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Review

Connecting the Ion Separation Factor to the Sorption and Diffusion Selectivity of Ion Exchange Membranes

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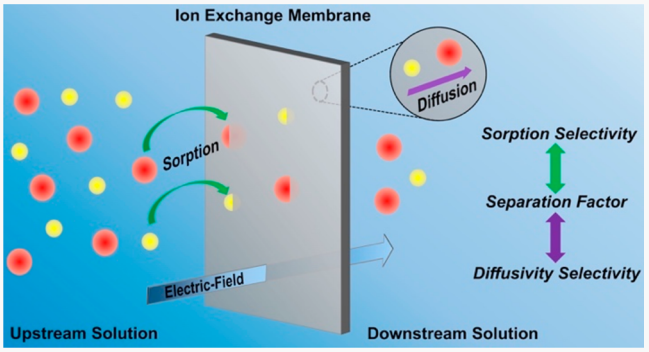
ABSTRACT: To optimize the productivity of ion exchange membranes used in electric field-driven ion separation processes, an understanding of the relationship between membrane structure−property metrics and a measure of ion separation is necessary. The membrane separation factor is a commonly used indicator of ion separation efficacy, and as outlined in this review, it can be related to the intrinsic sorption and diffusion selectivity properties of the membrane. Doing so connects the separation factor to key theories that describe ion transport, and this connection facilitates an analysis of the implications of these theories on electric field-driven ion separations. The process of electrodialysis and ion exchange membranes can be applied for both desalination and ion separation applications, and this review discusses relationships between commonly used metrics for electric field-driven transport (e.g., transport number) and properties commonly used in desalination contexts (e.g., sorption and diffusivity selectivity). These relationships provide context for commonly observed experimental trends. Additionally, some common assumptions (and their implications for describing membrane transport properties related to a multicomponent ED system) are discussed. This review also links fundamental membrane properties (such as sorption and diffusivity selectivity) to ion separation-critical properties (such as the ion exchange affinity). While the diffusivity selectivity may be more important at lower current density values, the sorption selectivity is expected to be important across a wider range of current density values. This review further highlights the interconnected manner by which ion exchange membrane properties and external process conditions couple to influence ion separation performance.



1. INTRODUCTION

Natural resources and energy, such as freshwater, minerals, and electricity, are indispensable to human life and the development of society, yet continuous global population growth continues to lead to increased demand that challenges the supply of each.[1−7] Polymer membrane-based separation processes are known for high efficiency, reliability, and cost-effectiveness, and they have been widely applied to mitigate stresses on the global supply of natural resources (particularly water) and are being considered to address challenges related to emerging production and storage of clean-energy.[8−11] For example, highly selective reverse-osmosis (RO) membranes can effectively desalinate water,[12−24] and ion exchange membranes (IEMs) can be used to selectively extract target ions from a mixture of electrolytes[25−31] or to serve as a selective, conductive barrier in batteries and fuel cells.[25,32−43] Among these membrane-based separations, electric field-driven membrane-based processes are of particular interest in the field of desalination,[44−50] specific ion separations,[31,51−66] and energy applications.[67−74] Processes, including electrodialysis (ED) (for desalination and/or specific ion separations) and reverse electrodialysis (for energy production), have been scaled up in response to this interest.

The electric field-driven nature of ED can lead to higher process costs in some cases as electricity can be more expensive compared to other driving forces (e.g., thermal energy and pressure) that are used to accomplish separations.[9,49,75] However, when ED is used in ion separation applications, the high cost of electricity could be overcome by the value of the recovered ions. This situation could be particularly true if the ions, e.g., lithium,[76−79] or rare Earth elements,[80−82] are sufficiently valuable.

In a typical ED application, cation exchange membranes (CEMs, which contain fixed negatively charged functional groups) and anion exchange membranes (AEMs, which

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contain fixed positively charged functional groups) are stacked in an alternating fashion. As a current is applied, cations will transport preferentially across the CEMs while anions will transport preferentially across the AEMs.[54,73,83,84] If the relative rates of transport of one cation, versus another, through the CEM (or one anion, versus another, through the AEM) are different, then ED can be used to fractionate ions and to enrich a target ion via the process. Different strategies, such as mixing nanomaterials into IEMs[85,86] or coating oppositely charged layers and/or layer-by-layer deposition of polyelectrolytes,[60,62−64,87−89] have been considered to enhance this form of selectivity. These modifications suggest promising strategies for developing novel IEMs that would enable the capture or enrichment of specific ions from a multielectrolyte solution.

Several critical challenges, such as membrane selectivity, productivity, and durability, still need to be addressed before this form of ion separation will likely be viable. First, many of the high value target ions (e.g., Li^+) are present at very low concentrations compared to other ions (e.g., Na^+ and Mg^{2+}) in the solution. Therefore, membranes offering high selectivity for the target ion over other ions are needed.[76−79] Also, the process must be productive enough to be viable. Low productivity in ED leads directly to higher energy consumption and operating costs.[76−79] Finally, membrane durability must also be considered when designing new IEMs. If, for example, ion selective surface coatings[60,62−64,87−89] become damaged over time,[90,91] repair or replacement of the membranes will result in greater cost over time.

Addressing these challenges could be facilitated by improved understanding of structure−property relationships in IEMs. For example, understanding what specific functional groups enhance the separation of specific ions would go a long way toward engineering new ion selective membranes. While efforts have been underway, for some time, to answer these questions, this area represents an opportunity for polymer science and engineering to understand how the interplay of chemistry and membrane structure contribute to transport mechanisms and ultimately transport properties.

Recently, the greater importance of water/salt selectivity compared to productivity has been emphasized.[92,93] It is likely that the corresponding view (that selectivity is particularly critical) may also be the case for IEMs used in electric field-driven processes because small molecule transport is highly analogous in these membranes. The ion selectivity of an IEM can be deconvoluted into sorption and diffusion selectivities,[94] and both of these selectivity values can be engineered to achieve selective transport of one ion over others. For example, the membrane could be engineered to preferentially sorb the target ion while excluding the others. Additionally or perhaps alternatively, it could be engineered to preferentially restrict the rate of transport of the other ions relative to the target ion. This review discusses the connections between sorption and diffusion selectivity and the overall ion selectivity of an ion exchange membrane.

Here, the ion selectivity and its sorption and diffusion selectivity contributors are discussed for ion exchange membranes using the framework of the solution-diffusion model. First, relevant theory is discussed followed by discussion of some implications of those theories. In addition to introducing and discussing the different ion selectivity measures for ion exchange membranes, we review several methods that are commonly used to quantify sorption and diffusion selectivity. We also review important assumptions and potential artifacts that are associated with the different methods for determining sorption and/or diffusion selectivity properties. Ultimately, the discussion connects measures of ion selectivity to sorption and diffusion contributors in an effort to provide insight for engineering next generation ion exchange membranes.

2. THEORY

2.1. Separation Factor. The separation factor (SF) describes the tendency of a target ion, i, to pass through a membrane relative to some other ion, j. Typically, the separation factor (sometimes also called the selectivity or permselectivity) is defined as a ratio of concentration normalized fluxes:[95,96]

$$\mathrm{SF} \equiv \frac{J_i/C_i^s}{J_j/C_j^s} \tag{1}$$

where J_i is the average flux of ion i, and C_i^s is the concentration of ion i in the upstream solution. Normalizing the flux by the ion concentration in the upstream solution accounts for differences in concentration, as J_i/C_i^s is effectively the permeance of ion i in the limit where the ion concentration on the upstream side of the membrane is much greater than that on the downstream side of the membrane.[6,9,97] Thus, SF can be viewed as a ratio of the permeance of i to that of j, and it is often used as a measure of the separation effectiveness (i.e., ion i is typically chosen to be the target ion so that SF > 1) of a membrane for ion separation applications (e.g., electrodialysis and Donnan dialysis).[76,98]

The separation of ions can also be evaluated using the separation efficiency parameter, S_{EP}, which is based on the initial concentrations of the ions in the dilute solution and the concentrations of the ions in the dilute solution after a fixed amount of operating time.[99,100] The two approaches for characterizing the ion separation are related. In an effective separation where i is the target component, the permeance of i is greater than that of component j. Therefore, in an effective separation process, one would expect the retention of component j at any time t to be greater than the retention of component i, and this situation results in a separation efficiency parameter greater than zero and a separation factor greater than unity. For the purpose of this review, we will focus on the separation factor (eq 1) as it describes the relative rates of transport of component i to that of component j.

