

Ion mobility and partition determine the counter-ion selectivity of ion exchange membranes

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Abstract

Ion (perm)selectivity and conductivity are the two most essential properties of an ion exchange membrane, yet no quantitative relation between them has been suggested. In this work, the selectivity between two different counter-ions is correlated to the membrane conductivity. We show that the counter-ion selectivity measured by conventional electrodialysis (ED) can be expressed by the product of two parameters: (a) the mobility ratio between these two different counter-ions in the membrane and (b) their partition coefficient between the solution and the membrane. This is reminiscent of the classical solution-diffusion model. Via the counter-ion mobility in the membrane, the selectivity could be simply expressed with the membrane conductivity and dimensional swelling degree at pure counter-ion forms and at mixed counter-ion form when the membrane has been equilibrated with 1:1 equivalence ratio of the two counter-ions in the solution. This correlation is validated experimentally for the ion selectivity of K^+/Na^+ in two commercial hydrocarbon-based cation exchange membranes (CEMs). For K^+/Na^+ in a commercial perfluorosulfonic CEM, and for Mg^{2+}/Na^+ in all the three types of CEMs, the correlation could predict the counter-ion partition very well; but there is an underestimation of the K^+/Na^+ and Mg^{2+}/Na^+ mobility ratios afforded by this correlation, which might be due to simplification of the cation activity coefficients in CEMs. This work offers a convenient method to decouple experimentally the effect of partition and mobility in controlling the membrane selectivity, and also proposes a new perspective to study the selectivity as well as conductivity of ion exchange membranes.

Keywords: ion (perm)selectivity, ion conductivity, ion exchange membranes, electrodialysis, characterization method, limiting current density

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1. Introduction

Ion exchange membranes (IEMs) have been established in electrolysis, electrodialysis (ED) and diffusion dialysis [1-3], and have been also under exploration for applications like fuel cells, redox flow batteries, reverse electrodialysis, membrane capacitive deionization and IEM bioreactors, among others [4, 5]. These applications in the field of saline water desalination [6], waste water treatment, energy storage and conversion [7] could help secure the water resources and energy supply for mankind [8, 9]. Therefore, the research about IEMs is of both practical and scientific significance.

Technically, IEMs are dense polymeric membranes bearing fixed ionogenic groups, which can ionize into fixed ionic groups and mobile counter-ions in the presence of polar solvents (*eg.* water) [10]. Due to the high volumetric concentration of fixed ionic groups in the polymer matrix, IEMs can facilitate the transport of counter-ions across the membrane, while effectively blocking the transport of co-ions that bear the same sign of charge as the fixed groups [11]. This is one kind of permselectivity based on the so-called Donnan exclusion and is an essential property that enables most of IEMs applications [2]. Literature almost exclusively focuses on this counter/co-ion permselectivity. However, very often not only one type of counter-ions is present in the aqueous solutions where IEMs are employed. For example, NaCl production by sea water desalination has to deal with the simultaneous presence of bivalent cations (Mg^{2+} , Ca^{2+}) together with the

target sodium ions (Na^+) [12, 13]. Mg^{2+} ions are much more concentrated than lithium ions (Li^+) in salt lake waters, which makes the lithium extraction by ED for example very challenging [14, 15]. For these processes, IEMs with the ability to discriminate between different counter-ions, hence having an excellent ion selectivity, are highly desired [5]. This requires further understanding of simultaneous (counter-)ion transport in IEMs and development of relevant techniques to conveniently characterize the ion selectivity.

Techniques available for the determination of ion selectivity between different counter-ions can be classified into two groups: ED and bi-ionic membrane potential, as summarized in our recent review [5]. ED is based on the determination of trans-membrane ionic fluxes driven by the potential gradient, which serves as the benchmark technique [12, 13] and will be detailed in Section 2.1. The bi-ionic membrane potential is a trans-membrane potential difference that arises due to the inter-diffusion of different counter-ions, when the two membrane surfaces are in contact with different ionic solutions [16-18]. The ion selectivity can be approximated by bi-ionic membrane potentials through ionic flux equations [19, 20]. This method can serve as a quick estimation [21, 22], though it is much less frequently used in practice. When the water transport is corrected for the ion selectivity obtained by ED, the ion selectivity afforded by these two methods are almost identical [1].

Besides selectivity, conductivity is the other essential property of IEMs [1, 4].

The ohmic resistance of an IEM is determined by the membrane thickness and resistivity (the reversal of which is conductivity), and it is generally expressed as a scalable parameter – area resistance with a unit of $\Omega \cdot \text{m}^2$. The membrane area resistance is the key parameter that determines the ohmic energy losses of electro-chemical processes as mentioned above [2]. As a result, the core fundamental research about IEMs is concerned with the conductivity, as well as the selectivity [23-26]. However, as one's attention could easily be drawn to the general trade-off between selectivity and conductivity, to the best of our knowledge, we find no studies that attempt to provide a different insight into the relation between these two essential properties. In this work, based on a completely different perspective to look at the relation between the two properties, we propose a new and easy approach to measure experimentally the counter-ion selectivity. Three representative types of cation exchange membranes (CEMs) are selected to study the selectivity of cation pairs $\text{Mg}^{2+}/\text{Na}^+$ and K^+/Na^+ . Results obtained by this conductivity approach are compared with those measured by the conventional ED method. The work presented below aims to motivate a new perspective to study the (perm)selectivity of IEMs.

2. Theory

2.1. Selectivity between different counter-ions

The selectivity between counter-ions i and j measured in ED, P_j^i , is defined as [12, 13]:

$$P_j^i = \frac{t_i^m/t_j^m}{c_i/c_j} \quad (1)$$

Where c_i is the equivalent counter-ion concentration at the membrane surface on the desalting side (equivalent m^{-3}) as shown in Figure 1 (b), t_i^m is the transport number of counter-ion i in the membrane phase, defined as [4]:

$$t_i^m = z_i F J_i^m / \sum_j (z_j F J_j^m) \quad (2)$$

z_i is the valence of counter-ion i , J_i^m is the ionic flux of counter-ion i in the membrane phase ($\text{mol m}^{-2} \text{s}^{-1}$), and F is the Faraday constant (96485 C mol^{-1}). When ion diffusion, compared to ion electromigration, can be neglected, the ionic flux in ED can be simplified from the Nernst-Planck Equation as [27, 28]:

$$J_i^m = -D_i^m z_i c_i^m \nabla \varphi \quad (3)$$

D_i^m is the diffusion coefficient of counter-ion i in the membrane phase ($\text{m}^2 \text{s}^{-1}$), c_i^m is the concentration of counter-ion i in the membrane phase (mol m^{-3}), and $\nabla \varphi$ is the electrical potential gradient in the membrane phase (V m^{-1}). In addition, the Nernst-Einstein relation correlates the counter-ion mobility in the membrane phase, u_i^m ($\text{m}^2 \text{s}^{-1} \text{V}^{-1}$), to its diffusion coefficient in the membrane phase D_i^m as [2]:

$$u_i^m = \frac{z_i F}{RT} D_i^m \quad (4)$$

R is the universal gas constant ($8.31 \text{ J mol}^{-1} \text{K}^{-1}$), T is the absolute temperature (K). For two types of counter-ions, i and j , in a CEM, the relation between counter-

ion concentration in the membrane phase, c_i^m and c_j^m (mol m⁻³), and the total equivalent counter-ion concentration of the CEM, c^m (equivalent m⁻³), is:

$$z_i c_i^m + z_j c_j^m = c^m \quad (5)$$

$$x_i^m = \frac{z_i c_i^m}{c^m} \quad (6)$$

x_i^m , defined by Equation 6, is the equivalent molar ratio of counter-ion i in the membrane phase. Equation 5 can then be expressed as:

$$\frac{x_i^m}{x_j^m} + 1 = 1 \quad (7)$$

Rearrangement of Equation 6 also gives:

$$z_i c_i^m = x_i^m c^m \quad (8)$$

Combining Equations 1-4 and 8, the ion selectivity can be expressed as:

$$P_j^i = \frac{z_i F J_i^m / (z_j F J_j^m)}{c_i / c_j} = \frac{u_i^m z_i c_i^m / c_i}{u_j^m z_j c_j^m / c_j} = \frac{u_i^m}{u_j^m} \cdot \frac{x_i^m / c_i}{x_j^m / c_j} \quad (9)$$

When the current density in ED is well below its limiting value, concentration polarization can be neglected (Figure 1), and c_i can be approximated with equivalent ion concentration in the solution bulk [28]:

$$c_i \approx c_i^s \quad (10)$$

So, P_j^i can be further expressed as:

$$P_j^i = \frac{u_i^m}{u_j^m} \cdot \frac{x_i^m / c_i^s}{x_j^m / c_j^s} \quad (11)$$

