Application of counter-ion condensation in calculating the ion activity coefficients for interpreting the membrane selectivity

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Abstract

The transport selectivity of different cations through cation exchange membranes (CEMs) could be estimated with the partition coefficient (K_j^i) and the cation mobility ratio in the membrane (u_m^i/u_m^j), which in turn can be related to corresponding membrane conductivity and dimensional swelling degree data [*Journal of Membrane Science*, 2020, 597, 117645]. This method has been validated in two hydrocarbon-based CEMs, and the obtained K^+/Na^+ selectivity equals to the one obtained with conventional electrodialysis (ED) method. However, the K^+/Na^+ selectivity of perfluorosulfonic acid (PFSA) membranes, and the bi-/monovalent cation (Mg^{2+}/Na^+) selectivity of all three types of CEMs estimated with this ionic conductivity experimental approach deviate noticeably from corresponding values obtained with ED. In this work, it is proved that this deviation is mostly due to the simplification of cation activity coefficients in the membrane. Here, the cation activity coefficients in three types of CEMs are calculated according to Manning's counter-ion condensation model. In this model, the Manning parameter (ξ) characterizing the dimensionless linear charge density is determined by the

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1 average distance between two adjacent fixed sulfonate groups (b) and the permittivity of hydrated
2 membranes (ϵ). In hydrocarbon-based CEMs, the average distance between fixed sulfonate groups
3 can be estimated by assuming homogeneous distribution of the fixed groups, while in PFSA
4 membranes three representative structure models are employed to estimate this average distance.
5 After accounting for the cation activity coefficients in the membrane, the cation transport selectivity
6 obtained with the ionic conductivity experimental approach agrees well with the selectivity obtained
7 with the ED method. This work shows the importance of cation activity coefficients in the membrane
8 phase in interpreting the membrane transport properties, and complements the proposed
9 conductivity approach to characterize the counter-ion selectivity of ion exchange membranes.

10 **Keywords:** cation exchange membrane, activity coefficient, selectivity, counter-ion condensation,
11 structure models of perfluorosulfonic acid membranes

1. Introduction

The transport characteristics of ions in ionomers and/or polyelectrolyte systems is interesting and also important [1]. Such systems can be seen in the biological field like the delicate sodium/potassium ion pump in cell membranes [2], and also can be witnessed in the artificial world including the synthetic ion exchange membranes (IEMs) [3, 4]. Though the ability of IEMs to control ion transport is not as perfect as their biological archetype in the cell membrane of living organisms, IEMs can still achieve ion transport selectivity at two levels [5]: 1. facilitate the transport of counter-ions while block the transport of co-ions (that bear the same sign of charge as the membrane fixed charges) [6]; 2. achieve partial fractionation between counter-ions of different valences [7, 8]. These two properties have already popularized IEMs in diverse applications for the water – energy nexus [9-11], for example redox flow batteries for the renewable energy storage. Therefore, further study of ion transport characteristics in such IEMs is definitely required to help reach the realm of perfect ion transport selectivity in synthetic membranes.

Study of ion transport in IEMs relies on experimental methods to characterize the ion transport selectivity [10, 12]. First of all, these methods shall be reliable, then ideally be convenient and swift. For the counter-/co-ion permselectivity of IEMs, extensive research efforts in the past have suggested the membrane potential method as a routine characterization method [5, 13]. For the selectivity of IEMs towards different counter-ions, a subject not fully studied yet, both electrodialysis (ED) [7, 8, 14] and the bi-ionic potential method [15] can be considered, with the former being the benchmark technique. As summarized in a recent review [10], ED is time-consuming and requires dedicated set-ups, and the bi-ionic potential method is not so popular though it is actually an easy estimation method. Alternatively, in a previous contribution [16] we propose that the membrane conductivity and dimensional swelling degree can predict the counter-ion selectivity of IEMs, by assuming linear dependence of membrane conductivity on the equivalent counter-ion composition in the membrane [17]. This new method will be referred as the ionic conductivity experimental approach in following discussions. The key idea of this method is to decouple the transport selectivity of two counter-ions into two parts: the partition selectivity between the membrane and contiguous aqueous solutions (K_j^i), and the mobility ratio of counter-ions in the membrane phase (u_i^m/u_j^m). The latter part

can be calculated from the ionic conductivity of membranes at corresponding counter-ion forms. While the former part, the partition selectivity, can also be obtained from the ionic membrane conductivity when the membrane is in equilibrium with a solution of two different types of counter-ions with a known equivalence ratio. Though this new method has been validated in two hydrocarbon-based cation exchange membranes (CEMs) for K^+/Na^+ transport, it is observed that the K^+/Na^+ mobility ratio in one perfluorosulfonic acid (PFSA) membrane and the Mg^{2+}/Na^+ mobility ratio in all the three types of CEMs are underestimated by this ionic conductivity experimental approach [16]. This underestimation of ion mobility ratio is very likely due to the simplification of cation activity in CEMs, which of course needs to be confirmed.

The ion activity, instead of ion concentration, is used to reflect the non-ideal behavior of ions in electrolyte solutions. The deviation of ion activity from ion concentration is quantified through the ion activity coefficient [18]. This is important for interpreting both the thermodynamic (ion partition) and kinetic (ion transport) properties of IEMs [19]. Even though swollen IEMs can be approximated as concentrated polyelectrolyte solutions [20], however, as compared to extensive study and theoretical frameworks for the ion activity coefficient in electrolyte solutions, there is much less research focused on ion activity coefficient in IEMs. Back in the 1950s, Mackie and Meares [21] applied the theory of Katchalsky and Lifson originally developed for polyelectrolyte solutions [22, 23] in one type of CEM, their theoretical results agreed well with experimental ion activity coefficients. However, with a similar approach, the results of Lakshminarayanaiah led to an opposite conclusion on the same type of CEM [24]. Shortly later, Gregor and his co-workers proposed a new model for the ion activity coefficient in IEMs [20], however this model found limited penetration in the field possibly due to its complexity. A significant advancement on this topic comes very recently. Kamcev and Freeman et al. adopted Manning's counter-ion condensation theory that was also originally for polyelectrolyte solutions in the calculation of ion activity coefficients in IEMs [25-32]. Without adjustable parameters, Manning's counter-ion condensation theory could predict both the magnitude and variation trend of ion activity coefficients as a function of the salt concentration in external solutions [26]. This approach has been applied in several hydrocarbon-based CEMs and anion exchange membranes (AEMs) for interpreting the ion partition [33], ion (especially co-ion) transport nicely [27, 28, 31, 34, 35]. The validity of this approach in another considerably different, yet important class of CEMs – PFSA

membranes (for example Nafion) – remains to be checked [36]. There are already a few literature reports that claim a large portion of protons (72 ~ 98%) in Nafion 117 equilibrating with pure water are condensed [37], though the conclusion is at question due to simplification of cation activity coefficient both in the membrane and in the solutions to be 1. A very recent work reports experimental evidence revealing similar condensation of counter-ions in Nafion membranes [38], which makes the application of Manning's counter-ion condensation theory in PFSA membranes quite interesting. Besides Manning's counter-ion condensation theory, for IEMs of low water contents (therefore small relative dielectric constants of hydrated membranes), Freger recently proposes a unified model that aims to describe the ion association between mobile ions and fixed charge groups within a charged membrane [39]. This seems an interesting step towards predictive modeling of ion transport in charged membranes, yet some necessary parameters that shall be determined by experiments are not available at the moment.