In addition to eq 1, the separation factor is, in some cases, also expressed as the ratio of the flux of i to that of j.[101] In this approach, the upstream solution concentrations are not used. This approach can be useful from a process engineering point of view because it provides direct insight into how many i ions transfer per each j ion.

Alternatively, when SF is defined as a ratio of ion permeances, it provides insight into how intrinsic membrane properties affect the ion separation. As a ratio of ion permeance values, eq 1 considers both the relative number of ions transferred (i.e., flux) and the ion availability (i.e., concentration). For example, in typical Li^+/Mg^{2+} separations, the feed solution typically contains much less Li^+ compared to Mg^{2+} (e.g., the molar ratio of Li^+/Mg^{2+} can be on the order of 0.1 depending on the source).[76] In a membrane separation process, the Li^+ flux would be expected to be much less than that of Mg^{2+} as a result of the smaller driving force for Li^+

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Table 1. Summary of the SF Expressions Discussed in section 2.1[a]

index for separation efficiency	definition/formula	applicability
	$\mathrm{SF} \equiv \frac{J_i/C_i^s}{J_j/C_j^s}$	general by definition
separation factor (SF)	$\mathrm{SF} = \frac{K_i D_i^m}{K_j D_j^m} = \frac{P_i}{P_j}$	dense membranes; transport driven by a concentration gradient
	$\mathrm{SF} \cong \frac{z_i}{z_j}\frac{K_i D_i^m}{K_j D_j^m}$	dense membranes; transport driven by an electric field
separation efficiency parameter (S_{EP})[99,100]	$S_{EP}(t) = \frac{\{c_j(t)/c_j(0)\} - \{c_i(t)/c_i(0)\}}{\{1 - c_j(t)/c_j(0)\} + \{1 - c_i(t)/c_i(0)\}} \times 100\%$	general by definition

[a]The separation efficiency parameter, S_{EP}, stems from an ion retention perspective and is based on the initial concentrations of the ions in the dilute solution and the concentrations of the ions in the dilute solution after a fixed amount of operating time.[99,100] The criteria for an effective separation, where component i is the target ion, are SF > 1 and S_{EP} > 0.

transport compared to that for Mg^{2+} transport. Consequently, comparing only the Li^+ and Mg^{2+} fluxes could lead to the conclusion that the membrane is ineffective, as a greater flux of Mg^{2+} (i.e., the interfering ion) is observed relative to that of Li^+ (i.e., the target ion). However, the process may actually enrich Li^+ (relative to Mg^{2+}) in the product solution if SF > 1. This enrichment means that Li^+ (i.e., the target ion) is concentrated in the product solution compared to the feed solution, which is the hallmark of an effective process.[76,98] Therefore, SF, as defined in eq 1, is a useful figure of merit to inform membrane performance for ion separations.

The definition of SF in eq 1 can be used to derive alternate expressions for the separation factor.[56,57] Often, arriving at these expressions requires knowledge of or assumptions about the ion transport mechanism in the membrane. Here we focus on dense, nonporous ion exchange membranes where transport is described using the solution-diffusion model.[102−104] While porous membranes have, in some cases, been used in electrodialysis applications,[51,105] the scope of this review is limited to dense, nonporous membranes. The solution-diffusion model describes cross-membrane ion transport as a three-step process.[102,103,106] First, ions sorb (or partition) into the membrane from the upstream solution. Next, the ion diffuses through the membrane, and finally, the ion desorbs into the downstream solution.

Fick's law is often used as the constitutive equation to relate flux to an external concentration difference driving force.[3,107] When the concentration difference across the membrane is approximately equal to the concentration on the upstream side of the membrane (i.e., $C_i^s \gg C_i^{s,downstream}$), Fick's law can be written as[107]

$$J_i = \frac{K_i D_i^m}{L} C_i^s \tag{2}$$

where D_i^m is the average diffusion coefficient of ion i in the membrane phase, L is the membrane thickness, and the ion sorption coefficient is defined as $K_i \equiv C_i^m/C_i^s$, where C_i^m is the concentration of i in the membrane phase at the upstream face.[102,106] The product of the sorption and diffusion coefficient (i.e., $K_i D_i^m$) is typically called the permeability of ion i, and this permeability therefore encapsulates the sorption and diffusion components of the solution diffusion model.[97,103] Correspondingly, the separation factor can be expressed as

$$\mathrm{SF} = \frac{K_i D_i^m}{K_j D_j^m} = \frac{P_i}{P_j} \tag{3}$$

where the separation factor is also equal to the ion i/j permeability selectivity (i.e., the ratio of the permeability of ion i, P_i, to that of ion j, P_j).

In ion separation processes seeking to separate ions of like charge, electric fields are often used to drive ion transport. Therefore, in the limiting case where ion transport is driven primarily by an electric field, the ion flux and separation factor can be expressed in terms of ion transport numbers as[89,108]

$$J_i = \frac{I t_i}{z_i F} \tag{4}$$

$$\mathrm{SF} = \frac{z_j}{z_i}\frac{t_i/C_i^s}{t_j/C_j^s} \tag{5}$$

where I is the current density, z_i is the valence of ion i, t_i is the transport number of i, and F is Faraday's constant. The appearance of the ion valences in eq 5 accounts for differences in the influence of the electric field on the transport of ions of different valence. The transport number describes the fraction of current carried by a particular ion and is defined as[25,94]

$$t_i = \frac{z_i^2 C_i^m D_i^m}{\sum_i z_i^2 C_i^m D_i^m} \tag{6}$$

Arriving at eq 5 requires an assumption that electric field-driven migration dominates over diffusive and convective ion transport.[89,108] This assumption may be valid when the concentration difference between the upstream solution and the downstream solution is relatively low (to suppress the contribution of diffusive transport) and the applied current density is sufficiently high.[94] The full expression for the Nernst−Planck equation,[107] described elsewhere, can be used in place of this assumption to simultaneously describe the contributions of diffusion, migration, and convection to the flux.[109]

By substituting eq 6 into eq 5, the separation factor can be expressed as

$$\mathrm{SF} \cong \frac{z_i}{z_j}\frac{K_i}{K_j}\frac{D_i^m}{D_j^m} \tag{7}$$

Both eqs 3 and 7 suggest that the separation factor can be expressed in terms of the sorption selectivity, K_i/K_j, and the

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diffusivity selectivity, D_i^m/D_j^m. Both of these selectivity values are intrinsic material properties of the membrane, though as will be discussed subsequently, the sorption selectivity may also depend on characteristics of the solution. A summary of different forms of the separation factor is provided in Table 1.

2.2. Ion Sorption Selectivity. The equilibrium ion sorption coefficient, K_i, is defined as the ratio of the concentration of i in the membrane relative to that in the external solution.[9,102,106] The partitioning process, or ultimately the concentration of i in the membrane, is affected by the specific properties of the membrane.[3,6,97] A particularly profound example of this situation is the one observed when comparing uncharged membranes and ion exchange membranes (IEMs). The fixed charge groups present in ion exchange membranes have a significant influence on ion sorption properties.[3,6,97] Furthermore, the choice of ion i and/or the way that K_i is used to analyze transport can depend on the application of interest. The following discussion further describes these differences.