In fact, the last term in Equation 11 is the partition coefficient of counter-ions i and j between the solution and the membrane phase, K_j^i

$$K_j^i = \frac{x_i^m / x_i^s}{x_j^m / x_j^s} = \frac{x_i^m / c_i^s}{x_j^m / c_j^s} \quad (12)$$

Therefore, the ion selectivity P_j^i can finally be calculated as [13]:

$$P_j^i = K_j^i \cdot \frac{u_i^m}{u_j^m} \quad (13)$$

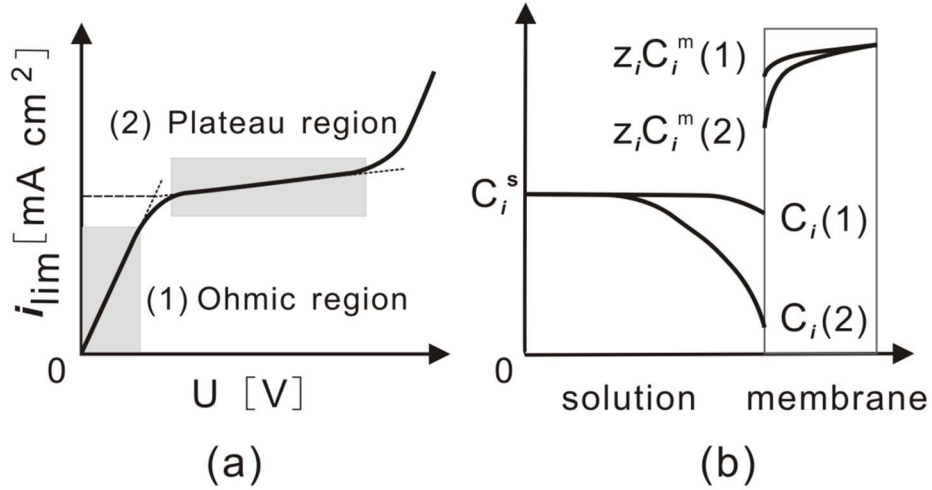


Figure 1. (a) An illustrative ion exchange membrane (IEM) current – voltage (I - V) curve in electrodialysis (ED) that shows the ohmic (1) and plateau (2) regions. (b) Illustration of the equivalent ion concentration profiles in ED at current densities below (1) and above (2) the limiting current density (i_{lim}). C_i^s is the equivalent ion concentration in the solution bulk, C_i equivalent ion concentration at the membrane surface, and $z_i C_i^m$ equivalent ion concentration in the membrane at the desalting side (c_i^m is the molar concentration).

2.2. Conductivity and counter-ion selectivity

The counter-ion mobility can be obtained from the membrane conductivity by the following correlation [29]:

$$\kappa_i^m = \frac{F c_i^m u_i^m}{F c^m u_i^m / z_i} = \quad (14)$$

κ_i^m is the conductivity of a CEM in counter-ion form i (S m⁻¹), c^m is the equivalent counter-ion concentration in the hydrated CEMs (equivalent m⁻³, Equation 5), and can be calculated by the following equations:

$$c^m = \frac{IEC \cdot \rho_{dry} \cdot V_{dry}}{V_{wet}} \quad (15)$$

$$SD = \frac{\delta_{wet} - \delta_{dry}}{\delta_{dry}} \times 100\% \quad (16)$$

IEC is the ion exchange capacity of an IEM based on the dry membrane weight (equivalence g⁻¹), ρ_{dry} is the dry membrane density (kg m⁻³), V denotes the membrane volume while the subscripts indicate the hydration state of membranes, δ is the membrane thickness (m). SD is the swelling degree of CEMs, in the normal direction of these flat-sheet membranes. SD depends not only on the CEM type, but also on the counter-ion type [30, 31]. By assuming isotropic swelling of CEMs, the volumetric swelling degree could be represented simply by the swelling degree of membranes thickness.

$$\frac{V_{dry}}{V_{wet}} = \frac{A_{dry} \delta_{dry}}{A_{wet} \delta_{wet}} = \left(\frac{\delta_{dry}}{\delta_{wet}} \right)^3 = \left(\frac{1}{1+SD} \right)^3 \quad (17)$$

$$c^m = IEC \cdot \rho_{dry} \cdot \left(\frac{1}{1+SD} \right)^3 \quad (18)$$

For a CEM with two counter-ions, i and j , the membrane conductivity $\kappa_{i,j}^m$ is the sum contributed by the two components. If the mobility of a counter-ion does not strongly depend on the membrane counter-ion composition, then there exists the following relation:

$$\kappa_{i,j}^m = F c^m x_i^m u_i^m / z_i + F c^m x_j^m u_j^m / z_j \quad (19)$$

x_i^m and x_j^m are the equivalent molar ratios of counter-ions i and j in the membrane phase, respectively, and their relationship is described by Equation 7. This assumption remains to be tested experimentally, and will be the first objective of this study. By combining Equations 7 and 19, it leads to:

$$x_i^m = \frac{\kappa_{i,j}^m / F c^m - u_j^m / z_j}{u_i^m / z_i - u_j^m / z_j} \quad (20)$$

Combine Equations 14, 18 and 20, and use SD_i , SD_j , and $SD_{i,j}$ to differentiate the membrane swelling degrees when the counter-ions are different, then x_i^m can be expressed as:

$$x_i^m = \frac{\kappa_{i,j}^m (1+SD_{i,j})^3 - \kappa_j^m (1+SD_j)^3}{\kappa_i^m (1+SD_i)^3 - \kappa_j^m (1+SD_j)^3} \quad (21)$$

The mobility ratio of counter-ions, $\frac{u_i^m}{u_j^m}$, can be obtained by combining Equations 14 and 18:

$$\frac{u_i^m}{u_j^m} = \frac{\kappa_i^m (1+SD_i)^3 z_i}{\kappa_j^m (1+SD_j)^3 z_j} \quad (22)$$

The ion partition coefficient, K_j^i , can be calculated as:

$$K_j^i = \frac{x_i^m / x_i^s}{(1-x_i^m) / x_j^s} = \frac{x_j^s}{x_i^s} \cdot \frac{\kappa_{i,j}^m (1+SD_{i,j})^3 - \kappa_j^m (1+SD_j)^3}{\kappa_i^m (1+SD_i)^3 - \kappa_{i,j}^m (1+SD_{i,j})^3} \quad (23)$$

By integration of Equations 22 and 23 into Equation 13, the counter-ion selectivity can be written as:

$$P_j^i = K_j^i \cdot \frac{u_i^m}{u_j^m} = \frac{x_j^s}{x_i^s} \frac{\kappa_{i,j}^m (1+SD_{i,j})^3 - \kappa_j^m (1+SD_j)^3}{\kappa_i^m (1+SD_i)^3 - \kappa_{i,j}^m (1+SD_{i,j})^3} \cdot \frac{\kappa_i^m (1+SD_i)^3 z_i}{\kappa_j^m (1+SD_j)^3 z_j} \quad (24)$$

It can be seen that the ion selectivity between two counter-ions i and j , P_j^i , can be obtained simply with the membrane conductivity and corresponding swelling degree data, provided that the counter-ion mobility does not strongly depend on the counter-ion composition in the membrane phase. For a specific situation when the CEM has been equilibrated with equivalent counter-ions in the solution ($x_i^s = x_j^s = 0.5$), P_j^i can be written as:

$$P_j^i = \frac{\kappa_{i,j}^m (1+SD_{i,j})^3 - \kappa_j^m (1+SD_j)^3}{\kappa_i^m (1+SD_i)^3 - \kappa_{i,j}^m (1+SD_{i,j})^3} \cdot \frac{\kappa_i^m (1+SD_i)^3}{\kappa_j^m (1+SD_j)^3} \quad (25)$$

As a summary of Section 2, it can be inferred that the selectivity between two different counter-ions, P_j^i , can also be

calculated from the membrane conductivity and the dimensional swelling degree (Equations 24 and 25). In the derivations, there is one basic assumption that the counter-ion mobility in the membrane phase (u_i^m) is independent of the membrane counter-ion composition (Equation 19). To unravel the question whether ion selectivity stems from mobility or partition selectivity, we propose the following methodology:

- (a) the equilibrium counter-ion composition in the membrane and corresponding membrane conductivity needs to be measured to substantiate or disprove the assumption of negligible ion interaction;
- (b) the thickness of hydrated CEMs with different counter-ion composition needs to be measured to calculate the dimensional swelling degree.
- (c) the ohmic membrane resistance obtained by impedance spectroscopy together with the hydrated membrane thickness will be used to calculate the membrane conductivity (see below, Equation 26).
- (d) For the benchmark values of P_j^i , the trans-membrane ionic fluxes need to be measured from the solution composition evolution in conventional ED experiments with a six-compartment cell (Figure 2).