In this work, the objective is to apply the Manning's counter-ion condensation theory for the calculation of cation activity coefficients in not only hydrocarbon-based CEMs, but also in PFSA membranes. Further, the inclusion of these cation activity coefficients in the proposed ionic conductivity experimental approach for the characterization of counter-ion transport selectivity in CEMs can testify whether the previously observed underestimation of cation mobility ratio in CEMs is due to the simplification of the cation activity. On one hand, this work can complement the proposed ionic conductivity experimental approach as a potentially reliable, swift and convenient approach for the counter-ion transport selectivity characterization. On the other hand, it is attempted in such a first trial to test the feasibility of applying the counter-ion condensation theory in PFSA membranes. It is necessary to note that the Manning's counter-ion condensation framework is based purely on electrostatic interactions, and there are other types of interactions – hydration, ion association (as called by Freger [39]) or non-electrostatic specific physical interaction (as termed by Weber et al. [40]), and internal pressure in membranes like Nafion [41, 42]. At the present stage, with the Manning's theoretical framework as a predictive model, it is meaningful to explore the potential of this model for the applications in PFSA membranes.

2. Background

2.1. The ionic conductivity experimental approach for the counter-ion selectivity determination

The transport selectivity between counter-ions i and j measured in electrodialysis (ED), P_j^i , is defined as [5, 7, 8]:

$$P_j^i = \frac{t_i^m/t_j^m}{z_i C_i/z_j C_j} \quad (1)$$

where t_i^m is the transport number of counter-ion i in the membrane phase, C_i stands for the molarity of counter-ion i (mol m⁻³) at the membrane surface on the desalination side, and z_i is the valence of the counter-ion. As is generally known, the transport selectivity of counter-ions measured in ED depends on the experimental conditions [10], which include but are not limited to the current density, the equivalence ratio of counter-ions in the solutions [43], the ionic strength of solutions, the mixing conditions (with or without flow) and the temperature. If one aims at characterizing the counter-ion transport selectivity of the membrane itself, it is necessary to choose carefully the experimental conditions to screen out the influence from other factors as much as possible. Though there are different practices in literature, we employ such one: equal equivalence ratio of counter-ions in the starting solutions (both the diluate and the concentrate), a current density well below its limiting value, fast liquid flow through the ED cell, duration that is long enough to determine the counter-ion concentration change in the solutions in ED (for several times of measurements at a regular time interval), but not so long that the counter-ion concentration changes exceed 5% as compared to their starting values (so c_i in Equation 1 can be approximated with the starting values). When the current density is well below the limiting one, it is rationale to approximate the counter-ion concentration at the membrane surface with its concentration in the bulk solution [44]. The counter-ion transport number in the membrane can be expressed with the ratio of ionic fluxes, which can be described by the Nernst-Planck equation [45]. With these considerations, the contribution of ionic diffusion and convection to the ionic fluxes can be neglected, then the counter-ion transport selectivity can be simplified to the following form [16]:

$$P_j^i = \frac{x_i^m/x_i^s}{x_j^m/x_j^s} \cdot \frac{u_i^m}{u_j^m} = K_j^i \cdot \frac{u_i^m}{u_j^m} \quad (2)$$

K_j^i is the partition coefficient of counter-ions i and j between the solution and the membrane phase, x_i^m is the **equivalent ratio** of counter-ion i among all counter-ions in the membrane phase, and x_i^s its equivalent ratio in the bulk solution. u_i^m is the mobility of counter-ion i in the membrane phase ($\text{m}^2 \text{s}^{-1} \text{V}^{-1}$), and it is related closely to the membrane conductivity, κ_i^m (S m^{-1}), as [18]:

$$\kappa_i^m = F a_i^m u_i^m = F \gamma_i^m C_i^m u_i^m \quad (3)$$

F is the Faraday constant (96485 C mol^{-1}), a_i^m is the activity of counter-ion i in the membrane, γ_i^m is the counter-ion activity coefficient in the membrane. In our previous work [16], the activity coefficient was simplified as 1. For the concomitant presence of two different counter-ions, i and j , in the membrane phase, if we assume the membrane conductivity ($\kappa_{i,j}^m$) is linearly dependent on the counter-ion activity (a more stringent assumption than the use of concentration as reported in [16]), then:

$$\kappa_{i,j}^m = F a_i^m u_i^m + F a_j^m u_j^m = F \gamma_i^m C_i^m u_i^m + F \gamma_j^m C_j^m u_j^m \quad (4)$$

A parameter, the equivalent concentration of all counter-ions in the membrane, C^m (equivalence· m^{-3}), is defined to unify the notations for both mono/bivalent counter-ions. It is defined as:

$$C^m = |z_i| C_i^m + |z_j| C_j^m \quad (5)$$

z_i is the valence of counter-ion i . Rearrangement of Equation 5 links the counter-ions' equivalent ratios as:

$$\frac{|z_i| C_i^m}{C^m} + \frac{|z_j| C_j^m}{C^m} = x_i^m + x_j^m = 1 \quad (6)$$

The equivalent concentration of all counter-ions, C^m , can also be calculated directly from the membrane parameters including ion exchange capacity (IEC , $\text{mmole} \cdot \text{g}^{-1}$ dry polymer), the dry polymer density (ρ_{dry} , kg m^{-3}), and the dimensional swelling degree (SD) by the following correlation [10]:

$$C^m = IEC \cdot \rho_{dry} \cdot \frac{V_{dry}}{V_{wet}} = IEC \cdot \rho_{dry} \cdot \left(\frac{1}{1+SD}\right)^3 \quad (7)$$

V is the volume of membranes (m^3), and the subscript denotes the hydration state (dry or wet). In the derivation of Equation 7, there is one another assumption that the membranes swell uniformly in three directions. Though there is proof that PFSA membranes have different dimensional swelling degrees in the normal and tangential directions to the membrane surface [46], we keep this assumption here to simplify the calculation. The combination of Equations 3 - 7 gives (the deduction details are given in the Supporting Information):

$$x_i^m = \frac{\kappa_{i,j}^m(1+SD_{i,j})^3 - \kappa_j^m(1+SD_j)^3}{\kappa_i^m(1+SD_i)^3 - \kappa_j^m(1+SD_j)^3} \quad (8)$$