To start, we restrict the discussion to single-electrolyte systems. In an uncharged membrane (i.e., a hydrophilic material that does not contain ionizable fixed charges), the equivalent cation and anion concentrations in the membrane must be equal according to the principle of electroneutrality.[106,110] For monovalent binary salts, this situation simplifies to say that the molar cation and anion concentrations are identical in the membrane.[110] In this case, defining K_i using either the anion or the cation yields the same result.[106,110]

In IEMs, the concentration of counterions (i.e., cations in cation exchange membranes or anions in anion exchange membranes) in the membrane phase is typically greater (and often much greater) than the concentration of co-ions (i.e., ions with the same charge as the fixed charge groups in the membrane).[106,110−112] When IEMs are used in desalination, co-ion sorption is particularly important because the co-ions are representative of the concentration of mobile salt (i.e., electrically neutral combinations of ions) in the membrane.[106,110−112] As such, the co-ion sorption coefficient in an IEM is equivalent to the salt sorption coefficient, K_S, which is useful for studying salt permeability properties of IEMs and ultimately salt rejection for desalination applications.[106,111,112]

When IEMs are used in electrodialysis, however, it is desirable to have the counterions carry the majority of the current (i.e., account for the majority of the ion transport).[25,113] As such, it is useful to consider the counterion sorption coefficient. For example, when defining the separation factor using eq 7, one would use the counterion sorption coefficient as counterion transport is desired in this case.[94,113]

The previous examples highlight the different contexts and/or uses of the ion sorption coefficient. Accordingly, the mobile salt (S), co-ion (X), or counterion (M) ion sorption coefficients (for ion i) are defined as[114]

$$K_{S,i} \equiv \frac{C_S^m}{C_i^s} \tag{8}$$

$$K_{X,i} \equiv \frac{C_X^m}{C_i^s} \tag{9}$$

$$K_{M,i} \equiv \frac{C_M^m}{C_i^s} \tag{10}$$

where in each case the sorption coefficient is the ratio of the membrane phase ion concentration to the solution phase ion concentration. Figure 1 further illustrates the nomenclature embodied by eqs 8−10.

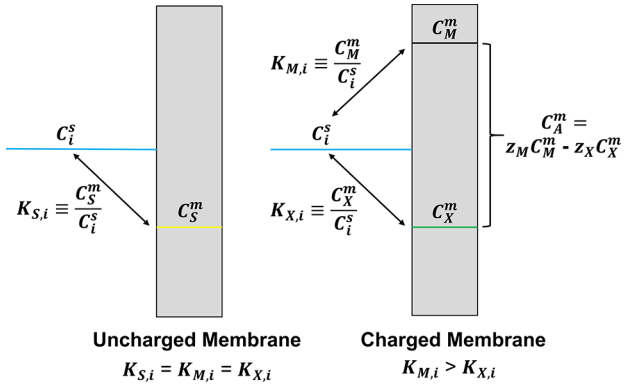

Figure 1. Nomenclature for the ion sorption coefficients and ion concentrations for both uncharged and charged (ion exchange) membranes exposed to a single-electrolyte solution. Often, uncharged membranes exclude salt, and $C_S^m < C_i^s$.[106,114] In charged (ion exchange) membranes, the counterion concentration, C_M^m, is often greater than C_i^s, and co-ions generally are excluded from the membrane (i.e., $C_X^m < C_i^s$).[106,115] In this example, the fixed charge group (the concentration of which is represented by C_A^m) is taken to be monovalent, which is commonly the case in IEMs.[76,94−96,113]

The charged (ion exchange) membrane depicted in Figure 1 contains fixed charge groups that have charges opposite to that of the counterions. To maintain electroneutrality, each fixed charge group (A) must be balanced by a counterion, and additionally, each co-ion must be balanced by a counterion. If the fixed charge group is monovalent, then the electroneutrality condition requires $C_A^m + z_X C_X^m = z_M C_M^m$.[114,116]

This charge balance can be divided by the external salt solution concentration to connect the charge balance to the ion sorption coefficient definitions as

$$K_{M,i} = \frac{z_X}{z_M} K_{X,i} + \frac{1}{z_M} \frac{C_A^m}{C_i^s} \tag{11}$$

where z_X is the co-ion valence, z_M is the counterion valence, and C_A^m is the membrane fixed charge concentration. For a monovalent (1:1 MX type) electrolyte (e.g., NaCl where M is Na^+ and X is Cl^-), eq 11 reduces to

$$K_{M,i} = K_{X,i} + \frac{C_A^m}{C_i^s} \tag{12}$$

The relationship for other types of electrolyte (e.g., M_2X) can be obtained in a similar manner from eq 11 by substituting the corresponding z_X and z_M values into the equation.

Theoretical models can be used, at least in principle, to calculate the value of $K_{X,i}$ (and therefore $K_{M,i}$) for a membrane equilibrated with a single-electrolyte solution. In perhaps the simplest case, the ion sorption process can be described as one where a charge is moved from one dielectric continuum (i.e., the external solution phase) to the membrane phase, which is also taken to be a dielectric continuum, and the Born model describes this relatively simple situation.[106,117−119] The observation of specific ion effects in ion exchange membranes suggests that dispersion energy may also be important for describing sorption of ions that exhibit Hofmeister series

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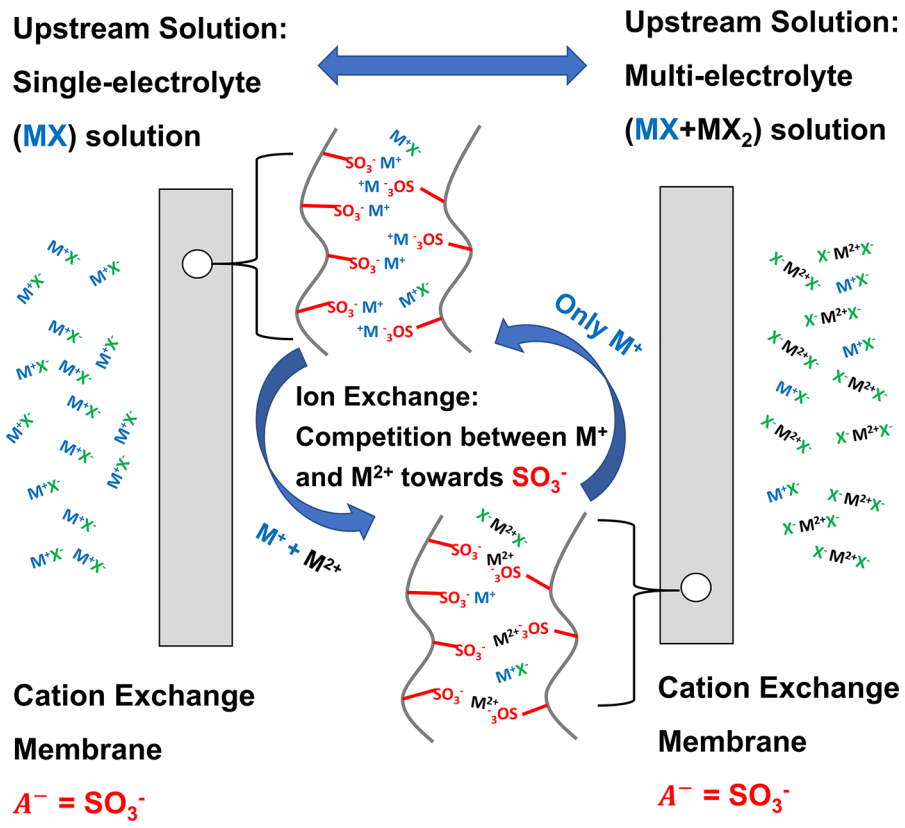