- (e) Before the ED experiments, the limiting current density of a specific membrane – electrolyte system shall be determined from the current – voltage (I - V) curve to avoid too strong polarization and low interfacial concentrations.

3. Experimental

3.1. Membranes

Three representative CEMs are selected for the study. Neosepta CMX (Astom Corporation, Japan) is a quasi-homogeneous IEM based on sulfonated polystyrene cross-linked with divinyl benzene, and reinforced with poly(vinyl chloride) [12]. It has been used as a standard CEM in desalination processes by ED. A homogeneous sulfonated poly(ether ether ketone) (SPEEK) CEM, and a perfluorosulfonic acid membrane F9120 are kindly provided by FumaTech GmbH, Germany. The F9120 membrane has an equivalent weight of 900 g mol⁻¹, which means a theoretical IEC of 1.11 mequ. G⁻¹. Important characteristics of CEMs are listed in Table 1. The IEC is measured by standard procedures as detailed in literature [32, 33]. The swelling degree values with standard deviations are based on data from 5 replicate samples.

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

Membranes	IEC [mequ·g ⁻¹ dry polymer]	ρ_{dry} [g·cm ⁻³]	Swelling degree [%]		
			K ⁺	Na ⁺	Mg ²⁺
CMX	1.66 ± 0.06	1.34	14.1 ± 1.0	11.1 ± 2.1	12.0 ± 1.2
SPEEK	1.62 ± 0.01	1.44	13.8 ± 3.3	9.4 ± 8.4	17.0 ± 10.0
F9120	1.03 ± 0.01	1.77	19.1 ± 1.3	21.3 ± 1.1	17.2 ± 5.2

3.2. Ion selectivity measurements by electro dialysis

ED is the conventional method to measure the ion selectivity between two different counter-ions [1, 2, 34]. However, the experimental setup and operation conditions have to be carefully selected for reliable selectivity values, which have been discussed in detail in our recent review [5]. The limiting current densities of an IEM – electrolyte system (Figure 1 (a)) should be determined first for appropriate ED experimental conditions in the selectivity measurements, because other complicating phenomena set in when the current density is above the limiting value [28, 35] and these phenomena will alter the ion selectivity [5].

Figure 2 shows illustratively a six-compartment cell used for the polarization I-V curve determination [10, 35], as well as for the selectivity measurement [34, 36]. The anode is a mixed-metal-oxide coated titanium mesh, and the cathode is a stainless steel plate. Neosepta CMX and AMX membranes are used as the auxiliary CEM and anion exchange membrane (AEM) in the cell, respectively. During the I-V measurements, the two electrodes are employed to deliver a DC current. The cell current density is increased stepwise by increasing the voltage (in between the electrodes) at a step length of 0.15 V in the under-limiting regime. At each step, the duration is 30 s. At the overlimiting regime, the voltage step length is 0.3 V and each voltage is kept for 60 s. The voltage drop across the investigated CEM is measured by two calomel reference electrodes (Prosense B.V., The Netherlands) extended with Haber-Luggin capillaries, and the capillary tips are positioned as close as possible to the

two membrane surfaces. The membrane voltage is recorded every second. At a specific current density, only the membrane voltages measured during the last 20 s are used in the calculation. Mixed electrolytes of equivalent Na^+ and K^+ (or Mg^{2+}) amount are used. The total sulphate concentration in the mixed electrolytes is 0.5 M. Before an ED test, membranes are conditioned in mixed electrolytes out of the cell for at least 24 h. The cell is connected to an ED rig, and the electrolyte is circulated between the cell and external reservoirs. The total electrolyte volume of every liquid stream is 1 L. The linear velocity of electrolyte in the two compartments adjacent to the CEM under investigation is kept constant at 3.85 cm s^{-1} . The electrolyte temperature is maintained at $25 \text{ }^\circ\text{C}$. The limiting current density of each membrane – electrolyte system is determined by two comparative data-processing methods. One is from the intersection of the linearized ohmic and plateau regions in the polarization I-V curve, as sketched by the dashed lines in Figure 1(a) [10, 34-36]. The other is by the Cowan-Brown method as detailed in literature [37], and a representative graph is given in the Supporting Information.

The ion selectivity measurements are performed in a galvanostatic mode. For comparison, the chosen current density in ED is 10 mA cm^{-2} , which is below the limiting values of all the tested systems. The experimental procedures are similar to those for the polarization I-V test, except that the cation concentration in the two liquid streams next to the investigated CEM is monitored. The effective membrane area available for the ion transport is 10.5 cm^2 . An ED experiment lasts for 5 h, the two liquid streams are sampled every 1 h. The composition of the solutions is analysed by conductivity measurements after the

separation with high performance liquid chromatography (HPLC). The samples are

diluted appropriately before injection into the HPLC system.

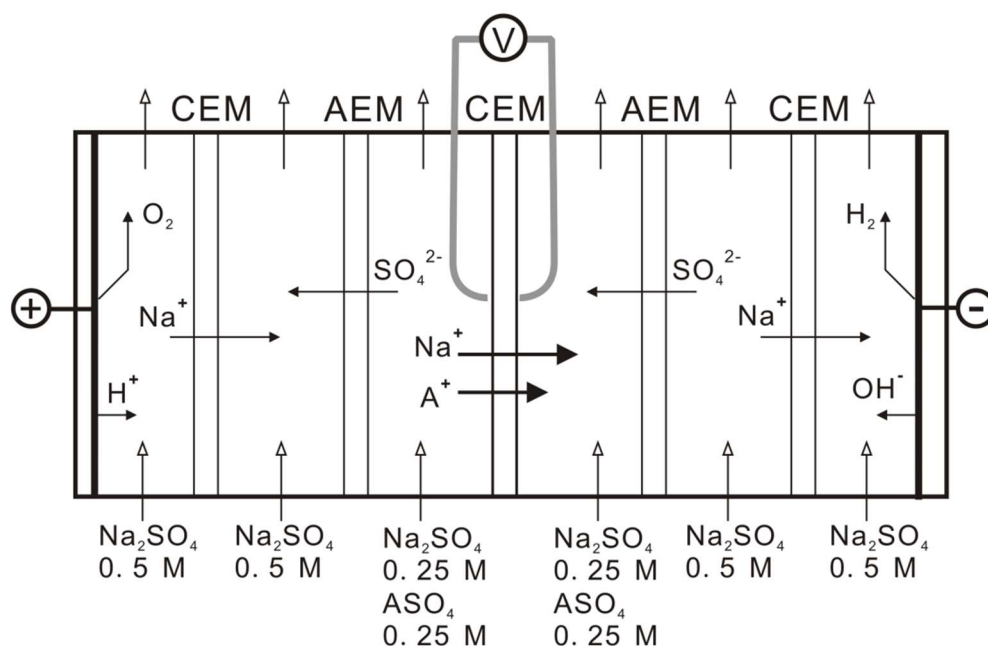


Figure 2. Illustrative of the six-compartment setup for the polarization I-V curve and ion selectivity measurements. The CEM under investigation is placed in the middle. Mixed electrolytes are employed in the two central compartments, ASO_4 indicates either $MgSO_4$ or Na_2SO_4 . CEM and AEM denote a cation and an anion exchange membrane, respectively.

3.3. Ion exchange

The equilibrium ion partition between a mixed electrolyte solution and the membrane phase is studied by ion exchange experiments. Received CEMs are cut into square samples (4×4 cm), immersed in 0.5 M NaCl for 48 h to convert them into Na^+ form. Then membrane samples are dried under vacuum at room temperature. For the perfluorosulfonic acid CEMs (F9120), they are standardized by boiling in acid as done for Nafion [38]. After ion-exchanged into Na^+ form, these perfluorosulfonic acid CEMs are briefly dried by pressing filtration papers upon them. Then the dried samples are brought into excessive (100 ml

for one sample) mixed electrolyte solutions of prescribed composition. All the mixed electrolyte solutions have a total sulphate concentration of 0.5 M. The mixed K_2SO_4/Na_2SO_4 electrolytes have a K^+ equivalence ratio of 0, 0.1, 0.2, 0.4, 0.6 and 1.0, respectively. While the mixed $MgSO_4/Na_2SO_4$ electrolytes have a Mg^{2+} equivalence ratio of 0, 0.1, 0.3, 0.5, 0.75 and 1.0, respectively. Afterwards, the samples are washed in deionized water for 24 h while renewing the solution multiple times. After removal from water, the samples are dried by pressing filtration papers upon them. Subsequently, each sample is ion exchanged with 25 ml 0.5 M $MgSO_4$ solution twice, and the sample is then washed with deionized water multiple times.