This means that the equivalent ratio of counter-ion i in the membrane, x_i^m , can be obtained from the membrane conductivity and dimensional swelling degree data, when $\gamma_i^m u_i^m$ is not dependent on the membrane counter-ion composition. This result is exactly the same as when the counter-ions' activity coefficients in the membrane are simplified to 1 (i.e., in Equations 3 and 4, $\gamma_i^m = \gamma_j^m = 1$) [16]. One step further, the partition coefficient in Equation 2 can be expressed as:

$$K_j^i = \frac{x_j^s}{x_i^s} \cdot \frac{\kappa_{i,j}^m(1+SD_{i,j})^3 - \kappa_j^m(1+SD_j)^3}{\kappa_i^m(1+SD_i)^3 - \kappa_j^m(1+SD_j)^3} \quad (9)$$

The deductions shown above for the partition coefficient with the simplification of counter-ion activity coefficients ($\gamma_i^m = \gamma_j^m = 1$) have been validated experimentally for K^+/Na^+ in cation exchange membranes (CEMs), and for Mg^{2+}/Na^+ in two hydrocarbon-based CEMs, as reported in our previous work [16]. However, the mobility ratios of K^+/Na^+ or Mg^{2+}/Na^+ obtained from the conductivity data are underestimated, when the cation activity coefficients are simplified [16]. Therefore, based on Equation 3, the counter-ion mobility ratio shall be expressed in the following way:

$$\frac{u_i^m}{u_j^m} = \frac{\kappa_i^m(1+SD_i)^3 |z_i|}{\kappa_j^m(1+SD_j)^3 |z_j|} \cdot \frac{\gamma_j^m}{\gamma_i^m} \quad (10)$$

As shown by Equation 2, the transport selectivity of counter-ions i and j can be expressed as the product of the partition coefficient (K_j^i) and the counter-ion mobility ratio in the membrane phase (u_i^m/u_j^m). Because the ionic conductivity experimental approach can already ensure the determination of the partition coefficient reasonably well (via Equation 9), so this study will then focus

on the counter-ion activity coefficients in the membrane phase, γ_i^m , to increase the accuracy when determining the counter-ion mobility ratio in the membrane phase via Equation 10. The calculation of counter-ion activity coefficients in the membrane phase is detailed in the following section.

2.2. Calculation of the counter-ion activity coefficient

The counter-ion (*gegen*-ion) and co-ion activity coefficients in an IEM, γ_g^m and γ_c^m respectively, can be calculated according to Manning's model [25, 28, 47] as:

$$\gamma_g^m = \left(\frac{\frac{C_A^m}{|z_g|\xi} + |z_g|\nu_g C_s^m}{C_A^m + |z_g|\nu_g C_s^m} \right) \exp \left[-\frac{\frac{C_A^m}{2}}{C_A^m + |z_g|\nu_g \nu_c \xi C_s^m} \right] \quad (11)$$

$$\gamma_c^m = \exp \left[-\frac{\frac{C_A^m}{2} \left(\frac{z_c}{z_g} \right)^2}{C_A^m + |z_g|\nu_g \nu_c \xi C_s^m} \right] \quad (12)$$

where C_A^m is the molarity of fixed charges in a hydrated membrane (mol m^{-3}), C_s^m is the mobile salt concentration in the membrane (mol m^{-3}), z_g and z_c are the *gegen*-ion and co-ion valences, respectively. ν_g and ν_c indicate the stoichiometric number of counter-ions and co-ions in one mobile salt, respectively, and $\nu = \nu_g + \nu_c$. ξ is the so-called Manning parameter that denotes the dimensionless fixed linear charge density on a polymer chain of the membrane [47].

When the amount of imbibed co-ion into an IEM can be neglected (namely $C_s^m \approx 0$), the counter-ion activity coefficient in the membrane can then be simplified as:

$$\gamma_g^m = \frac{1}{|z_g| \xi} \exp\left(-\frac{1}{2}\right) \quad (13)$$

Under such a condition, the counter-ion activity coefficient is only related to the counter-ion valence and the Manning parameter, and the latter is defined as follows [47]:

$$\xi = \frac{e^2}{4\pi\epsilon_0\epsilon kTb} = \frac{\lambda_B}{b} \quad (14)$$

where e is the elementary charge (1.60×10^{-19} C). ϵ_0 is the vacuum dielectric constant (8.85×10^{-12} F m⁻¹), ϵ is the relative dielectric constant (permittivity) of the hydrated membrane. k is the Boltzman constant (1.38×10^{-23} J K⁻¹), T stands for the absolute temperature (K). b is the average distance between two adjacent fixed charges in a hydrated membrane (m). λ_B is the Bjerrum length (m) that characterizes the critical distance at which the thermal energy of a counter-ion is equal to the attractive electrostatic energy between this counter-ion and an interacting fixed charge group. When the distance between a counter-ion and a fixed charge group (eg. on a polymer chain) is smaller than the Bjerrum length, the counter-ion is considered as “condensed” with the fixed charge group. When the distance is larger than the critical value, the counter-ion is regarded as “free”. In Manning’s model, the dimensionless linear charge density ξ is in fact the ratio of Bjerrum length to the average distance between two adjacent fixed charge groups (on a polymer chain).

The model has an important idea of the critical linear charge density, ξ_{crit} , which discriminates the situation whether or not a counter-ion will be condensed with these consecutive fixed charge groups on a polymer chain. The critical linear charge density is correlated to the valence of the counter-ion and corresponding fixed charge groups as [47]:

$$\xi_{crit} = \frac{1}{|z_g z_p|} \quad (15)$$

z_p is the valence of the fixed charge groups on polymer chains. For fixed sulfonate groups ($z_p = -1$) and a monovalent cation (eg. Na⁺), the critical linear charge density is 1; for the same fixed charge

groups and a bivalent cation (eg. Mg^{2+}), the value is 0.5. Within this framework, counter-ions will be condensed when the Manning parameter is larger than its critical value, and these condensed counter-ions could then neutralize some fixed charges and increase the average distance between two adjacent fixed charge groups, consequently the Manning parameter is reduced until its critical value is reached. Though Manning's theory was originally developed for polyelectrolyte systems, it has also been proved valid in similar systems like highly hydrated IEMs, since these IEMs can be treated as crosslinked ionomers with high fixed charge concentrations. Kamcev and Freeman et al. have recently extended Manning's theory to IEMs, and obtained excellent results in interpreting the thermodynamic [25, 29] and transport properties [28, 31] of several types of hydrocarbon-based CEMs.