Figure 2. Difference in CEM ion sorption behavior between a single-electrolyte system and a multielectrolyte system. In the multielectrolyte system, both cations are present in the membrane phase, and an ion exchange equilibrium constant is generally used to describe the relative composition of the counterions associated with the fixed charges.

behavior.[114,119−122] Activity coefficient effects, long neglected in the analysis of ion sorption in polymers, are critical for accurately modeling ion sorption in hydrated polymers, and the Donnan-Manning model can be effective at quantitatively predicting the ion sorption properties of some highly swollen IEMs.[111,112,123,124]

The aforementioned models have been applied to describe single-electrolyte systems. Additional complications arise when considering the multielectrolyte partitioning problem, which is at the core of ion separation processes.[76,98,105] A significant difference between ion partitioning in multielectrolyte systems and single-electrolyte systems is competition between different counterions (e.g., Li^+ and Mg^{2+}) for association with the membrane fixed charge groups (e.g., A^- or SO_3^- in the cation exchange membrane example shown as Figure 2).[125,126] This competition, arising from different affinities between the counterions and the membrane fixed charge groups, can be described by an ion-exchange equilibrium constant.[116,127]

Ion exchange equilibrium between a cation exchange membrane (CEM) and an electrolyte containing two cations (M_i and M_j), where M_i is a monovalent cation ($z_i = 1$) and M_j is a divalent cation ($z_j = 2$) can be described as[127,128]

$$2(A^-M_i^+) + M_j^{2+} \rightleftharpoons 2M_i^+ + (A^-)_2M_j^{2+} \tag{13}$$

This equilibrium relationship can be used to define the ion exchange equilibrium constant, K_{iex}, which is typically defined using concentrations as opposed to thermodynamic activity values, as[128]

$$K_{iex} = \frac{C_j^m}{C_j^s}\left(\frac{C_i^s}{C_i^m}\right)^2 = \left(\frac{C_j^m}{C_j^s}\right)^{|z_i|}\left(\frac{C_i^s}{C_i^m}\right)^{|z_j|} \tag{14}$$

The expression can be generalized in terms of $|z_i|$ and $|z_j|$ (as shown on the right-hand side of eq 14). The value of K_{iex} can be determined experimentally,[127,128] but values are reported often for ion exchange resins prepared using chemistry that is similar to that used in many ion exchange membranes.[129]

The ion exchange equilibrium constant can be expressed using dimensionless ion concentrations to facilitate use with ion exchange isotherms. In the solution phase, the dimensionless composition of counterion j (in a mixture of counterions i and j) can be written as

$$x_j = \frac{|z_j|C_j^s}{|z_j|C_j^s + |z_i|C_i^s} \tag{15}$$

The concentration of cations in the solution phase, in units of equivalents of charge per volume, can be written as

$$C_0 = |z_j|C_j^s + |z_i|C_i^s \tag{16}$$

For example, in the multielectrolyte (M_iX and M_jX_2) system described in Figure 2, $C_0 = 2C^s_{M_{j2+}} + C^s_{M_{i+}}$. The corresponding dimensionless composition of counterion j in the membrane phase can be written as

$$y_j = \frac{|z_j|C_j^m}{C_A^m} \tag{17}$$

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where the fixed charge group has been taken to be monovalent, i.e., $|z_A| = 1$. The value of y_j represents the fraction of fixed charge equivalents that are associated with counterion j, and if only two counterions are present (i and j), then $y_i = 1 - y_j$ and represents the fraction of fixed charge equivalents that are associated with counterion i. Using eqs 15−17 and by taking counterion i to be a monovalent ion (i.e., $|z_i| = 1$), eq 14 can be simplified by introducing the dimensionless concentrations:[51]

$$K_{iex} = \frac{(1 - x_j)^{|z_j|} y_j}{x_j (1 - y_j)^{|z_j|}} \left(\frac{C_0}{C_A^m} \right)^{|z_j|-1} \tag{18}$$

If counterion j is a monovalent ion (i.e., $|z_j| = 1$), then the value of K_{iex} does not depend on either the membrane fixed charge concentration, C_A^m, or the equivalent counterion concentration in the solution, C_0.[127] However, if counterion j is a divalent (i.e., $|z_j| = 2$) or a trivalent (i.e., $|z_j| = 3$) ion, then K_{iex} is affected by the ratio of C_0/C_A^m, either linearly or quadratically.[51] To account for this dependence, K_{iex} can be further normalized by C_0/C_A^m to yield the dimensionless ion exchange affinity, α_i^j:[127]

$$\alpha_i^j = K_{iex} \left(\frac{C_0}{C_A^m} \right)^{1-|z_j|} = \frac{(1 - x_j)^{|z_j|} y_j}{x_j (1 - y_j)^{|z_j|}} \tag{19}$$

Therefore, if the value of α_i^j is known, one can calculate the dimensionless counterion composition in the membrane phase, y_j, given a particular solution composition, x_j. If the values of y_j and y_i are known at given values of x_j and x_i, then the dimensionless counterion composition values can be used to calculate sorption coefficients for each counterion:[127]

$$K_i = \frac{(1 - y_j) C_A^m}{(1 - x_j) C_0} \tag{20}$$

$$K_j = \frac{y_j C_A^m}{x_j C_0} \tag{21}$$

The ratio of these sorption coefficients can be taken to define the membrane sorption selectivity of counterion i relative to counterion j.

$$K_j^i \equiv \frac{K_i}{K_j} = \frac{x_j (1 - y_j)}{y_j (1 - x_j)} \tag{22}$$

The expression of K_j^i in eq 22 is related to the expression of α_i^j in eq 19. The relationship between K_j^i and α_i^j will be discussed in further detail in section 3.1.

2.3. Counterion/Counterion Diffusivity Selectivity. The counterion/counterion diffusivity selectivity, D_i^m/D_j^m, represents the relative kinetic rates of diffusion or mobility of counterion i relative to counterion j in the membrane.[84,94] Unlike ion sorption selectivity in multielectrolyte systems, where the selectivity often is determined experimentally, the ion diffusivity selectivity for multielectrolyte systems can be either experimentally measured or, in some cases, calculated via theory. This section describes two theoretical models (the theory of Mackie and Meares and free volume theory) that are used to calculate ion diffusion coefficients and experimental approaches to measure ion diffusivity properties.

2.3.1. Theory of Mackie and Meares. The theory of Mackie and Meares is a statistical description of small molecule diffusion in a mixture of polymer and solvent.[130,131] The theory is based on the assumption that the swollen membrane is a homogeneous mixture of polymer and sorbed water.[130] This mixture is represented on a lattice, and lattice positions occupied by polymer are considered impermeable. Therefore, small molecules can only diffuse by executing diffusional jumps between lattice positions that do not contain polymer.

The physical implication of this treatment is that cross-membrane transport occurs through the volume of the swollen material that is occupied by the sorbed water. As such, the presence of the polymer has two effects on transport. First, the presence of the polymer reduces the effective cross-sectional area available for transport, and second, it increases the tortuosity.[130] Both of these effects lead to reduction in diffusivity.

The Mackie and Meares model connects the membrane phase diffusion coefficient, D_i^m, to that in the external solution via the volume fraction of water as

$$\frac{D_i^m}{D_i^s} = \left(\frac{\phi_W}{2 - \phi_W} \right)^2 \tag{23}$$

where D_i^s is the diffusion coefficient in bulk solution, and ϕ_W, the only variable in the model, is the membrane water volume fraction.[130,131] An important feature of eq 23 is that it ensures the diffusion coefficient in the membrane converges to the diffusion coefficient in bulk solution as ϕ_W approaches unity (i.e., the pure solution limit).[106] In general, the Mackie and Meares model is most likely to be suitable for describing diffusion in highly swollen membranes ($\phi_W > 0.5$)[112,113] and systems with negligible ion−polymer interactions,[106] and in these cases, the effects described by the Mackie and Meares model can be much greater than electrostatic effects.