All the elution solutions are combined and the total volume is fixed to 500 ml with pure water to give a final Mg^{2+} concentration of around 3 g L^{-1} . The Na^+ and/or K^+ concentrations are analysed by HPLC. As a supplementary method, the K^+ concentration is also assessed by an analytic kit (LCK 328, HACH Lange GmbH, Germany), details are provided in the Supporting Information. All these experiments are performed at room temperature.

3.4. Conductivity measurements by impedance spectroscopy

The ohmic resistance of IEMs equilibrated with pure and mixed electrolyte solutions is investigated by electrochemical impedance spectroscopy (EIS). A customized four-electrode cell with two chambers and a cell rack are constructed. Details can be found in the reference [32]. The mixed electrolyte solutions have a total sulphate concentration of 0.5 M as used for the ion exchange and ED experiments. In fact, the salt concentration has also to be carefully chosen for reliable and reproducible conductivity measurements [39]. Before measurements, the membranes are equilibrated in the solutions for at least 48 h to allow equilibration. During measurements, a membrane sample is sandwiched between the two chambers. The diameter of the effective membrane area in EIS measurement is 16 mm. A potentiostat/galvanostat (320N, Metrohm Autolab) with a frequency response analyser unit is used to apply an AC current of 20 mV amplitude in the frequency range 100 Hz ~ 100 kHz, between the working and the counter electrodes next to the two ends of the cell. The impedance between the

reference and sensor electrodes close to the CEM in the middle of the cell is recorded and the imaginary part of the impedance complex is plotted against its real part to obtain the so-called Nyquist plot. The intercept of the spectra on the real axis in the plot represents the ohmic resistance between the reference and sensor electrodes. The membrane ohmic resistance is obtained by the difference with and without the membrane in the cell. All the measurements are performed at room temperature. The membrane conductivity can then be calculated from the membrane ohmic resistance as:

$$\kappa_i^m = \frac{1}{R_i} \cdot \frac{\delta_{wet}}{A} \quad (26)$$

R_i is the ohmic resistance of hydrated CEMs when the counter-ion is i (Ω), A is the effective cross-sectional area of hydrated CEMs in EIS (2 cm^2). The reported data are based on 3 replicate samples with multiple measurements. By careful experimentation, the accuracy of membrane resistance measurements could be around 20 m Ω .

4. Results and Discussions

4.1. Counter-ion selectivity measured by electro dialysis

In conventional ED methods for the counter-ion selectivity measurements, the current density has to be carefully chosen to make sure the measurements are performed below the limiting current density of the membrane – electrolyte system. One should also not use very low electrolyte concentrations, because next to concentration polarization there is also a resistance contribution due to the Helmholtz double layer from the surface of

IEMs [40, 41], which should be avoided. In this work, the mixed electrolytes have a total sulphate concentration of 0.5 M, and the equivalent ratio of two cations is 1:1. Table 2 lists the limiting values of the studied systems, with results from two different data processing methods (details are provided in the Supporting Information). It is clear that a current density of 10 mA

cm⁻² is well below these limiting values, therefore the approximation of counter-ion concentration at the membrane surface with its concentration in the solution bulk (Figure 1(b), Equation 10) is rationalized.

Table 2. The limiting current densities of different CEM-electrolyte systems

Membranes	i_{lim} (K ⁺ /Na ⁺)		i_{lim} (Mg ²⁺ /Na ⁺)	
	[mA cm ⁻²]		[mA cm ⁻²]	
	I-V curve	Cowan-Brown[37]	I-V curve	Cowan-Brown
CMX	43.3	39.3	31.9	27.3
SPEEK	40.7	37.5	30.2	24.9
F9120	36.4	36.6	24.9	23.8

The cation selectivity is measured by monitoring the concentration evolution of electrolyte streams in ED. As shown in Figure 3, the cation concentrations in the dilute stream decrease linearly as a function of time. The starting solution has two types of cations with 1:1 equivalence concentration, because Mg²⁺ is bivalent, so the starting molar concentration of Mg²⁺ is half of the Na⁺ concentration. The data on the other two types of CEMs (SPEEK and F9120) are provided in the Supporting

Information. The cation flux in ED can be represented by the slope of the linear fitting as shown in the figure. The cation selectivity, as defined by the ratio of concentration-normalized fluxes (Equation 1), is then obtained by the ratio of slopes that normalized by the actual starting cation concentrations. The results are tabulated in Table 3. All the three types of CEMs are more selective towards K⁺ than Na⁺, and also more selective to Mg²⁺. These results are consistent with observations reported in literature [5].

Table 3. The ion selectivity obtained by ED

Membranes	K ⁺ /Na ⁺			Mg ²⁺ /Na ⁺		
	$J_{Na^+}^m \times 10^3$ [mol m ⁻² s ⁻¹]	$J_{K^+}^m \times 10^3$ [mol m ⁻² s ⁻¹]	$P_{Na^+}^{K^+}$ [-]	$J_{Na^+}^m \times 10^3$ [mol m ⁻² s ⁻¹]	$J_{Mg^{2+}}^m \times 10^3$ [mol m ⁻² s ⁻¹]	$P_{Na^+}^{Mg^{2+}}$ [-]
CMX	3.7	5.2	1.43	3.4	2.3	1.34
SPEEK	4.5	5.9	1.31	4.4	2.4	1.09
F9120	4.3	5.5	1.30	4.6	2.6	1.32

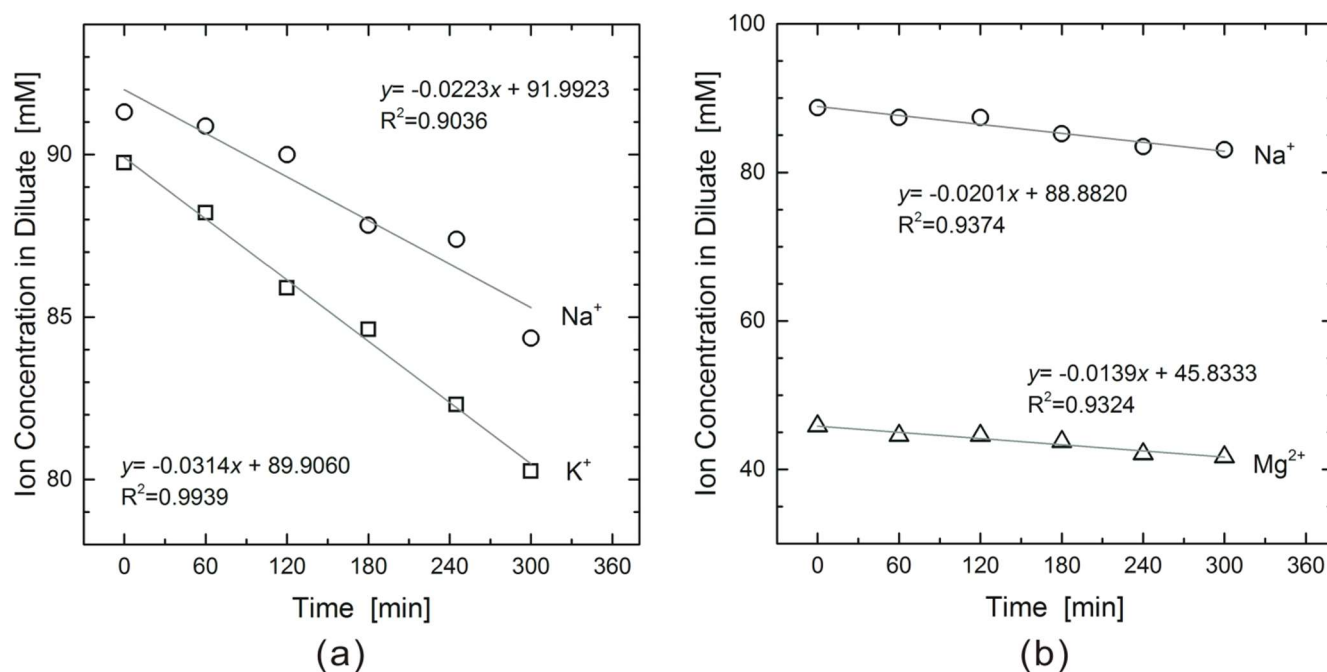


Figure 3. (a) Ion concentration evolution in the dilute solution during ED with mixed ionic solutions. The solution on the feed side contains 1:1 (in equivalence) K⁺ and Na⁺ ions, and the anion is sulphate. (b) Ion concentration evolution in the dilute solution during ED with mixed ionic solutions. The solution on the feed side contains 1:1 (in equivalence) Mg²⁺ and Na⁺ ions, and the anion is sulphate. The current density in ED is 10 mA cm⁻².