In Equation 14, the permittivity of a hydrated membrane (ε) can either be measured experimentally [48-50], or alternatively be approximated by the following additive rule [25]:

$$\varepsilon = \Phi_w \varepsilon_w + \Phi_p \varepsilon_p \quad (16)$$

Φ_i is the volume fraction of component i in a hydrated membrane, ε_i is the permittivity of component i . The subscripts w and p stand for water and polymer, respectively. The value of ε_w is chosen at 78, the permittivity of bulk water at room temperature. In Equation 14, the average distance between two adjacent fixed charge groups in an IEM (b) can be estimated geometrically, based on known knowledge of the chemical structure and the membrane composition for hydrocarbon-based IEMs [25]. However, for PFSA membranes with significant hydrophobic and hydrophilic nanophase separation upon hydration, structure models are necessary for estimating the parameter b .

3. Characteristics of cation exchange membranes

The chemical schemes of three representative types of CEMs are shown in Figure 1. CMX (Astom Corp., Japan) is made from sulfonated polystyrene crosslinked by divinylbenzene (Figure 1, a), and further reinforced with polyvinyl chloride fabric. It is conventionally used as a standard CEM in

ED. SPEEK is short for sulfonated poly(ether ether ketone) (Figure 1, b), and it is representative of homogeneous CEMs. PFSA membranes are another important class of CEMs, including Nafion from DuPont and F9120 from Fumatech, and so on. The difference of these PFSA membranes is the density of side chains (m, n values), and the length of side chains (x, y values in Figure 1, c) [46]. The spanning length of a monomer residue (b_0) in CMX and SPEEK is also shown in the figure.

Figure 1. Chemical schemes of the three different types of cation exchange polymers that form the corresponding cation exchange membranes (CEMs): a. CMX, b. SPEEK and c. perfluorosulfonic acid (PFSA) polymers including F9120. All the polymers are shown in their proton forms.

Table 1 lists the basic physicochemical characteristics of CEMs, including the density of the dry polymer membrane (ρ_{dry}), the water contents and the dimensional swelling degree. The data of water contents and swelling degree are based on 10 samples for each condition. The standard deviations of water contents are all less than 3.5%. The numbers of water molecules per fixed sulfonate groups (λ) in different CEMs are listed in the Supporting Information (Table S1). The swelling degree is obtained by measuring the thickness of membranes before and after hydration. There is such a concern that PFSA membranes are anisotropic in swelling [51], which is also reflected by the inconsistency between F9120 swelling degree in the normal direction and water contents if isotropic swelling was assumed (Table S2). In this work, the change of membrane thickness is still chosen as the representative swelling degree because of the convenience in its measurements. Delicate measurements in the future are necessary to clarify the swelling behaviour of PFSA membranes.

Table 1. The characteristics of cation exchange membranes (CEMs)

Membranes	ρ_{dry} [g cm ⁻³]	Water contents			Swelling degree (<i>SD</i>)		
		[g H ₂ O · g ⁻¹ dry polymer, %]			[%]		
		K ⁺	Na ⁺	Mg ²⁺	K ⁺	Na ⁺	Mg ²⁺
CMX	1.34	18.2	22.0	21.9	14.1 ± 1.0	11.1 ± 2.1	12.0 ± 1.2
SPEEK	1.44	15.4	25.1	22.8	13.8 ± 3.3	19.4 ± 8.4	17.0 ± 10.0
F9120	1.77	7.6	16.9	17.4	19.1 ± 1.3	21.3 ± 1.1	17.2 ± 5.2

4. Structure models of perfluorosulfonic acid membranes

The average distance between two adjacent fixed sulfonate groups is an important parameter in the Manning's counter-ion condensation theory, as detailed in Section 2.2. In the case of hydrated PFSA membranes, ion clusters have been observed [46, 52], which indicates that this average distance can't be estimated based on the assumption that fixed sulfonate groups are homogeneously distributed. To this end, knowledge of the PFSA membrane microstructure is necessary. However, the microstructure of PFSA membranes has long been a subject of hot debate, one possible reason of which might be the adaptive nature of the PFSA membrane structure as a response of environmental stimuli, especially the water contents [51].

In this work, three important and influential structure models have been included for the estimation, and their characteristic features are illustrated in Figure 2. The first one is the famous and generally accepted cluster-network model proposed by Gierke *et al.* (Figure 2, a) [53]. In this model, spherical inverted micelles (called clusters) distribute with a paracrystalline pattern through the membrane, and these clusters are interconnected by narrow cylindrical channels with a diameter of around 1 nm (which also depends on the hydration level) [52]. Upon further hydration, clusters grow and coalesce. The second model introduced by Schmidt and Chen in 2008 is the first quantitative model obtained by fitting the small angle X-ray scattering (SAXS) data of a hydrated Nafion [54], and has attracted a lot of attention by far. This model proposes cylindrical water nanochannels arranged

in parallel, with cylinder lengths on the order of some 20 nm [54]. Swelling results in generally the enlargement of the cylinder diameter (Figure 2, b). This model could explain the fast ion transport in these PFSA membranes naturally. Despite its popularity, the parallel cylindrical water channel model is also at question. Kreuer points out that the hydration level of the exact sample whose data have been employed by Schimdt and Chen in their simulation is not correct, and also the simulation is limited to only one sample [51]. With the same approach of direct numerical simulation of the scattering data, Kreuer further developed his semi-quantitative structure model of PFSA membranes. It is found that the microstructure of the water domains in PFSA should be locally flat, without any curvature as proposed in the case of cluster-network and parallel cylindrical water channel models [51]. Because the swelling is observed to be in one direction, so the locally planar water channels increase their spacing distance as a result of swelling (Figure 2, c) [51]. Such planar structures might be with a length on the order of 30 -100 nm, as reflected by the tortuosity of PFSA membranes deduced from SAXS data [51].

Figure 2. Three representative structure models of PFSA membranes and the structure evolution upon swelling with water. (a) The classical cluster-network model proposed by Gierke *et al.* (modified from Reference [52] with permission), (b) the newly introduced model of parallel cylindrical water channels (simplified from Reference [54] with permission) and (c) the structure model with locally flat water layer as suggested by Kreuer (modified from Reference [51] with permission).