Applying the Mackie and Meares model for two different counterions, i and j, and assuming the volume fraction of water in the membrane, ϕ_W, is independent of the presence of the ions, the ion diffusivity selectivity reduces to

$$\frac{D_i^m}{D_j^m} = \frac{D_i^s}{D_j^s} \tag{24}$$

This expression suggests that the membrane ion diffusivity selectivity is identical to the diffusivity selectivity observed in solution, i.e., the membrane provides no additional diffusivity selectivity. Such a condition, which might be realized for some highly swollen membranes, is often not valid for many electrodialysis membranes, which typically have lower water content (e.g., $\phi_W \sim 0.3$)[104] and potentially non-negligible ion−polymer interactions. Nonetheless, the ion diffusivity selectivity obtained from the Mackie and Meares model can be treated as a limiting value for the membrane ion diffusivity selectivity as it represents the limiting case where the membrane makes no contribution to the diffusivity selectivity.

2.3.2. Free Volume Theory. Yasuda et al. studied NaCl transport in a series of hydrogels[132] and suggested that cross-membrane transport can be described using a free volume-based model:[133,134]

$$D_i^m \sim \exp\left[-\frac{V^*}{V_f} \right] \tag{25}$$

where V^* is the minimum free volume size required by a penetrant, and V_f is the total free volume of the membrane.

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Yasuda et al. assumed that the membrane free volume was proportional to the hydration, H, as[133]

$$H \equiv \frac{\text{mass of water}}{\text{mass of hydrated polymer}} \tag{26}$$

$$V_f = (1 - H)V_{f,P} + HV_{f,W} \tag{27}$$

where $(1 - H)$ is the mass fraction of polymer in the membrane, $V_{f,P}$ is the polymer free volume, and $V_{f,W}$ is the free volume of water. Yasuda et al. further assumed that salt alone would not diffuse through the nonhydrated regions (or free volume) of the polymer.[133] Therefore, the free volume available for salt transport, in eq 27, was taken to be $HV_{f,W}$ or $V_f \sim HV_{f,W}$. Equations 25 and 27 lead to a useful correlation, where H is the only variable, for D_i^m/D_i^s:[132]

$$\frac{D_i^m}{D_i^s} = \exp\left[b\left(1 - \frac{1}{H}\right)\right] \tag{28}$$

and b is an adjustable parameter related to the size of the penetrant.

Although Yasuda's free volume-based theory was initially applied to hydrogels, it has also been successfully applied to predict the penetrant diffusivity in IEMs. Xie et al. investigated the dependence of membrane salt diffusivity on average free volume element size for a series of sulfonated polysulfone membranes and found that the experimentally measured diffusivity values correlated, in a manner consistent with the free volume-based theory, as[135]

$$D_i^m = A \exp\left[-\frac{\gamma V^*}{V_F^H}\right] \tag{29}$$

where A is a polymer related constant, γ is a correction factor to prevent double counting the free volume elements, and V_F^H is the average free volume element size in the hydrated polymer.

The value of V^* necessarily depends on the penetrant. For example, if NaCl is used as the model penetrant, the V^* value in eq 29 can be taken as the volume for the hydrated sodium ion.[136] This value is used rather than the combined volume of the hydrated sodium and chloride ions since the former is larger than the latter (i.e., as long as a free volume element is sufficiently large to permit a hydrated sodium ion to execute a diffusional jump, it could also permit a hydrated chloride ion to execute a diffusional jump).[135] Based on eq 29, the membrane ion diffusivity selectivity, $\alpha_{D(i/j)}$, can be expressed as

$$\alpha_{D(i/j)} = \frac{D_i^m}{D_j^m} = \exp\left[\frac{\gamma(V_j^* - V_i^*)}{V_F^H}\right] \tag{30}$$

where V^* is appropriately defined for either counterion i, V_i^*, or counterion j, V_j^*.

Use of eq 30 requires knowledge of the free volume of the hydrated polymer, V_F^H, and this information can, at least in principle, be obtained from positron annihilation lifetime spectroscopy (PALS) measurements[135,137−143] or molecular dynamics (MD)[144,145] simulations. However, both the PALS and MD approaches have some limitations that result in a situation where V_F^H data are not always available or easily obtained for many membranes of interest. This situation limits, at least to some extent, the use of eq 30.

An alternate approach is to measure the diffusivity selectivity of other molecules. For example, one could measure the water/salt diffusivity selectivity using measurements commonly made on desalination membranes.[115,146] That information, in principle, can be used to calculate γ/V_F^H using eq 30. This approach will be discussed in more detail in section 3.2.

2.3.3. Conductivity Measurements. In addition to the approaches discussed previously, the membrane ion diffusivity selectivity can also be determined experimentally. For example, ion transport can be measured using nuclear magnetic resonance (NMR),[147−149] neutron spin echo,[150] and/or conductivity measurements.[43,59,60,94−96] Among these experimental techniques, membrane conductivity measurements regularly are used to determine ion diffusivity in ion exchange membranes. When migration dominates over concentration-driven transport, the ion diffusion coefficients in the membrane are linked to the ionic conductivity as[116]

$$\kappa = \frac{F^2}{RT}\sum_i z_i^2 C_i^m D_i^m \tag{31}$$

where κ is the ionic conductivity of the membrane, F is Faraday's constant, R is the gas constant, and T is the absolute temperature. For a single electrolyte system, eq 31 becomes

$$\kappa = \frac{F^2}{RT}(z_M^2 C_M^m D_M^m + z_X^2 C_X^m D_X^m) \tag{32}$$

Typically, solving for both D_M^m and D_X^m requires two measurements (typically a conductivity measurement and a concentration-driven permeation measurement).[113] In the concentration-driven permeation measurement, the salt permeability is measured, and then, it is used to calculate the salt diffusion coefficient, which can be further deconvoluted into D_M^m and D_X^m.[113] Once the value of D_M^m is known for each counterion (e.g., i and j), the ion diffusivity selectivity, D_i^m/D_j^m, can be calculated.

In the absence of the concentration-driven permeation measurement, an approximation can be used to calculate D_M^m using eq 32. In ion exchange membranes, due to the presence of fixed charged groups in the polymer matrix, C_M^m is typically much greater than C_X^m (i.e., $z_M C_M^m = z_X C_X^m + C_A^m$ or $C_A^m > C_X^m$).[3,6,97] Consequently, the contribution of co-ion migration to the membrane ionic conductivity is often assumed to be negligible.[108] In other words, the co-ion migration term is dropped in eq 32, and D_M^m can be determined using a single measurement. This approach only works if the counterion transport number is sufficiently close to unity.

This assumption can lead to an overestimation of the membrane ion diffusivity and could be propagated forward as error when determining the membrane ion diffusivity selectivity. Therefore, in section 3.3, we will discuss the importance of accounting for co-ion migration while determining counterion diffusion coefficients via conductivity measurements. Specifically, we will discuss the effects of solution composition and membrane physicochemical properties on co-ion transport.