4.2. Ion partition isotherm

As revealed by Equation 13, the cation selectivity is a product of the ion partition coefficient and their mobility ratio in the membrane phase. So, the thermodynamic equilibrium ion partition of K⁺/Na⁺ and Mg²⁺/Na⁺ between the mixed electrolytes and CEMs needs to be determined. The counter-ion composition in the CEMs can be obtained by ion exchange and analysed by either HPLC and/or precipitation measurements. The equivalent K⁺ ratio in the membrane phase ($x_{K^+}^m$) determined by HPLC is plotted against its equivalent ratio in the solution phase ($x_{K^+}^s$), which is displayed in Figure 4 (a) for the three CEMs. The dashed diagonal indicates no

preferential partition between the two phases. For brevity, the results obtained by precipitation measurements are provided in the Supporting Information. The two methods give almost identical results. Figure 4 suggests that there is no obvious partition of K⁺ in CMX and only slight enrichment of K⁺ in SPEEK. Interestingly, in the mixture with Na⁺, K⁺ is preferentially present in the perfluorosulfonic acid membrane F9120. This indicates that the affinity between K⁺ and the sulfonic groups in perfluorinated F9120 membrane is stronger as compared with the affinity between Na⁺ and these sulfonic groups. These observations are in line with the experimental results reported by Pintauro et al [42, 43]. The ion partition of K⁺/Na⁺ in these three representative types of CEMs in

general is in accordance with the known principle of ion exchange: cations of larger hard sphere radius are preferentially present in the CEMs [44]. However, as shown by the experimental results here, there is significant difference in ion exchange between the perfluorosulfonic acid CEMs and other non-fluorinated hydrocarbon-based CEMs. Such differences need to be resolved in the future: for the purpose of

demonstrating the proposed methodology, we accept this as experimental evidence merely.

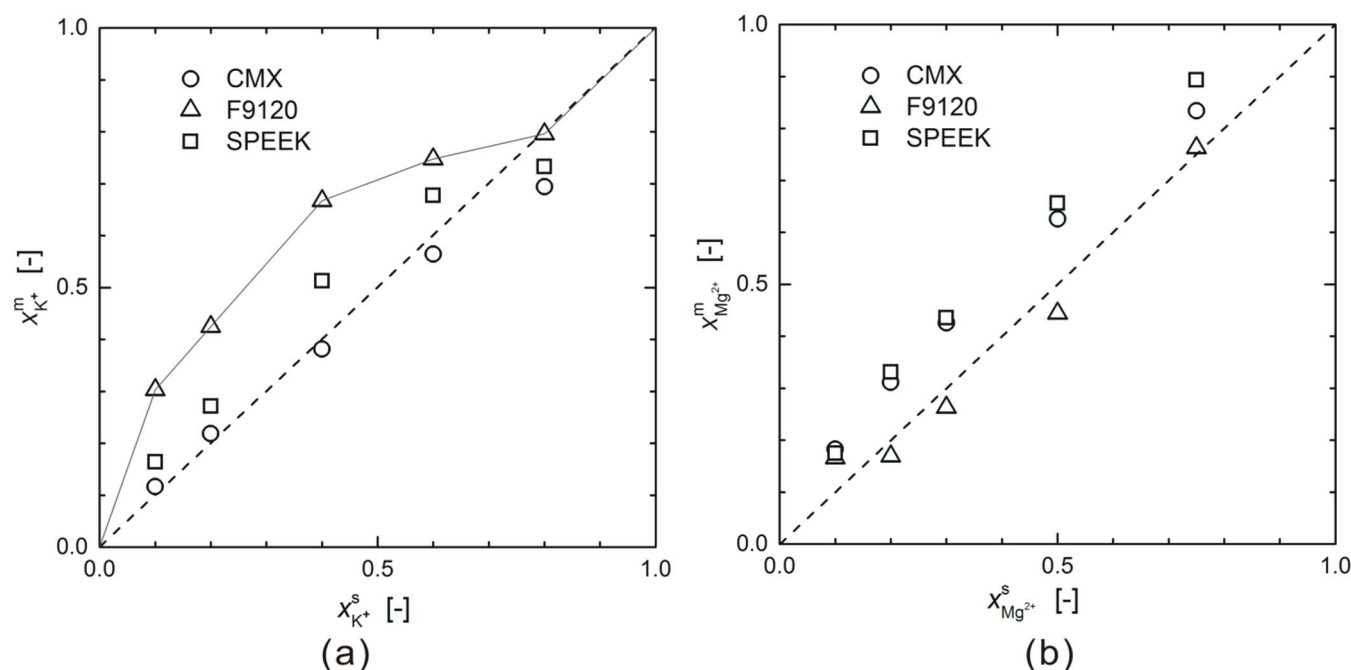


Figure 4. (a) Partition of K^+ ions between the solution and the membrane phase. The equivalent K^+ ratio in the membrane phase, $x_{K^+}^m$, is plotted against its equivalent ratio in the solution $x_{K^+}^s$. The other counter-ion is Na^+ . The line connecting data points is to guide the eyes. (b) Partition of Mg^{2+} ions between the solution and the membrane phase. The equivalent Mg^{2+} ratio in the membrane phase, $x_{Mg^{2+}}^m$, is plotted against its equivalent ratio in the solution $x_{Mg^{2+}}^s$. The other counter-ion is Na^+ . The dashed diagonal indicates no preferential partition between the two phases.

The equilibrium Mg^{2+} partition, with the concomitant presence of Na^+ , between CEMs and the solution phase is presented in Figure 4 (b). Mg^{2+} ions are enriched in CMX and SPEEK membranes, as compared to the solution composition. The partition of Mg^{2+} in CMX and SPEEK is also almost identical. This observation is also consistent

with the generally accepted principle of ion exchange: ions of higher valence are preferentially present in ion exchange membranes [44]. However, as shown in Figure 4 (b), the Mg^{2+} composition in the F9120 membrane and in the solution is almost identical, which means that there is no preferential partition of Mg^{2+} in this

perfluorosulfonic acid CEM. Also these results indicate that there is significant difference between the perfluorosulfonic acid CEM and the non-fluorinated hydrocarbon-based CEMs (CMX and SPEEK) with regard to the cation partition.

4.3. Membrane conductivity

The through-plane resistance of CEMs is measured by electrical impedance spectroscopy EIS. A group of representative Nyquist plot data are shown in Figure 5.

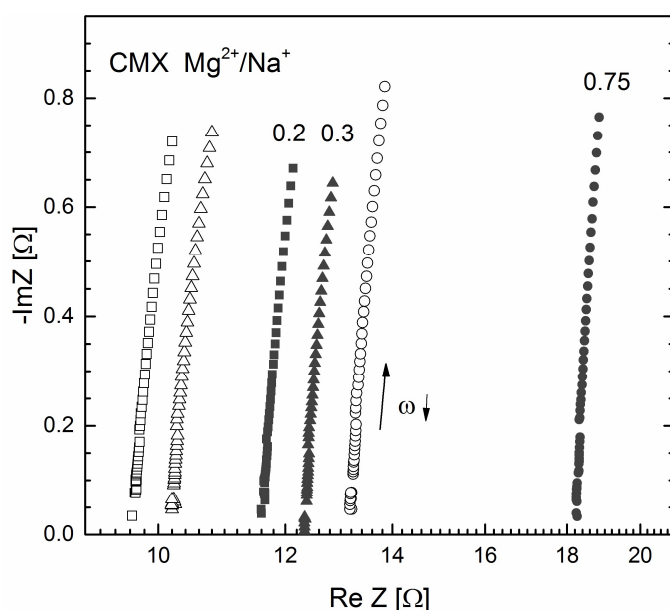


Figure 5. The imaginary vs. the real part of measured impedance (Nyquist plots) with (filled symbols) and without (hollow symbols) the cation exchange CMX membranes. The electrolytes are mixed MgSO_4 and Na_2SO_4 solutions, with the equivalent Mg^{2+} ratio in total cations as indicated by the numbers in the graph. For brevity, only parts of these plots are shown here.