5. Results and Discussions

5.1. The ion partitioning selectivity factor and the ion mobility ratio

Figure 3 shows the equilibrium partition coefficient of Mg^{2+} over Na^+ (a), of K^+ over Na^+ (b) between three types of CEMs and the surrounding aqueous solution with varying equivalent ratios of two different cations. The definition of the partition coefficient is given in Equation 2. For the CMX and SPEEK membranes, Mg^{2+} ions are preferentially distributed in the membrane phase for the whole solution composition range investigated, and the partition coefficient $K_{Na^+}^{Mg^{2+}}$ decreases with the increase of equivalent Mg^{2+} ratio in the solution. This is in accordance with the general principle of ion exchange [55]. However, for the PFSA membrane F9120, the partition coefficient drops from 1.6 at an equivalent solution Mg^{2+} ratio of 0.1 to values below 1 when the equivalent solution Mg^{2+} ratio is not less than 0.2. This reversal of the counter-ion partition selectivity in the membrane phase is not frequently seen, and a reasonable explanation has not been achieved yet. As shown in Figure 3(b), there is no preferential partition of K^+ between the CMX membrane and the solution, while K^+ ions are clearly enriched in the membrane phase of SPEEK and F9120. The partition coefficients $K_{Na^+}^{K^+}$ in the F9120 membrane are quite large, especially at low equivalent solution K^+ ratios. Because ion exchange membranes prefer the counter-ion with smaller equivalent solvated volume when different counter-ions have the same valence [55], therefore K^+ is preferentially enriched over Na^+ in the membrane. The underlying reason for this preference of IEMs is the favorable elastic relaxation of the polymeric matrix when the more hydrated counter-ions are replaced by less hydrated ones [55]. The large partition coefficients $K_{Na^+}^{K^+}$ at low equivalent solution K^+ ratios for the F9120 membrane as compared to the SPEEK membrane indicate that the polymeric matrix of the F9120 membrane tends to reorganize relatively easier. This is in line with the observation that the

polytetrafluorene ether side chains in PFSA membranes (Figure 1, c) are easier to reorganize as compared to the stiffer poly(ether ether ketone) hydrocarbon chains [56], which is also reflected by their corresponding glass transition temperatures.

Figure 3. The equilibrium partitioning selectivity factor of (a) Mg^{2+} over Na^{+} ($K_{Na^{+}}^{Mg^{2+}}$), and (b) K^{+} over Na^{+} ($K_{Na^{+}}^{K^{+}}$) between three CEMs (CMX, SPEEK and F9120) and aqueous solutions with varying equivalent cation ratios. The anion is sulfate, and its total molar concentration is 0.5 M. The dashed lines in the figures indicate no preferential partitioning of cations between the membrane and the solution phases.

The cation mobility ratio in the membrane phase (u_i^m/u_j^m) can be calculated *via* Equation 2, when the partition coefficient of cations (K_j^i) and the transport selectivity (P_j^i) are known. Due to experimental difficulties in measuring the actual partition coefficient *during* electrodialysis (ED), the equilibrium partition coefficient is generally used instead [7]. Table 2 lists the transport selectivity of Mg^{2+}/Na^{+} and K^{+}/Na^{+} measured by ED. Mg^{2+} ions are preferentially transported as compared to Na^{+} ions through all three types of CEMs, and so are K^{+} ions. In the ED process, when the current density is well below its limiting value, the partition of counter-ions between the membrane and the solution phase can be considered as close to equilibrium [44, 57]. In our ED experiments the current density at 10 mA cm⁻² is well below the limiting current densities of systems investigated [16], so the

experimentally measured equilibrium partition coefficients (as shown in Figure 3) can be used to calculate the counter-ion mobility ratio in the membrane $u_i^m/u_j^m(ED)$, via Equation 2. As also shown in Table 2, the Mg^{2+}/Na^+ and K^+/Na^+ mobility ratios determined with the ED selectivity data are larger than 1, except for the Mg^{2+}/Na^+ pair in the SPEEK membrane and the K^+/Na^+ pair in the F9120 membrane. The unusual phenomenon of smaller K^+ mobility as compared to Na^+ in the membrane phase has also been observed in other PFSA membranes like Nafion [58]. On the other hand, the cation mobility ratios in the membrane can also be calculated from the membrane conductivity data at pure counter-ion forms (Equation 10, without cation activity coefficients), the results of $u_i^m/u_j^m(\kappa)$ are tabulated in Table 2. It is clear that only the K^+/Na^+ mobility ratios in the CMX and SPEEK membranes are close to those calculated with the ED selectivity data. The Mg^{2+}/Na^+ mobility ratios and the K^+/Na^+ mobility ratio in the F9120 membrane calculated from the membrane conductivity data (without cation activity coefficients) are all smaller than corresponding values calculated from the ED selectivity data. This discrepancy should be due to the simplification of cation activity coefficients in the CEMs when the membrane conductivity data are employed for the calculation of cation mobility ratios in the membrane. Therefore, the calculation of cation activity coefficients in these CEMs becomes necessary.

Table 2. The measured cation transport selectivity and calculated cation mobility ratio for CEMs

Membranes	$P_j^i(ED)$		$u_i^m/u_j^m(ED)$		$u_i^m/u_j^m(\kappa)$	
	Mg^{2+}/Na^+	K^+/Na^+	Mg^{2+}/Na^+	K^+/Na^+	Mg^{2+}/Na^+	K^+/Na^+
CMX	1.34	1.43	1.07	1.51	0.17	1.62
SPEEK	1.09	1.31	0.83	1.11	0.15	1.19
F9120	1.32	1.30	1.48	0.89	0.37	0.34

5.2. The average distance between two adjacent fixed sulfonate groups

The average distance between two adjacent fixed sulfonate groups (Equation 13, b) in CEMs is necessary for the calculation of cation activity coefficients in CEMs. For the hydrocarbon-based CEMs (CMX and SPEEK) it is calculated based on the assumption that these ionic groups are

distributed randomly throughout the whole membrane, and the distribution can be considered as homogeneous on a microscopic scale. Therefore, with known molar ratio of charged and non-charged groups, the b values can easily be estimated. Table 3 lists the parameters necessary for the calculation in the hydrocarbon-based CEMs. The CMX membranes are made from sulfonated polystyrene cross-linked with divinyl benzene (Figure 1), and these cross-linked copolymers are further reinforced with inert fabric. The weight fraction of styrene and divinyl benzene copolymers in the composite membrane is reported to be 45 – 65% [59], and an average value of 55% is used here. The homogeneous distribution of fixed charge groups in these hydrocarbon-based ionomers is a rationale assumption, because it is already known that fixed charge groups in these ionomers are more distributed and show no ion clustering [56]. This assumption has also been adopted by Kamcev et al. in their calculations, and the calculated cation activity coefficients in the hydrocarbon-based CEMs show remarkably good agreement with experimental values [25]. As shown in Table 3, though the CMX and SPEEK membranes have similar IECs, the b value of SPEEK is larger than that of CMX because the unit distance (b_o) in SPEEK is much larger (Figure 1). A recent study on the small angle X-ray scattering profiles of SPEEK membranes reveals a scattering peak corresponding to the average distance between two adjacent sulfonate groups on the polymer backbone [60]. For SPEEK membranes with IEC in the range of 1.3 - 1.6 mmol·g⁻¹, the average distance is around 2.4 nm [60], which accredits the value calculated in this study.

Table 3. The average distance between two adjacent fixed sulfonate groups (b) in CEMs

Membranes	IEC [mmol·g ⁻¹ dry polymer]	n_{non}^* [mmol·g ⁻¹]	n_c/n_{non}^* [-]	b_o [nm]	b [nm]
CMX	1.66 ± 0.06	1.62	0.98	0.25 [25]	0.50
SPEEK	1.62 ± 0.01	1.28	0.79	1.70 [61]	3.04

* n_c and n_{non} stand for the molar amount of charged and non-charged groups per 1 g of the whole dry ion exchange polymer. b_o is the unit distance between two adjacent fixed charge groups as schemed in Figure 1.

