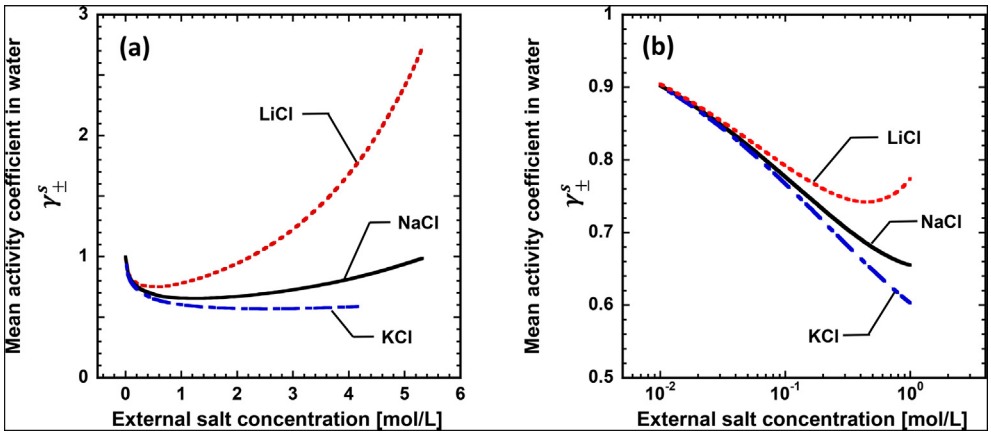


Fig. 5. (a) Mean activity coefficients of LiCl, NaCl, and KCl in water as a function of molar concentration up to the point beyond which the Pitzer model is not valid (5.3 mol/L for LiCl) or up to the solubility limit (5.3 M for NaCl and 4.2 M for KCl) [35]. (b) Mean activity coefficients of LiCl, NaCl, and KCl in water over the concentration range considered in this study [62].

(5.3 M for NaCl and 4.2 M for KCl) [52,63]. Interestingly, the activity coefficient of LiCl in water develops an upward curvature at the same salt concentration (~0.5 M) where the slope of LiCl sorption coefficient in a series of XLPEGDA polymers changes (cf. Fig. 4). As shown in Fig. 4, the salt sorption coefficient of LiCl increases rather linearly on a semi-log plot from 0.01 to 0.3 M, but the slope becomes steeper between 0.3 and 1.0 M. This correspondence between the two concentration ranges strongly suggests that salt sorption behavior in these hydrated polymers is influenced by salt activity coefficients in the external solution. This phenomenon is not observed in NaCl sorption in polymers because, presumably, the upturn of the NaCl activity coefficient in aqueous solution (cf. Fig. 5(a) and (b)) is not as sharp as that of LiCl and occurs at higher concentration (i.e., ~2.0 M).

The mean activity coefficients of salt in water calculated by the Pitzer model and experimentally determined ion concentrations in the membrane were used to obtain the mean activity coefficients of salt in the membrane, $\gamma_{\pm}^{m}$, using Eqn. (8). The concentration of salt in the polymer can be defined in at least two ways when calculating $\gamma_{\pm}^{m}$. One is based on total swollen polymer volume (i.e., polymer + water + ions), mols salt/(liter of swollen polymer), $C_s^{m,p}$, and the other is based on volume of water sorbed in the swollen polymer, mols salt/(liter of sorbed water), $C_s^{m,w}$. Experimentally determined salt concentration described in the salt sorption measurement procedure is based on total swollen polymer volume. The water volume fraction data were then used to calculate the salt concentration in the membrane based on water in the swollen polymer as follows [61]:

$$C_s^{m,w} = \frac{C_s^{m,p}}{\varphi_w} \tag{9}$$

For comparison, the mean activity coefficients of NaCl in XL-0 calculated using these two bases are shown in Fig. 6. Depending on volume references, salt concentration as well as mean activity coefficients values in the polymer change. Either concentration choice is acceptable, and the trend is qualitatively similar for both volume references. However, defining the concentration of salt based on the volume of water in the swollen polymer is more appropriate for describing equilibrium phenomenon since the system volume of water should be chosen for both phases to have the same standard reference state [64]. Therefore, subsequent analysis of the membrane activity coefficient will be based on water volume in the swollen polymer, and values for $\gamma_{\pm}^{m}$ and $C_s^{m,p}$ based on total swollen membrane are presented in the Supplementary Material.