After obtaining the membrane ohmic resistance as described in Section 3.4, the through-plane membrane conductivity is calculated with Equation 26. The results about CEMs with K^+/Na^+ ions are shown in Figure 6. As can be seen, for two monovalent cations, the membrane conductivity of all the three types of CEMs is a linear function of the equivalent membrane cation composition. The straight lines are least-square linear fitting of experimental data points, the regression functions together with coefficients of

determination are shown in the figure. For the CMX and SPEEK membranes, the membrane conductivity increases as the equivalent K^+ ratio in the membrane phase increases. This results from higher mobility of K^+ ions in the membrane as compared with Na^+ ions, which is also consistent with the mobility of these two ions in aqueous solutions at infinite dilution [5, 29]. Quite interestingly, the membrane conductivity of the perfluorosulfonic membrane F9120 decreases with an increase of equivalent K^+ ratio. This means that K^+ ions in this type of membranes are less mobile than Na^+ ions, which is opposite to the situation in aqueous

solutions. Shi et al. have observed that similar perfluorosulfonic CEM (Nafion) shows cation-content dependent membrane conductivity; and at high membrane hydration levels (eg. in water), the membrane conductivity is more controlled by the membrane water contents [45]. In our study, the equilibrium water content of

F9120 in Na⁺ form is 16.9 wt.%, while the value of K⁺ form F9120 is much less and is only about 7.6 wt.% (Supporting Information, Table S1). We think that the lower K⁺ mobility in this type of perfluorosulfonic CEM can be also ascribed to the low hydration ability of K⁺ ions in these membranes, as compared to Na⁺ ions.

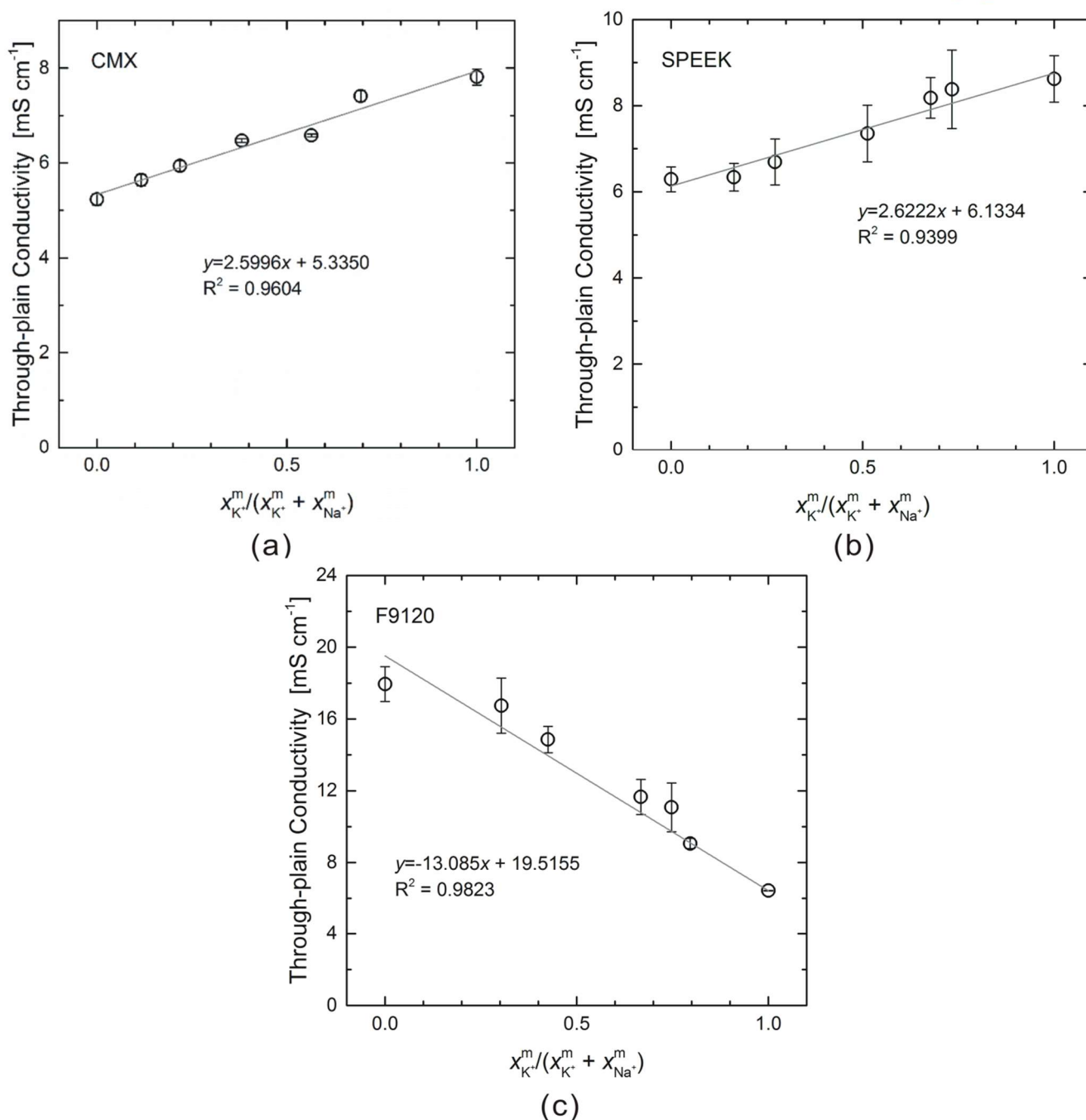


Figure 6. The through-plane ionic conductivity of CMX (a), SPEEK (b) and F9120 (c) CEMs as a function of the equivalent cation composition in the membrane phase. These CEMs have been equilibrated in K₂SO₄/Na₂SO₄ solutions with varying K⁺/Na⁺ equivalence ratios.

The straight lines are linear fittings of experimental data points. The error bars represent standard deviations of data based on three replicate samples.

Figure 7 shows the through-plane conductivity of CEMs with varying $\text{Mg}^{2+}/\text{Na}^+$ equivalence ratios in the membrane phase. Interestingly, the conductivity of CMX and SPEEK has also excellent linear correlation with the equivalent Mg^{2+} ratio in the membrane phase. It is necessary to stress that the conductivity is plotted against the equivalent Mg^{2+} ratio, not the molar ratio of Mg^{2+} . It is not a big surprise that membrane conductivity changes linearly with the equivalent ratio of K^+ in a counter-ion mixture with two monovalent cations (Figure 6). However, for the monovalent Na^+ and bivalent Mg^{2+} considered here, these results indicate that the membrane conductivity is also a linear function of the equivalent counter-ion composition. Therefore, the assumption necessary for the counter-ion selectivity calculation by the conductivity data (**Equation 19**) is validated experimentally, at least for the $\text{Mg}^{2+}/\text{Na}^+$ pair in two types of CEMs. Actually Le et al. already observed the linear dependence of membrane conductivity on the equivalent membrane $\text{Ni}^{2+}/\text{H}^+$ composition in a CEM very similar to CMX [46]. So, it is reasonable to

envision that this linear dependence is valid in hydrocarbon-based CEMs, because the rearrangement of fixed ionic groups in these CEMs is not as easy as in their perfluorosulfonic analogues [47]. As indicated by Figure 7(c), the conductivity of the F9120 membrane can hardly be correlated in a linear fashion with the membrane counter-ion composition, especially there is large deviation of measured conductivity when some Mg^{2+} ions are present in a Na^+ -enriched membrane. Only obvious is the lower mobility of Mg^{2+} ions as compared with Na^+ ions in the membrane phase. In summary, the linear dependence of membrane conductivity on the equivalent counter-ion composition in the membrane phase (**Equation 19**) has been confirmed experimentally, except for $\text{Mg}^{2+}/\text{Na}^+$ in the perfluorosulfonic CEM F9120 (Figures 6 and 7). Therefore, it is possible to obtain the membrane counter-ion composition by the membrane conductivity data, for both mono-/mono- and mono-/bivalent counter-ion pairs, except for the mono-/bivalent counter-ion pair in perfluorosulfonic acid CEMs.