Different from the situation in the hydrocarbon-based CEMs, estimation of the average distance between two adjacent fixed sulfonate groups in PFSA membranes relies on the membrane structure models derived from the scattering data [51, 52, 62]. Since ion clustering is observed in these membranes, the assumption of homogeneous distribution of fixed charge groups throughout the whole membrane does not hold any more. The cluster-network model initiated by Gierke et al. [52], the parallel cylindrical water channel model [54] and the layered locally planar channel model proposed by Kreuer et al. [51, 56, 62] are typical examples. In these models, the water volume fraction of the hydrated membranes (ϕ_w) is the most important parameter. As shown in Table 1, the water content of the F9120 membrane in Na^+ form is 16.9 wt.%, which is close to 17.8 wt.% of Nafion in Na^+ form with an equivalent weight of $1200 \text{ g}\cdot\text{mol}^{-1}$ (Table 1 from Ref. [52]). For this type of Nafion membrane at such a hydration level, Gierke et al. estimated a cluster diameter of 3.88 nm and 73 fixed charge sites within a single cluster [52]. By assuming homogeneous distribution of fixed charge groups within a single spherical cluster (as sketched in Figure 2(a)), an average distance of 0.91 nm between these fixed charge groups can be obtained. Though the equivalent weight of the F9120 membrane ($950 \text{ g}\cdot\text{mol}^{-1}$) used in this study is different from this type of Nafion described in literature, we assume that the microstructure of the F9120 membrane resembles this type of Nafion, because of their similar water contents at Na^+ form. Following the same procedure of Gierke, and use the equivalent weight of $950 \text{ g}\cdot\text{mol}^{-1}$ for the calculation of fixed charge group numbers, the cluster diameter and the number of fixed charge groups per cluster of the F9120 membrane in Na^+ and K^+ forms are obtained, and results are presented in Table 4. The calculation details are provided in the Supporting Information. There are no scattering data about Mg^{2+} -form Nafion membranes [52], consequently the Bragg spacing distance necessary for the estimation of the cluster spacing distance in Nafion is not available. Alternatively, the Bragg spacing distance measured from

Na⁺-form Nafion is adopted for the calculation. Because of similar water contents, the b value of the Mg²⁺-form F9120 membrane is almost identical to that of the Na⁺-form membrane.

Table 4. The average distance between two adjacent fixed sulfonate groups (b) in PFSA

Structure model	Cation	Cluster/cylinder	Fixed charges per	b [nm]
		diameter [nm]	cluster/cylinder [-]	
Cluster-network [52]	K ⁺	3.22	93	0.67
	Na ⁺	3.73	81	0.83
	Mg ²⁺	3.75	81	0.84
Parallel cylindrical water channels [54]	K ⁺	1.91	3.98×10^6	0.56
	Na ⁺	2.76	3.98×10^6	0.69
	Mg ²⁺	2.80	3.98×10^6	0.68
Layered locally planar channels [51]	K ⁺	0.4*	/	0.79
	Na ⁺	1.0	/	0.79
	Mg ²⁺	1.0	/	0.79

* This is the water layer thickness in the layered locally planar channels model.

The parallel cylindrical water channels model suggests that the water nanochannels in PFSA membranes are parallel cylinders of a few nanometer diameter. This model is based on the direct numerical simulation of small angle X-ray scattering data of a Nafion117 membrane with 20 vol.% of water [54]. For such a membrane, the authors find the average diameter of cylinders to be 2.4 nm [54]. The length of these cylindrical water nanochannels is around 20 nm, however whether these nanochannels align along the normal direction to the membrane surface is not clear [54]. To simplify

the calculation, it is assumed that these nanochannels align almost in series across the whole membrane thickness. So, the estimated value of the nanochannel length is the minimum (and also equals to the hydrated membrane thickness), and consequently the estimated value of the average distance between two adjacent fixed charge groups is also the minimum. With the amount of fixed charge groups (IEC value), the number of fixed charge groups within such a water-filled cylindrical nanochannel (Figure 2, b) penetrating the membrane thickness is calculated as much as 4.20×10^6 , by taking into account of 20 vol.% water in the membrane. Then the average distance between two adjacent fixed charge groups is estimated to be 0.62 nm. This structure model is also transferred to the F9120 membrane by comparing the water volume fractions, together with the adoption that PFSA membranes swell/shrink in a fashion that only the diameter of cylindrical water nanochannels increases/decreases (Figure 2, b). For the K^+ -form of the F9120 membrane with 7.6 wt.% of water (12.7 vol.%, Table 5), the diameter of the water nanochannels in the F9120 membrane is 1.91 nm, and the average distance between two adjacent fixed charge groups is 0.56 nm. In a similar way, the average distances in Na^+ -form and Mg^{2+} -form F9120 membranes are obtained, and these two values are quite close (Table 4) because of similar water contents in these two membranes.

Even though the parallel cylindrical water nanochannels model of Nafion is the first quantitative structure model and has become popular, it is still at criticism because only a few scattering patterns were employed for the comparison of simulation and experimental results, and the water volume fraction of the important sample was also faulty [51]. Kreuer et al. propose a different structure model by simulations of the scattering patterns in a similar fashion, but with an array of membrane samples with large variations of the water volume fraction and pre-treatment/relaxation history [51]. Their results exclude the possibility of the parallel cylindrical water nanochannels model, and instead suggest cautiously that the water domain is locally flat, and the water and the polymer domains are most likely layered lamella [51]. According to this model, only the thickness of the water layers changes with the alteration in the membrane water contents. Therefore, the calculated average thickness of the water layers changes as the counter-ions of the F9120 membrane change (Table 4). However, the average distance between two adjacent fixed charge groups pervading homogeneously on the planar water-polymer interface (Figure 2, c) is not affected, and is constant at around 0.79 nm.

1 These estimated values of b , based upon three different structure models of PFSA membranes,
2 are all at the same order of magnitude as the reported 0.47 nm obtained by molecular dynamics
3 simulations [40, 46, 63, 64]. This agreement substantiates our estimations.