Fig. 7 presents the mean activity coefficients of LiCl, NaCl, and KCl in a series of XLPEGDA polymers as a function of external salt concentration. In all cases, the mean activity coefficients in the membrane are greater than 1. Activity coefficient values being greater than 1 mean that ions thermodynamically prefer to partition into the external salt solution than into the membrane [35]. That is, uncharged XLPEGDA

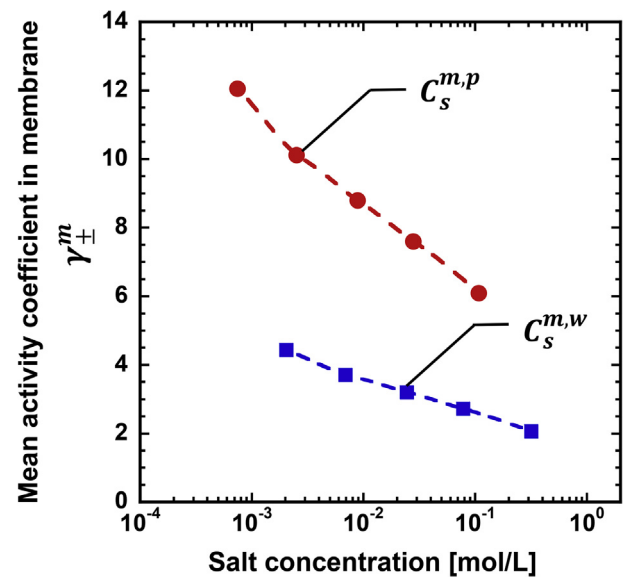


Fig. 6. Mean activity coefficients of NaCl in XL-0 as a function of salt concentration in the membrane based on swollen polymer volume, $C_s^{m,p}$, and based on the volume of water in the swollen polymer, $C_s^{m,w}$. The dashed lines were drawn to guide the eye.

polymers provide a less favorable environment for ions than the external solution phase. The salt mean activity coefficients decrease as water volume fraction in the hydrated polymers increases in all cases. More water in the hydrated polymer results in an environment more favorable for ion partitioning, as indicated by lower ion activity coefficients in XL-40 than in XL-20 and lower activity coefficients in XL-20 than in XL-0. Thus, ions interact relatively more favorably with higher water content membranes, resulting in reduced mean activity coefficients.

The relative order of mean activity coefficient in all three polymers is: NaCl > LiCl > KCl, which is consistent with the proposed interaction mechanism (cf. Fig. 1), where the weakest interactions are those between Na^+ ions and the polymer, which results in NaCl having the highest activity coefficients among the three salts. The mean activity coefficients of salts decrease as external salt concentration increases. Relatively speaking, salt partitioning at higher external salt concentration is energetically more favorable than salt partitioning at lower external salt concentration.

3.6. χ parameter determination and water volume fraction modeling

The value of the Flory-Huggins interaction parameter (i.e., χ) is sensitive to polymer concentration and the measurement methods used

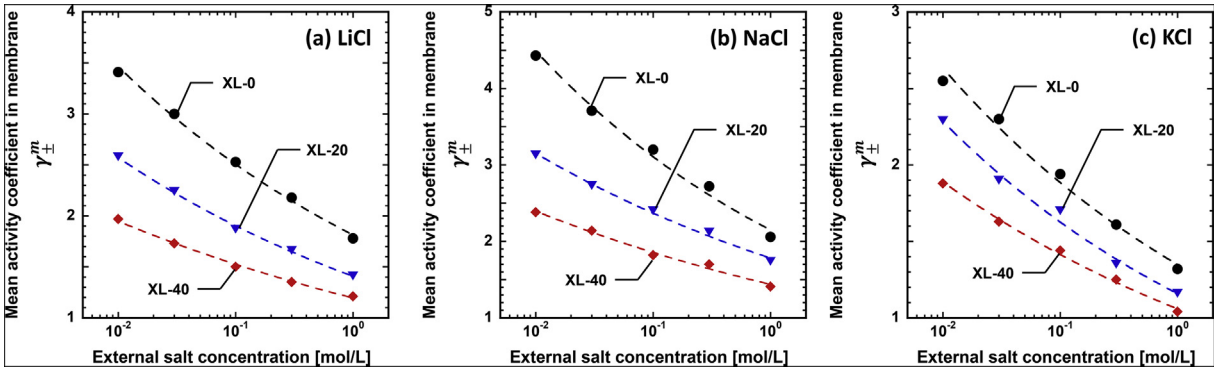


Fig. 7. Mean activity coefficients of alkali metal chlorides as a function of external salt concentration for: (a) LiCl, (b) NaCl, and (c) KCl. The mean activity coefficient is calculated based on the volume of water in the swollen polymer, $C_s^{m,w}$. The dashed lines were drawn to guide the eye.

to determine it. In previous studies, the χ value of linear poly(ethylene oxide) (PEO) in water was applied to cross-linked PEO/water systems [27,65]. The χ values for solution of linear PEO/water reported in the literature are 0.426 or 0.45, and these values are measured for polymer volume fractions from 0.04 to 0.2 [66,67]. It is well known that the χ value is a function of volume fraction polymer [31,68]. The polymers considered in this study have polymer volume fractions of 0.5–0.65 when equilibrated with water [66,67]. In addition, XLPEGDA contains approximately 18 wt% of ethyl-ester groups that may influence polymer-water interactions. Therefore, using the χ values for linear PEO/water may not be appropriate for this study.