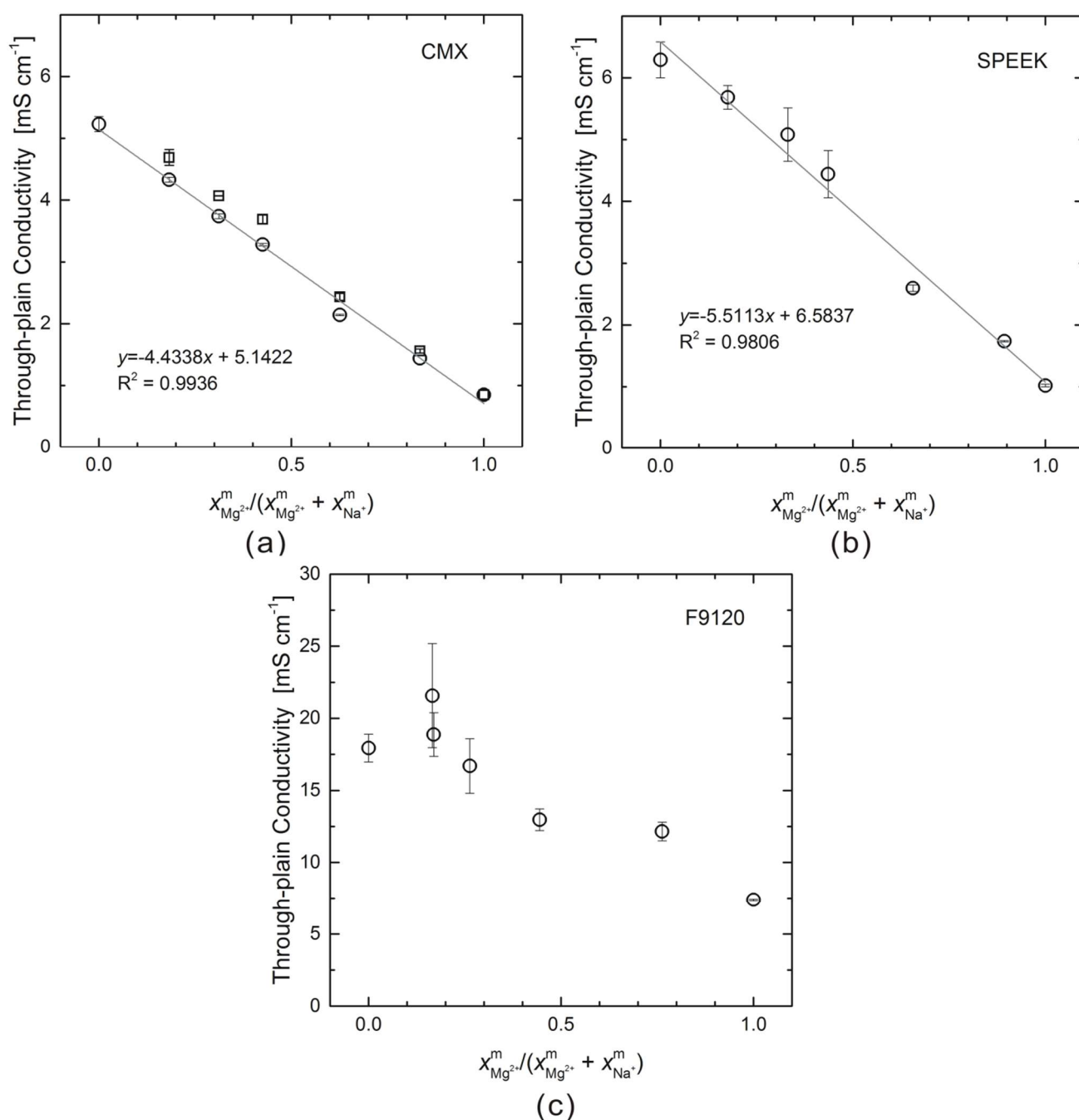


Figure 7. The through-plain ionic conductivity of CMX (a), SPEEK (b), and F9120 (c) as a function of the equivalent cation composition in the membrane phase. These CEMs have been equilibrated in MgSO₄/Na₂SO₄ solutions with varying Mg²⁺/Na⁺ equivalence ratios. The straight lines are linear fittings of experimental data points.

As predicted by Equation 25, the selectivity between two different counter-ions can be calculated with the membrane conductivity and the swelling degree (SD) at pure counter-ion forms and at mixed

counter-ion forms. The membrane conductivity values when the solution has 1:1 equivalence ratio of two counter-ions ($\kappa_{0.5}^m$) are listed in Table 4, together with the SD under such conditions ($SD_{0.5}$). The

reported $SD_{0.5}$ in mixed K^+/Na^+ solutions are based on 5 samples, standard deviations are also provided in the table.

Table 4. Experimental membrane conductivity and swelling degree (SD) data

Membranes	K^+/Na^+				Mg^{2+}/Na^+		
	$\kappa_{Na^+}^m$ [mS cm^{-1}]	$\kappa_{K^+}^m$ [mS cm^{-1}]	$\kappa_{0.5}^m$ [mS cm^{-1}]	$SD_{0.5}$ [%]	$\kappa_{Mg^{2+}}^m$ [mS cm^{-1}]	$\kappa_{0.5}^m$ [mS cm^{-1}]	$SD_{0.5}$ [%]
CMX	5.23	7.81	6.86	12.5±1.3	0.85	2.14	13.7
SPEEK	6.29	8.62	7.66	14.9±3.9	1.02	2.60	19.0
F9120	17.94	6.43	13.65	20.2±0.9	7.40	12.97	20.4

4.4. Counter-ion selectivity obtained by conductivity measurements

The linear dependence of membrane conductivity on the equivalent counter-ion composition in the membrane phase (Equation 19) has been confirmed experimentally, except for Mg^{2+}/Na^+ in the perfluorosulfonic CEM F9120 (Figures 6 and 7). Then it is possible to extract the membrane counter-ion composition directly from the measured membrane conductivity data (Equation 23), and consequently it is possible to calculate the counter-ion selectivity with the experimental conductivity and SD data as summarized in Table 4, by Equations 24 or 25.

Table 5 tabulates the calculated cation mobility ratios, partition coefficients and selectivity values. The selectivity values measured by ED are also shown here as comparison. The mobility ratio between K^+ and Na^+ in CEMs is calculated, by Equation 22, with the conductivity and SD data of membranes at pure counter-ion forms. The equilibrium partition coefficient K_j^i (Equation 23) is also reckoned with these two parameters when the membranes are equilibrated with known equivalence ratio

of the two counter-ions in the solution. To compare the selectivity values obtained by ED and the conductivity approach at identical conditions, the membrane conductivity equilibrated with 0.5 equivalent K^+ ratio in the solution is needed. These values are approximated by averaging the conductivity at solution K^+ ratios of 0.4 and 0.6. Because the accuracy of measured SD data have large impact on the calculation results, the SD of CEMs in solutions with 0.5 equivalent K^+ ratio is measured experimentally. The calculated partition coefficients of K^+/Na^+ for CMX and SPEEK are close to unity, their respective values are very close to experimental values (Figure 4(a), calculated *via* Equation 12, 1.02 for CMX and 1.18 for SPEEK). For the perfluorosulfonic CEM F9120, the partition coefficient calculated with the conductivity data also confirms the enrichment of K^+ ions in the membrane phase, and the calculated value is also quite close to the experimental one (1.46). The K^+/Na^+ selectivity values $P_{Na^+}^{K^+}$ of CMX and SPEEK calculated from the conductivity data is remarkably close to those measured directly by ED, as displayed in Table 5. Since the partition coefficients of K^+/Na^+ calculated from the conductivity data agree well with the experimental values, the

excellent accuracy of K^+/Na^+ selectivity calculation by the conductivity data suggests that the calculated mobility ratio of these two ions in the membrane also reflects the actual mobility ratio of these two ions within such CEMs in practical ED process. However, for the F9120 membrane, the K^+/Na^+ selectivity calculated from the conductivity data is substantially smaller than the value obtained by ED. This discrepancy could only be ascribed to the underestimation of the K^+/Na^+ mobility ratio by the membrane conductivity data. The selectivity obtained by ED and the measured partition coefficient for F9120 indicate that the actual mobility of K^+ within the membrane should be only slightly smaller compared with Na^+ in the ED process. There might be two possible explanations to this. The first one is the difference of mobility values measured under conditions of direct current (DC) and alternating current (AC) [29]. The counter-ions electromigrate through the CEMs in the ED process driven by constant electric gradient, while in EIS the counter-ions are expected to oscillate in the membrane matrix as are influenced by the applied oscillating electric field. Due to the high

possibility of interference imposed by surrounding ionic atmosphere in an oscillating field [29], the mobility measured by EIS might be smaller than the value obtained by ED. Because EIS gives reasonably good mobility ratios of K^+/Na^+ in the other two CEMs (CMX and SPEEK), only the microstructure difference between perfluorosulfonic CEMs and other hydrocarbon-based CEMs [47], or the greater significance of ion hydration in perfluorosulfonic CEMs might support this explanation [38, 48]. The second explanation is the difference of activity coefficients for K^+ and Na^+ in the membrane. This could account for the observed discrepancy rationally. All the parameters that might influence the ion mobility can be included into the activity coefficients of ions, like ion – sulfonate group interaction, ion hydration and so on [42, 43]. Nevertheless, at the present stage, we could conclude that it is possible to obtain the selectivity of two monovalent cations in hydrocarbon-based CEMs by the membrane conductivity and SD data.