5 5.3 The Manning parameter and cation activity coefficients

6 With the estimated average distance between two adjacent fixed sulfonate groups (b) in CEMs,
7 it is then possible to calculate the cation activity coefficients in these CEMs. According to Equation
8 14, the Manning parameter (ξ) can be calculated when the b values and the permittivity of hydrated
9 membranes (ε) are known. The values of ε can be measured experimentally [48-50] or alternatively
10 can be approximated with the average of the membrane polymer and the water permittivity (Equation
11 16). Table 5 lists the approximated ε values, Bjerrum length (λ_B) and ξ values for the three types of
12 CEMs. For the calculation of the water volume fraction in the hydrated membranes (Φ_w), the water
13 density of $1 \text{ g}\cdot\text{cm}^{-3}$ is chosen. The permittivity of water at room temperature is 78, and for simplicity,
14 the permittivity of the dry membrane polymer is chosen at 6 as in Reference [25]. One recent work
15 reports different experimental dielectric constants of crosslinked poly(glycidyl methacrylate)
16 polymers and Nafion 117 at similar water volume fraction, which suggests that polymer water content
17 alone may be insufficient for estimating the permittivity of hydrated polymers [50]. This means that
18 polymer chemistry is also influencing. However, in this work, all the cation exchange polymers have
19 the same functional groups (sulfonate groups, though slightly different pK_a values) and the additivity
20 rule has been proved valid in similar CEMs [25], we keep the use of additivity rule at the present
21 stage.

Table 5. The calculated Bjerrum length (λ_B) and Manning parameter (ξ) in CEMs

Membranes	Cations	Φ_w [%]	ε [-]	λ_B [nm]	ξ [-]
CMX	K ⁺	19.6	20.1	2.79	5.6
	Na ⁺	22.8	22.4	2.50	5.0
	Mg ²⁺	22.7	22.3	2.51	5.0
SPEEK	K ⁺	18.2	19.1	2.93	0.86
	Na ⁺	26.5	25.1	2.23	0.66
	Mg ²⁺	24.7	23.8	2.35	0.69
F9120	K ⁺	12.7	15.1	3.70	5.52/6.61/4.68
	Na ⁺	26.5	25.1	2.23	2.69/3.23/2.83
	Mg ²⁺	27.2	25.6	2.19	2.61/3.22/2.77

As can be seen in Table 5, most of the λ_B values are in the range of 2.20 – 3.00 nm, because similar ε values are found for these hydrated CEMs at room temperature. However, the ξ values differ. For the CMX membrane, the Manning parameters are all larger than corresponding critical values (1 for K⁺ and Na⁺, 0.5 for Mg²⁺), so the three types of cations in the CMX membrane are all condensed. A recent work reports that the Manning parameter (ξ) for the CMX membrane is 1.0 ± 0.1 , obtained by fitting the experimental co-ion (Cl⁻) concentrations in the membrane according to the counter-ion condensation theory [33]. This difference is mainly due to smaller water contents in our case (18.0 – 22.0%) as compared to more absorbed water in literature (around 40%), because more concentrated external salt solutions of bivalent sulphate anions (therefore larger ionic strength) are employed in this work. While for the SPEEK membrane, only bivalent Mg²⁺ ions are condensed because ξ is larger than 0.5. The K⁺ and Na⁺ ions in the SPEEK membrane are not condensed, just

because the average distance between two adjacent fixed sulfonate groups (b values) is large (Table 3), and which is a result of the relatively low IEC values for these SPEEK membranes. For the F9120 membrane, b values estimated from 3 different structure models (Table 4) are used to calculate the Manning parameter, and the results are grouped in Table 5. As shown, all three types of cations are condensed in the F9210 membrane, irrespective of which structure model is employed.

When the counter-ions are not condensed, i.e. the Manning parameter $\xi < \xi_{crit}$, then the counter-ion activity coefficient in the membrane phase is calculated with the following formula [47]:

$$\ln \gamma_g^m = -\frac{1}{2}\xi \frac{C_A^m}{C_A^m + 2C_S^m} \quad (17)$$

Since the free salt concentration in the membrane phase can be neglected ($C_S^m \approx 0$) when bivalent co-ion SO_4^{2-} at a total molar concentration of 0.5 M is employed in this study, Equation 17 can then be simplified as:

$$\gamma_g^m = \exp\left(-\frac{1}{2}\xi\right) \quad (18)$$

For the case of the SPEEK membranes with K^+ or Na^+ ions, the cation activity coefficients should be calculated with Equation 18, instead of Equation 13 [47]. The calculated results are listed in Table 6. As can be seen, when the cations are condensed in the membrane, the resultant activity coefficients are generally only about 10 – 25% of the ideal values (1), which is in general agreement with the results published in literature [25, 47]. For the Mg^{2+} ions in the SPEEK membrane, the Manning parameter is slightly larger than the critical value (0.5), so limited portion of counter-ions are condensed and the Mg^{2+} activity coefficient is therefore larger than 0.5. While for the K^+ and Na^+ ions in the SPEEK membrane, because these cations are not condensed at all in this CEM with a large distance between two adjacent fixed sulfonate groups, their activity coefficients are as large as 0.651 and 0.719, respectively. In a word, with the aid of Manning's counter-ion condensation theory, all the cation activity coefficients in CEMs are obtained.

Table 6. The cation activity coefficients in CEMs calculated via Manning's theory

Membranes	Structure model	γ_g^m		
		K ⁺	Na ⁺	Mg ²⁺
CMX	/	0.131	0.147	0.074
SPEEK	/	0.651	0.719	0.533
	Cluster-network	0.110	0.225	0.116
F9120	Parallel cylindrical channel	0.092	0.188	0.094
	Layered locally planar channel	0.130	0.214	0.110

5.4 The revised ion mobility ratio and resultant ion transport selectivity

As shown in Section 5.1, the cation mobility ratios calculated from the membrane ionic conductivity data are obviously smaller than corresponding values obtained from the ED data, except for the cases of K⁺/Na⁺ transport in the CMX and SPEEK membranes (Table 2). This discrepancy could be ascribed to the simplification of the cation activity coefficients in CEMs. Now these cation activity coefficients have been obtained with the Manning's counter-ion condensation theory, and are listed in Table 6. Then the revised mobility ratios ($u_j^i(\kappa, \gamma)$) with the consideration of the cation activity coefficient can be calculated with Equation 10, and the results are shown in Table 7. For the F9120 membrane, only the results based on the cluster – network structure model are presented in Table 7. The revised mobility ratios are generally in quantitative agreement with the mobility ratios calculated from the ED data. As compared to the non-revised mobility ratios, the revised Mg²⁺/Na⁺ mobility ratios of the CMX and SPEEK membranes have increased, but are still smaller than the corresponding ratios from the ED data. At the present stage, we think this might possibly be due to oversimplification in estimating the average distance between adjacent fixed sulfonate groups (b) by assuming homogeneous distribution of fixed charge groups in these hydrocarbon-based CEMs. In the future, it is necessary to figure out how to include the influence of membrane water volume

fraction (ϕ_w) on the average distance between fixed sulfonate groups (b) in these hydrocarbon-based CEMs.