Furthermore, conductivity measurements also can be used to determine the counterion sorption selectivity of the membrane (for counterions i and j).[94,116,125] In the limit where the transport number is sufficiently close to unity, a single-electrolyte conductivity measurement can be used to measure the counterion diffusion coefficients for both

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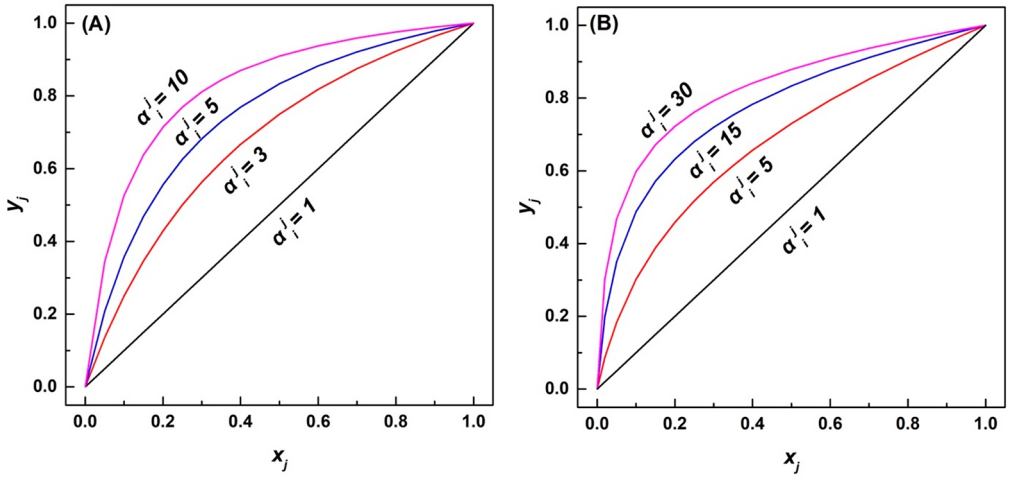

Figure 3. Ion exchange isotherms for systems containing (A) two monovalent counterions and (B) a divalent (j) and a monovalent (i) counterion. In both cases, counterion i was set as a monovalent ion, and values of α_i^j values were chosen to span the range of values reported by Miyoshi et al.[127]

counterions (i.e., D_i^m and D_j^m). Also in this limit, eq 31 can be written in terms of the two counterions:

$$\kappa = \frac{F^2}{RT}(z_i^2 C_i^m D_i^m + z_j^2 C_j^m D_j^m) \tag{33}$$

The Nernst−Einstein relation can be used to express the ion diffusion coefficients as ionic mobilities:[113]

$$u_i^m = \frac{z_i F}{RT} D_i^m \tag{34}$$

$$\kappa = C_A^m F((1 - y_j)u_i^m + y_j u_j^m) \tag{35}$$

where u_i^m is the membrane phase mobility of ion i, and $(1 - y_j)$ is the dimensionless composition of i in the membrane (per eq 17). Arriving at eq 33 from eq 31 requires the assumption that co-ion migration is negligible in the binary electrolyte system. This assumption commonly is used for multielectrolyte systems,[94] since the concentration-driven permeation measurements are less standard for multielectrolyte systems compared to single electrolyte systems. When D_i^m and D_j^m are available, u_i^m and u_j^m are calculated using eq 34, and the value of y_j can be obtained using eq 35. This approach results in a situation where the value of K_j^i can be calculated from eq 22. Although the mathematical formula for eq 35 is rather simple, several underlying conditions and assumptions (e.g., solution compositions and ion−polymer interactions) need to be understood to use eq 35 properly. Those conditions and assumptions will be discussed further in section 3.4.

3. IMPLICATIONS

The current density is important when performing electric field-driven experiments to determine the ion separation factor. This consideration is particularly important for characterizing novel membranes and for operating electric field-driven processes. For example, potentiostatic polarization coupled with impedance spectroscopy can result in transport numbers that vary with current density.[151] Many electric field-driven membrane characterization experiments, however, are run below the limiting current density to avoid concentration polarization effects and/or other electrochemical phenomena that occur at elevated current densities. The ion diffusivity and sorption selectivity values are expected to be important at these lower current density values, and the sorption selectivity is expected to remain important at higher current density values.[151] In this section, we discuss the implications of common assumptions and/or analysis/experimental routes on selectivity characterization from the perspective of both the diffusivity and sorption selectivity properties while recognizing that the significance of the diffusivity selectivity may be limited to lower current density situations.

3.1. Relationship between the Dimensionless Ion Exchange Affinity and the Counterion/Counterion Sorption Selectivity. In section 2.2, we suggest that counterion sorption in multielectrolyte systems can be determined from ion exchange isotherms. Specifically, the dimensionless ion exchange affinity, α_i^j, is interconnected to the counterion/counterion sorption selectivity, K_j^i. Qualitatively, K_j^i is inversely related to α_i^j. This relationship can be realized by considering a given solution composition. An increase in α_i^j suggests that the interactions between counterion j and the membrane fixed charge groups become more preferential compared to the interactions between counterion i and the membrane fixed charge groups.[116,127] Consequently, counterion j is enriched in the membrane phase relative to counterion i, which corresponds to a decrease in K_j^i.

A more quantitative interpretation of the relationship between K_j^i and α_i^j requires knowledge of the valence of counterion j. When j is a monovalent ion (i.e., $|z_j| = 1$), K_j^i is equal to the reciprocal of α_i^j (i.e., $K_j^i = 1/\alpha_i^j$ as can be seen by comparing eqs 19 and 22). Hence, K_j^i is a constant when α_i^j is a constant regardless of the solution composition. When j is a multivalent ion, the only difference between the reciprocal of K_j^i (i.e., K_j^i) and α_i^j is the valence of counterion j. In this case, the value of K_j^i varies with the solution composition when $\alpha_i^j \neq 1$, which can be found by combining eqs 19 and 22. For example, if $\alpha_i^j = 5$ for a system containing divalent (j) and monovalent (i) counterions, then K_j^i would increase from 0.26 to 0.43 when x_j increases from 0.1 to 0.9. In general, when the multivalent ions are considered, the counterion/counterion sorption selectivity will depend on the solution composition.

The value of α_i^j provides insight into the relationship between y_j and x_j (in addition to its relationship to the counterion/counterion sorption selectivity). Miyoshi et al. reported α_i^j values for a series of commercial ED membranes.[127] Using this range of α_i^j values, ion exchange

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isotherms were generated using eq 19 for systems containing two monovalent counterions (Figure 3A) or a divalent (j) and a monovalent (i) counterion (Figure 3B). These two types of systems are often of interest for practical separation applications.

When α_i^j is unity (and, accordingly, $K_j^i = 1$), the dimensionless composition of counterion j in the membrane phase is identical to its composition in the solution. In other words, counterion sorption or ion exchange into the membrane phase does not result in a situation where counterion j is enriched relative to the composition in the external solution. This situation is the case regardless of whether the solution contains two monovalent counterions (Figure 3A) or a divalent and a monovalent counterion (Figure 3B). When α_i^j is greater than 1 (and, accordingly, $K_j^i < 1$), the dimensionless composition of counterion j in the membrane phase is always greater than its concentration in the solution (i.e., counterion j is enriched in the membrane phase and counterion i is excluded by the membrane phase). When α_i^j values are sufficiently large (e.g., >5 for a monovalent−monovalent ion pair or >15 for a divalent−monovalent ion pair), the dimensionless composition of counterion j in the membrane phase becomes close to unity (i.e., $y_j > 0.9$, the majority of the counterions in the membrane are counterion j) when the dimensionless composition of counterion j in the solution is greater than 0.7. This situation is often encountered in practical ion separation processes when the nontarget ions, which often have high α_i^j values, are the dominating species in the solution.[76,98,152]

For example, in the Li^+/Mg^{2+} separation, the molar ratio of Li^+/Mg^{2+} is around 0.1 in the external solution.[76] In that case, the dimensionless composition of Mg^{2+} in the solution is $x_j = 0.947$, and the binding affinity of Mg^{2+} toward sulfonate groups is greater than that of Li^+,[129] so the majority of the counterions in the membrane will be Mg^{2+} (i.e., $y_j \geq 0.947$). Consequently, the contribution of Mg^{2+} to the membrane ionic conductivity will be close to 100% (eq 35). Although this behavior does not affect the determination of the ion sorption selectivity using ion exchange experiments, it could result in challenges when determining the ion sorption selectivity from conductivity measurements, as discussed in section 3.4.