In this study, we use rubber elasticity theory to estimate cross-link density, and combine this result with equilibrium water swelling data to determine χ [27,69]. This approach assumes that the cross-link density estimated from mechanical tests is consistent with that obtained from water swelling studies. Some literature reports that polymer chain disentanglement during mechanical testing, which is absent in solvent swelling studies, induces a discrepancy between the two methods [70]. However, DMA may minimize polymer chain deformation during modulus measurements, where the sample responds to deformation only by conformational changes without bending or breaking of bonds [69]. In this case, the tensile storage modulus, E', at the rubbery plateau has a relationship with cross-link density, v_e, as shown in Eqn. (4) ($v_e = E'/3RT$).

Equilibrium solvent swelling of a cross-linked polymer network can be described by Flory-Rehner theory. In Eqn. (10), the terms on the left-hand side represent the mixing free energy of the polymer network and the solvent, and the terms on the right-hand side describe the change in the elastic free energy due to polymer network swelling [31].

$$-\left[ln(1-\varphi_{p2}) + \varphi_{p2} + \chi\varphi_{p2}^2\right] = v_e V_w \left[\left(\frac{\varphi_{p2}}{\varphi_{p1}}\right)^{1/3} - \frac{1}{2}\left(\frac{\varphi_{p2}}{\varphi_{p1}}\right)\right] \tag{10}$$

where V_w is the molar volume of water (18 cm^3/mol), φ_{p1} and φ_{p2} are the polymer volume fractions of the hydrogel in the relaxed (i.e., before being swollen in water) and swollen states (i.e., when equilibrated in water), respectively. φ_{p1} was approximated as the volume fraction of PEGDA in the prepolymerization mixture and φ_{p2} was determined by equilibrium water uptake experiments [27].

The χ values obtained using this method were 0.839, 0.770, and 0.703 for XL-0, XL-20, and XL-40, respectively. These χ values are greater than the values reported for linear PEO/water systems, presumably, due to different polymer volume fractions between the two systems [66,67]. Additionally, hydrophobic ethyl ester linkages in XLPEGDA would also contribute to increasing the value compared to linear PEO. The χ values for XLPEGDAs with different cross-link densities considered in this study are somewhat different despite similar chemical compositions. This result can also be attributed to the difference in polymer volume fraction in each polymer.

The change in the chemical potential of water in the membrane, μ_w^m, equilibrated with electrolyte solution can be described by three terms, which represent the changes due to the mixing of polymer and water, $(\Delta\mu_w^m)_p$, to mixing with the ionic constituents, $(\Delta\mu_w^m)_i$, and to the elastic deformation of the network, $(\Delta\mu_w^m)_{el}$ [31]:

$$\mu_w^m - \mu_w^0 = (\Delta\mu_w^m)_p + (\Delta\mu_w^m)_i + (\Delta\mu_w^m)_{el} \tag{11}$$

where μ_w^0 is the standard state chemical potential of water. At equilibrium, the chemical potential of water in the membrane must be equal to that in the external solution (i.e. $\mu_w^m = \mu_w^s$). Using this relation and defining $(\Delta\mu_w^s)_i$ as $\mu_w^s - \mu_w^0$, we can rearrange Eqn. (11) as follows:

$$(\Delta\mu_w^s)_i - (\Delta\mu_w^m)_i = (\Delta\mu_w^m)_p + (\Delta\mu_w^m)_{el} \tag{12}$$

where the terms on the right hand side are given in Eqn. (10). Generally, the chemical potential change of water in solution is written as [31]:

$$(\Delta\mu_w^s)_i = \mu_w^s - \mu_w^0 = gRTlnN_w^s \tag{13}$$

where g is the osmotic coefficient, and N_w^s is the mole fraction of water in the solution. The osmotic coefficient in the external solution is calculated from the Pitzer model [51,52], and the osmotic coefficient in the membrane is approximated as 1 since the salt concentration in the membrane is dilute [31]. Within the salt concentration range considered in this study, the relation $lnN_w^s \cong -V_w \sum_j C_j^s$ is valid, where the summation is over all ionic species. Then, we can write

$$(\Delta\mu_w^s)_i \cong -V_w gRT \sum_j C_j^s \tag{14}$$

Similarly, the chemical potential change from the mixing with the ionic constituents, $(\Delta\mu_w^m)_i$, is [31].