Table 5. Ion selectivity calculated from the experimental membrane conductivity

Membranes	$x_{K^+}^s$	$u_{K^+}^m/u_{Na^+}^m$	$K_{Na^+}^{K^+}$	$P_{Na^+}^{K^+}$	$P_{Na^+}^{K^+}$ (ED)
CMX	0.4 & 0.6	1.62	0.92	1.48	1.43
SPEEK	0.4 & 0.6	1.19	1.16	1.37	1.31
F9120	0.4 & 0.6	0.34	1.39	0.47	1.30
Membranes	$x_{Mg^{2+}}^s$	$u_{Mg^{2+}}^m/u_{Na^+}^m$	$K_{Na^+}^{Mg^{2+}}$	$P_{Na^+}^{Mg^{2+}}$	$P_{Na^+}^{Mg^{2+}}$ (ED)
CMX	0.5	0.33	2.06	0.69	1.34
SPEEK	0.5	0.31	2.30	0.70	1.09
F9120	0.5	0.74	0.87	0.65	1.32

For a mono-/bivalent cation pair, Mg^{2+}/Na^+ , the selectivity values calculated

from the membrane conductivity data are in general smaller than the ones measured by

ED. For CMX and SPEEK, even there is slight overestimation of the partition coefficients as compared with experimental values (Figure 4(b), calculated *via* Equation 22, 1.25 for CMX and 1.31 for SPEEK), the selectivity values calculated from the membrane conductivity data are still smaller. This means that for all the three types of CEMs the Mg^{2+}/Na^+ mobility ratios in the membrane phase are underestimated. Notably a selectivity value by ED is roughly twice of its corresponding value derived from the conductivity data: this implies that only the difference of activity coefficients

To exclude the possible influence of experimental errors on this underestimation of Mg^{2+}/Na^+ mobility ratios in the CEMs, a comparison of the Mg^{2+}/Na^+ mobility ratios, partition coefficients and selectivity values calculated as discussed above (with only 3 solution compositions, $x_i^s = 0, 0.5$ and 1) and by a linear regression of the experimentally obtained conductivity data (with 7 solution compositions, Figures 6 and 7) is shown in Table 6. The regression

of Mg^{2+} and Na^+ could provide rational explanations. Another observation necessary to stress is the larger Mg^{2+}/Na^+ mobility ratio in F9120 as compared with the ratios in the other two CEMs, this is in accordance with the fact that perfluorosulfonic CEMs have larger ionic channels in the membrane matrix when fully hydrated [49, 50]. The F9120 membranes with Mg^{2+} and Na^+ counter ions are in general more conductive than corresponding hydrocarbon-based CEMs (SPEEK and CMX).

function could then be used to give more accurate single ion mobility values and then provide mobility ratios that are less influenced by experimental errors. As shown in Table 6, the Mg^{2+}/Na^+ ratios obtained by two methods differ negligibly, even though the partition coefficients obtained from the regression data are closer to experimental values. This further excludes the possible influence of experimental errors on the mobility ratios.

Table 6. Calculation of the counter-ion selectivity from experimental conductivity data with and without regression

Membr.	With Regression(n=7)*				Without Regression (n=3)		
	$x_{Mg^{2+}}^s$	$u_{Mg^{2+}}^m/u_{Na^+}^m$	$K_{Na^+}^{Mg^{2+}}$	$P_{Na^+}^{Mg^{2+}}$	$u_{Mg^{2+}}^m/u_{Na^+}^m$	$K_{Na^+}^{Mg^{2+}}$	$P_{Na^+}^{Mg^{2+}}$
CMX	0.5	0.28	1.44	0.41	0.33	2.06	0.69
SPEEK	0.5	0.31	1.89	0.58	0.31	2.30	0.70
F9120	0.5	-	-	-	0.74	0.87	0.65

*n indicates the number of different solution compositions employed in the CEM equilibration for the conductivity measurements.

The results presented in this section prove that the selectivity of the mono-/monovalent cation pair, K^+/Na^+ , can be readily calculated from the membrane conductivity and swelling degree data for hydrocarbon-based CEMs (CMX and SPEEK), not for the perfluorosulfonic CEM (F9120). While for the bi-/monovalent cation pair, Mg^{2+}/Na^+ , the selectivity calculated from the membrane conductivity data is generally smaller compared with the results measured by ED. This underestimation of Mg^{2+}/Na^+ selectivity is due to smaller Mg^{2+}/Na^+ mobility ratios calculated from the membrane conductivity data. The underestimation of the bi-/monovalent cation selectivity in all CEMs, and the discrepancy of mono-/monovalent cation selectivity in perfluorosulfonic CEM possibly stem from the activity coefficients for cations with different valences, and the cation activity coefficients in CEMs with different chemistry [51-53]. This will be the focus of our next report to complement the proposed methodology for the convenient characterization of the counter-ion selectivity.

It is also necessary to stress that, in this work, the combination of conductivity measurements on CEMs with pure counter-ions for their mobility ratio in the membrane (Equation 22) and conductivity measurements on CEMs with mixed counter-ions for their partition coefficient between the membrane and the solution (Equation 23) can decouple the effect of partition and mobility in controlling the selectivity. This can hardly be achieved by the conventional ED method.

5. Conclusions

The selectivity of mono-/monovalent cations (K^+/Na^+) and bi-/monovalent cations (Mg^{2+}/Na^+) for three representative types of cation exchange membranes (CEMs) is studied theoretically and experimentally. From the ion flux equation in electrodialysis (ED) for the conventional counter-ion selectivity measurements, it is deduced that the measured selectivity coefficient can be expressed as the product of two terms: the partition coefficient of the two different counter-ions between the solution and the membrane phase (K_B^A), and the mobility ratio of these two counter-ions in the membrane phase (u_A^m/u_B^m). Linked through the ion mobility in the membrane phase, the selectivity of counter-ions could be related to the membrane conductivity. Under the assumption that the membrane conductivity varies linearly with the equivalent counter-ion ratio in the membrane, the counter-ion selectivity can be simply expressed by the membrane conductivity and swelling degree when the membranes are respectively equilibrated with solutions of counter-ion A, B and mixed A/B. This proves in theory that the counter-ion selectivity of ion exchange membranes could be calculated from the membrane conductivity with different mixture compositions and swelling degree data, which is the basis for such a simple and convenient characterization method.

The assumption is validated experimentally with K^+/Na^+ and Mg^{2+}/Na^+ ion pairs for two CEMs based on hydrocarbon polymers (CMX and SPEEK membranes), with K^+/Na^+ for one type of perfluorosulfonic acid CEM (F9120). However, there exists strong mutual

influence of Mg^{2+} and Na^+ in the F9120 membrane, which makes the membrane conductivity not linearly-dependent on the equivalent cation composition.

The K^+/Na^+ selectivity coefficient calculated from the membrane conductivity data is identical to the one measured from ED, which strongly substantiates the theory proposed in this study. However, for the perfluorosulfonic membrane F9120, even though the K^+/Na^+ partition coefficient calculated from the membrane conductivity data agrees well with the experimental value, the K^+/Na^+ mobility ratio is underestimated by the conductivity data. It is also observed experimentally that the K^+ mobility in perfluorosulfonic acid CEM is lower than the Na^+ mobility, contrary to the situation in other hydrocarbon-based CEMs and in the bulk solution.

For bi-/monovalent cations Mg^{2+}/Na^+ , the counter-ion selectivity coefficients calculated from the conductivity data for all three types of CEMs are roughly half of their corresponding ones measured from ED. This might be ascribed to the influence of ion activity coefficients in the membrane. K^+ and Na^+ likely have activity coefficients close to each other, therefore the influence cancels each other in the calculation; while the activity coefficient of Mg^{2+} is probably roughly half of the Na^+ activity coefficient, and the influence is then revealed. This will be the focus of further research to complement the method proposed in this study for the counter-ion selectivity characterization.

In general, this work offers a convenient method to decouple experimentally the effect of partition and mobility in controlling the membrane

selectivity, and also provides a perspective to link the selectivity and conductivity of ion exchange membranes, which hopefully helps future studies to gain deeper insight into the transport properties of novel ion exchange membranes.

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