3.2. Using Free Volume Theory to Relate Measures of Diffusivity Selectivity. In section 2.3, we suggested a free volume theory-based framework that would allow the membrane counterion/counterion diffusivity selectivity, $\alpha_{D(i/j)}$, to be estimated from a measure of the water/salt diffusivity selectivity, $\alpha_{D(W/S)}$ (or, in principle the selectivity of any two other small molecules). One reason to connect $\alpha_{D(i/j)}$ and $\alpha_{D(W/S)}$ is that some IEMs, and in particular some CEMs,[153−155] are of interest for both desalination and electric field-driven ion separation applications. Using two other probe molecules (e.g., water, W, and a single electrolyte, S) to measure diffusivity selectivity ($\alpha_{D(W/S)}$ in this case) could provide insight into hydrated polymer free volume as

$$\frac{\gamma}{V_F^H} = \frac{\ln(\alpha_{D(W/S)})}{(V_S^* - V_W^*)} \quad (36)$$

The ratio γ/V_F^H is a characteristic of the membrane, and it could then be used in eq 30 to estimate the counterion/counterion diffusivity selectivity as

$$\alpha_{D(i/j)} = \exp\left[\ln(\alpha_{D(W/S)})\frac{(V_j^* - V_i^*)}{(V_S^* - V_W^*)}\right] \quad (37)$$

Figure 4 shows an example of this relationship where eq 37 connects transport property data obtained within the context

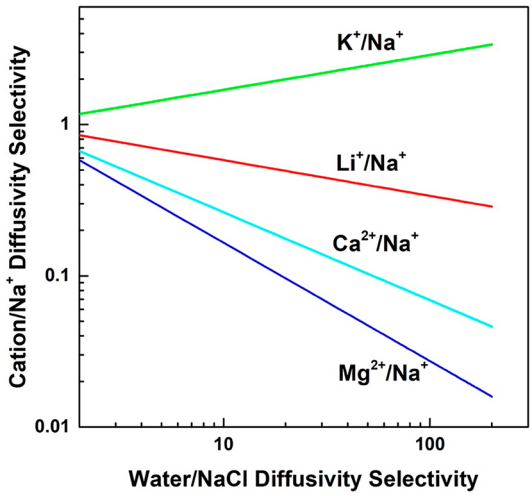

Figure 4. Counterion/counterion diffusivity selectivity values calculated using the water/salt diffusivity selectivity (eq 37). The counterion j was taken as Na^+, and the salt (water/salt diffusivity selectivity) was taken as NaCl. The range of the water/salt diffusivity selectivity values was chosen based on data reported for a series of sulfonated polysulfones.[135]

of desalination membranes to that within the context of electric field-driven counterion separations.

When the membrane water/salt diffusivity selectivity is 2, which is the limiting value based on water and NaCl diffusion coefficients in bulk solution, the counterion/counterion diffusivity selectivity for all of the ion pairs considered reduces to a value close to the corresponding diffusivity selectivity in bulk solution (Figure 4).[106] This free volume-based approach also predicts that selectivity for the smaller counterion relative to the bigger counterion increases as the membrane water/salt diffusivity selectivity increases. It also predicts that the diffusivity selectivity is greater when the size difference between the ions is greater. Both of these observations are generally aligned with Cohen-Turnbull theory, which forms the basis of the free volume-based theory.[134]

As an example of this approach, the water and salt diffusion coefficients for the Neosepta CMX membrane are reported to be 2.5×10^{-6} cm^2/s and 2.1×10^{-7} cm^2/s, respectively, so $\alpha_{D(W/S)} = 12$ for the CMX membrane.[104] According to eq 37, the values of $\alpha_{D(K^+/Na^+)}$ and $\alpha_{D(Mg^{2+}/Na^+)}$ are 1.77 and 0.147, respectively, when $\alpha_{D(W/S)} = 12$. These values, predicted using eq 37, only differ by approximately 10% from the corresponding values measured using a conductivity technique: $\alpha_{D(K^+/Na^+)} = 1.62$ and $\alpha_{D(Mg^{2+}/Na^+)} = 0.165$.[94]

While eq 37 reveals a connection between a measure of diffusion selectivity, commonly considered for desalination membranes, and a measure of counterion/counterion selectivity that is useful in electric field-driven ion separation applications, the approach does have limitations. Equation 37 suggests that desalination membranes with high $\alpha_{D(W/S)}$ values should also have high $\alpha_{D(i/j)}$ values. While this design criterion results directly from the theory, it may not tell the entire story

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from a practical perspective. For example, a desalination membrane with a high $\alpha_{D(W/S)}$ value may have very low ionic conductivity due to the lack of fixed charge carriers.[12,13] This potential situation highlights the need to consider both the selectivity and productivity (in this case, ionic conductivity) properties of membranes for separation applications.

Additionally, the approach to selecting specific values of V_j^* and V_i^* presently is not well-defined. When free volume theory is applied to a desalination membrane, the V^* value represents the minimum free volume element size for a molecule to execute a diffusional jump.[135] In electrodialysis, both diffusion and migration occur,[156] and this situation might suggest different interpretation of the V^* values. For the purpose of the example discussed previously, we applied the same interpretation of the V^* values to the counterions and the water and single electrolyte used to obtain the desalination-based diffusivity selectivity. While this approach appeared to be sufficient for connecting the two measures of diffusivity selectivity for the Neosepta CMX membrane, additional verification of this V^* value analysis could be necessary for different membranes or ions.

3.3. Influence of Co-ion Transport on Diffusion Coefficients Determined Using Conductivity Measurements. As discussed in section 2.3.3, conductivity measurements can be used to measure counterion diffusivity (without the use of an additional experiment, e.g., concentration-driven permeation measurements) if the contribution of co-ion migration to conductivity is negligible. This approximation can lead to an overestimation of individual counterion diffusivity values, and if these values are used to calculate counterion/counterion diffusivity selectivity, this overestimation may lead to errors in the membrane ion diffusivity selectivity. This overestimation artifact becomes more significant when the membrane counterion transport number decreases and the fraction of the current carried by the co-ions increases. This section discusses an approach to estimate the extent to which neglecting co-ion transport affects the counterion diffusivity calculation.

3.3.1. Theory to Support Analysis. The co-ion concentration in a charged ion exchange membrane, in the simplest case, is described by Donnan theory.[3,9,97,116,157] When an IEM is brought into equilibrium with an electrolyte solution, an electric potential (i.e., the Donnan potential) is established at the IEM/electrolyte interface.[116,158] This Donnan potential occurs due to the difference in the thermodynamic activity of the ions inside the membrane relative to their corresponding thermodynamic activity values in the external solution caused by the presence of fixed charge groups in the ion exchange membrane.[116,158] The result of this Donnan potential is that co-ions are excluded from sorbing into the membrane.[116,158]

The strength or effectiveness of Donnan exclusion increases with the absolute value of the Donnan potential, so co-ion sorption is suppressed to a greater extent in situations where the Donnan potential at the IEM/electrolyte interface is higher.[116] Next, for a given IEM/electrolyte system, the Donnan potential increases (and co-ion sorption decreases) with increases in the difference between the counterion activity in the membrane and that in the external solution.[116] The Donnan potential also decreases as the counterion valence increases meaning that co-ion sorption tends to be more significant when the multivalent counterions are exposed to the membrane.[116] At the same time, Donnan exclusion is more effective at reducing the sorption of multivalent co-ions.[116] Therefore, co-ion sorption (and, thus, co-ion transport) is affected by both solution and membrane factors.