Table 7. The revised cation mobility ratios considering the cation activity coefficients

Membranes	u_i^m/u_j^m (ED)		u_i^m/u_j^m (κ)		u_i^m/u_j^m (κ, γ)	
	Mg ²⁺ /Na ⁺	K ⁺ /Na ⁺	Mg ²⁺ /Na ⁺	K ⁺ /Na ⁺	Mg ²⁺ /Na ⁺	K ⁺ /Na ⁺
CMX	1.07	1.51	0.17	1.62	0.34	1.82
SPEEK	0.83	1.11	0.15	1.19	0.20	1.31
F9120	1.48	0.89	0.34	0.34	0.72	0.70

The ion transport selectivity values obtained by the conventional ED method and the ionic conductivity experimental approach we proposed before are illustrated in Figure 4, and numerical values are provided in the Supporting Information (Table S3). The benchmark values are those obtained by ED. The cation transport selectivity values $P_{Na^+}^{Mg^{2+}}$ and $P_{Na^+}^{K^+}$ for the three types of CEMs are all larger than 1 (indicated by the dashed horizontal line in Figure 4). The $P_{Na^+}^{Mg^{2+}}$ calculated from the membrane conductivity data (κ) without the consideration of cation activity coefficients are all significantly smaller than their corresponding reference values (Figure 4, a). While for the $P_{Na^+}^{K^+}$ calculated in the same fashion, the selectivity values are quite close to the reference values for the CMX and SPEEK membranes, however not for the F9120 membrane (Figure 4, b). With the inclusion of the cation activity coefficients in the calculation, the $P_{Na^+}^{Mg^{2+}}$ for CEMs all increase to values quite close to the references. For the F9120 membrane, because 3 different structure models are employed, so there are 3 different values. The $P_{Na^+}^{Mg^{2+}}$ value revised with the layered locally planar channel model deviates obviously from the other two values, which results from the inefficiency of the third structure model in predicting the change of b values (Table 4). For the CMX and SPEEK membranes, the $P_{Na^+}^{K^+}$ values revised with the cation activity coefficients are close to the

1 references, while the $P_{Na^+}^{K^+}$ values of the F9120 membrane are still slightly smaller than the
 2 reference value. Nevertheless, in general the $P_{Na^+}^{Mg^{2+}}$ and $P_{Na^+}^{K^+}$ values calculated from the
 3 conductivity data are close to the reference values after the cation activity coefficients have been
 4 included in the calculation. It is also necessary to note that the $P_{Na^+}^{Mg^{2+}}$ of SPEEK membrane
 5 measured by ED is only 1.09 (also shown in Table 2), indicating no significant preferential transport
 6 of bivalent Mg^{2+} ions across the membrane. We confirmed this unusual behavior with repeated ED
 7 experiments. After the cation activity coefficients in the SPEEK membrane have been calculated,
 8 now the reason for this unusual behavior is clear: part of the Mg^{2+} ions in the SPEEK membrane are
 9 condensed to the fixed sulfonic groups (Table 5, $\xi > 0.5$), and the overall Mg^{2+} activity coefficient is
 10 0.533; however, all the monovalent Na^+ ions in this membrane are not condensed (therefore being
 11 mobile), and the Na^+ activity coefficient is 0.719, larger than that of Mg^{2+} . On the other hand, the
 12 partition coefficient $K_{Na^+}^{Mg^{2+}}$ of the SPEEK membrane is around 1.3 when the solution equivalent Mg^{2+} :
 13 Na^+ ratio is 1 (Figure 3, a). As a result, the $P_{Na^+}^{Mg^{2+}}$ of the SPEEK membrane is only 1.09. With the
 14 help of Manning's counter-ion condensation theory to calculate the cation activity coefficient, such an
 15 unusual transport selectivity is now rationalized.

17 **Figure 4.** The cation transport selectivity (a) of Mg^{2+} over Na^+ ($P_{Na^+}^{Mg^{2+}}$), and (b) of K^+ over Na^+ ($P_{Na^+}^{K^+}$)
 18 for three types of CEMs (CMX, SPEEK and F9120) obtained by the conventional ED method (circles),

by the ionic conductivity experimental approach without (black squares) and with (square) the correction of cation activity coefficient in the membrane phase (γ_i^m) calculated via Manning's counter-ion condensation theory.

Conclusions

The $\text{Mg}^{2+}/\text{Na}^+$ and K^+/Na^+ transport selectivity through three types of cation exchange membranes (CEMs) obtained from our newly proposed ionic conductivity experimental approach, after accounting for the cation activity coefficients in CEMs with Manning's counter-ion condensation theory, is compared to the results obtained via conventional electrodialysis (ED) method. The new ionic conductivity experimental approach is able to decouple the partition coefficient (K_j^i) and mobility ratio (u_i^m/u_j^m) components of cation transport selectivity. It is found that calculation of the mobility ratios of two cations in the membrane (u_i^m/u_j^m) via the membrane conductivity has to include the cation activity coefficients in the membrane phase. While for the calculation of the partition coefficients of two cations between the solution and the membrane phase (K_j^i), the formula is the same whether or not the cation activity coefficients are included in the expression of the membrane conductivity, as long as the counter-ion mobility in the membrane phase is not strongly dependent on the counter-ion composition. The studied CEMs include CMX, SPEEK and one type of perfluorosulfonic acid (PFSA) membrane F9120. The K^+/Na^+ selectivity obtained by the ionic conductivity experimental approach without the consideration of cation activity coefficients in the membrane phase are not significantly different from the selectivity with the inclusion of cation activity coefficients, and this is coincidentally due to the close values of K^+ and Na^+ activity coefficients in the membrane. However, for the bivalent/monovalent $\text{Mg}^{2+}/\text{Na}^+$ ion pair, the selectivity obtained by the ionic conductivity experimental approach without the consideration of cation activity coefficients are almost half of their corresponding values obtained by the ED method. When both the Mg^{2+} and Na^+ activity coefficients are included, the revised $\text{Mg}^{2+}/\text{Na}^+$ selectivity values are close to the values obtained by ED. To further improve the accuracy of our proposed ionic conductivity experimental

approach for the determination of cation transport selectivity in PFSA membranes, the anisotropic swelling characteristics of these membranes have to be considered.

It is also shown in this work that the Manning's counter-ion condensation theory could not only be applied to hydrocarbon-based CEMs, but also can be used in PFSA membranes to calculate the cation activity coefficients. To do so, the average distance between two adjacent fixed sulfonate groups in the hydrocarbon-based CEMs (CMX and SPEEK) can be estimated by assuming homogeneous distribution of the fixed charge groups in the membrane. However, for the PFSA membrane F9120, models describing the membrane microstructure as a result of the hydrophobic – hydrophilic microphase separation have to be employed. It is found that the classical cluster-network model and the recent parallel cylindrical water channel model can give reasonable values of the average distance and its change as a response of the change in the membrane water contents. However, the layered locally planar water channel model is presently not effective in predicting the change of this average distance, and more details have to be included to substantiate this structure model of PFSA membranes. This work stresses the importance of including the cation activity coefficients in the interpretation of the membrane counter-ion transport selectivity.

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