$$(\Delta\mu_w^m)_i \cong -V_w RT \sum_j C_j^m \tag{15}$$

Combining these expressions with Eqn. (10) in Eqn. (12) yields [31].

$$RT\sum_j (gC_j^s - C_j^m) = \frac{RT}{V_w}\left[ln(1-\varphi_{p2}) + \varphi_{p2} + \chi\varphi_{p2}^2\right] - RTv_e\left[\left(\frac{\varphi_{p2}}{\varphi_{p1}}\right)^{1/3} - \frac{1}{2}\left(\frac{\varphi_{p2}}{\varphi_{p1}}\right)\right] \tag{16}$$

Eqn. (16) was solved numerically using Mathematica to calculate the polymer volume fraction in the membrane, φ_{p2}, as a function of external salt concentration for given values of g, C_j^s, C_j^m, χ, and v_e. The resulting polymer volume fractions are converted to water volume fractions (i.e., $\varphi_w = 1 - \varphi_{p2}$) and presented as a function of external salt concentration in Fig. 8 along with the experimental data.

Reasonable agreement is observed between the values obtained by

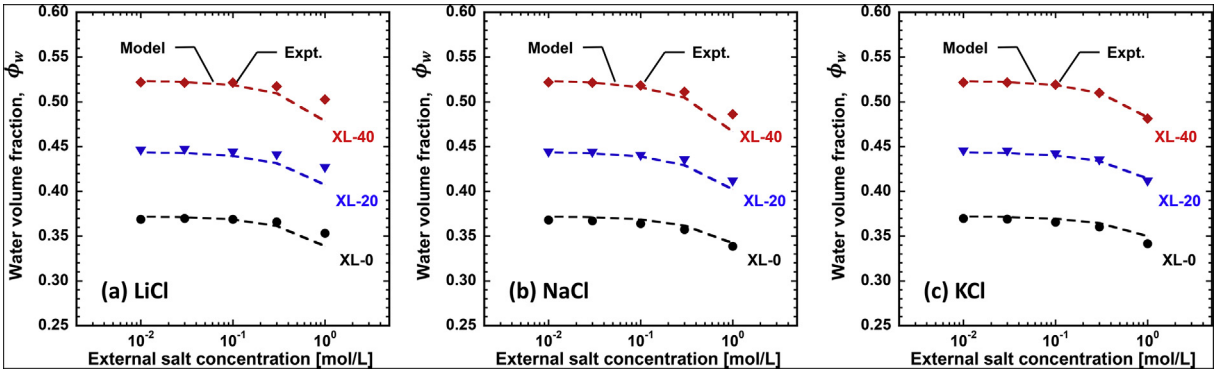


Fig. 8. Water volume fraction in XLPEGDA polymers as a function of external salt concentration for: (a) LiCl, (b) NaCl, and (c) KCl. The symbols are experimentally obtained values (XL-0 (black ●), XL-20 (blue ■), and XL-40 (red ♦)) and the dashed lines are model predictions from Eqn. (16).

the approach described above and those obtained experimentally. The decrease in water volume fraction at high salt concentrations (i.e., 0.3 and 1.0 M) as the cross-link density of the polymer decreases is captured by the model. Presumably, this result suggests that the χ values obtained by the approach described above are reasonable. Some ion specific deviations, however, are observed at high external concentrations. For example, the agreement between the model and experimental data for KCl is very good, whereas LiCl shows greater deviations. Further study is needed to better understand the origin of this discrepancy.

4. Conclusions

Uncharged XLPEGDA polymers having different water contents were synthesized and their sorption properties were characterized with alkali metal chloride solutions. The state of water in these polymers varies as cross-link density changes. A good correlation exists between the water content and membrane salt sorption properties, where increased membrane water content leads to increased salt sorption. Increasing water content of the polymer induces more favorable partitioning of salt as shown by decreasing salt activity coefficients in the polymers. The order of salt sorption in these of XLPEGDA polymers was: KCl > LiCl > NaCl, which was influenced by ion hydration and polymer-ion specific interactions. The unusual sorption isotherm of LiCl arises from an increasing LiCl activity coefficient in the external solution at high concentrations. The activity coefficients of all salts in the membranes were greater than 1, so ions prefer partitioning in aqueous solution than in these uncharged XLPEGDA polymers. The Flory-Huggins interaction parameter and cross-link density were estimated using dynamic mechanical analysis and rubber elasticity theory. Using these values in the Flory-Rehner theory gave reasonable agreement between the experimental and model water volume fraction values over the range of external salt concentration considered in this study (i.e., 0.01–1.0 M), but some observed deviations require further studies.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.polymer.2019.121554.

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