Donnan theory can be used to develop an expression for the co-ion sorption coefficient:[3,116]

$$K_{X,i} = \frac{C_X^m}{C_i^s} = \sqrt[2]{\left[\frac{1}{4}\left(\frac{C_A^m}{C_i^s}\right)^2 + \left(\frac{\gamma_\pm^s}{\gamma_\pm^m}\right)^2\right]} - \frac{1}{2}\frac{C_A^m}{C_i^s} \tag{38}$$

where $\gamma_\pm^s$ is the mean ionic activity coefficient in the solution, and $\gamma_\pm^m$ is the mean ionic activity coefficient in the membrane. The value of C_A^m is the fixed charge concentration of the membrane, and the value of $\gamma_\pm^s$ can be determined using the Pitzer model.[159−161] Determining the value of $\gamma_\pm^m$, however, is less straightforward.

Manning's counterion condensation theory describes the thermodynamic circumstances that lead to a situation where counterions condense or undissociate in the material.[162] The theory was developed for polyelectrolytes in solution, so it assumes that the fixed charge groups are distributed evenly along the polymer backbone.[162] The so-called Manning parameter, ξ, defines a critical point at which counterion condensation occurs in the membrane:

$$\xi = \frac{\lambda_B}{b} = \frac{e^2}{4\pi\varepsilon_0\varepsilon kTb} \tag{39}$$

where λ_B is the Bjerrum length (i.e., $\lambda_B = e^2/4\pi\varepsilon_0\varepsilon kT$), b is the spacing between two adjacent charge groups on the polymer backbone, e is the elementary charge, ε_0 is the permittivity of free space, ε is the relative dielectric permittivity (or dielectric constant) of the hydrated membrane, and k is Boltzmann's constant.[111,162] Above the critical point (i.e., when $\xi > \xi_{crit}$, where $\xi_{crit} = 1$ if the fixed charge group is monovalent), counterion condensation occurs such that the value of ξ is to ξ_{crit}.[162] Thus, this condensation process acts to reduce the fixed charge group concentration in the membrane (i.e., C_A^m decreases as a result of counterion condensation).[111,162] Recently, Kamcev et al. used Manning's counterion condensation theory to calculate the value of $\gamma_\pm^m$. Their Donnan-Manning model effectively described co-ion sorption in some highly swollen commercial IEMs.[111]

Another result of counterion condensation is that the counterions in the membrane may exist in one of two different forms.[113] The condensed form is the situation where the counterions interact strongly with the fixed charged groups and may reduce the effective membrane fixed charge concentration, and the uncondensed form is the situation where the counterions are considered to be dissociated from the fixed charged groups.[113] Condensed counterions may have unique transport behavior compared to uncondensed counterions. When transport is driven by a concentration gradient, the condensed counterions are assumed to be immobile since they are localized near the polymer backbone.[112] When the transport is driven by an electric field, however, these condensed counterions are mobile[163−166] and may have greater mobility compared to the uncondensed counterions.[113]

3.3.2. Analysis for an Idealized Cation Exchange Membrane. With that framework in mind, we return to the analysis about the extent to which neglecting co-ion transport affects the calculation of the counterion diffusion coefficient obtained using a single ionic conductivity measurement. To analyze this scenario, we will consider an idealized case where ion−polymer interactions are negligible, and the membrane is

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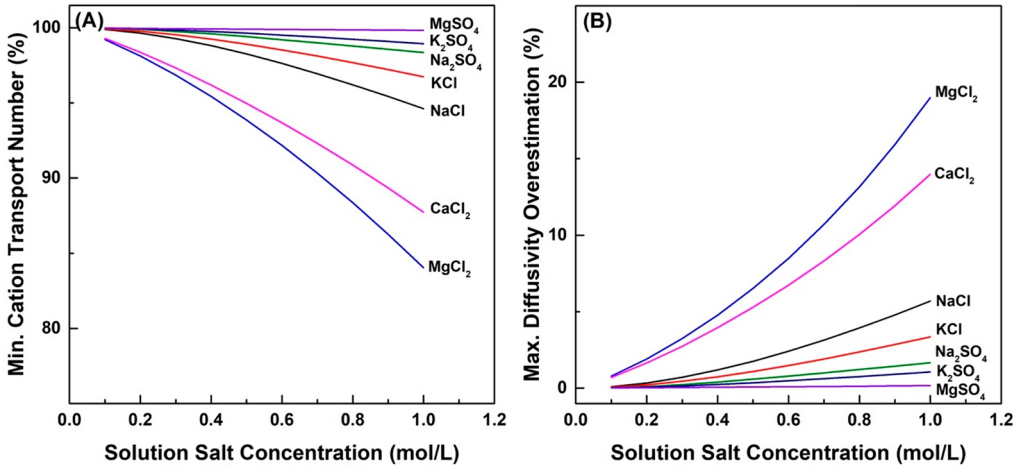

Figure 5. Minimum counterion transport number (calculated using eq 40) (A) and the maximum diffusivity overestimation (calculated using eq 41) (B) in a CEM presented as a function of salt solution concentration for different electrolytes. In those calculations, the co-ion concentration in the membrane was calculated using the Donnan-Manning model,[111] the solution activity was calculated using the Pitzer model,[159−161] and the membrane fixed charge concentration and dimensionless linear charge density values were taken as 6.21 mol/L and 1.5, respectively, to be consistent with the Selemion CMV membrane.[104]

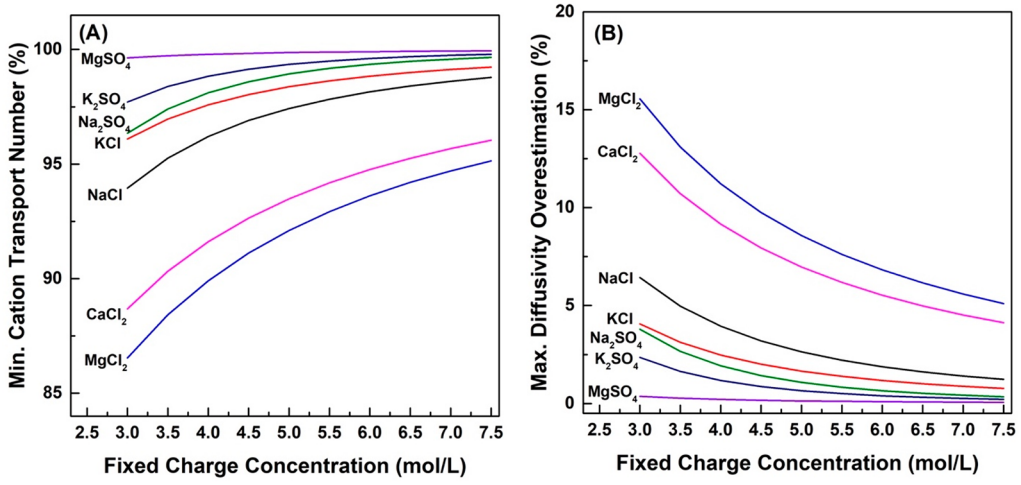

Figure 6. Minimum counterion transport number (calculated using eq 40) (A) and the maximum diffusivity overestimation (calculated using eq 41) (B) in a CEM presented as a function of fixed charge concentration for different electrolytes. The salt solution concentration was fixed at 0.5 M, and the other details of the calculation are provided in the Figure 5 caption.

a CEM with monovalent fixed charge groups and uncondensed counterions. Therefore, we will use the theory of Mackie and Meares[130,131] to describe the diffusion coefficients in the membrane relative to those in bulk solution. Additionally, we will calculate the membrane phase co-ion concentration, C_X^m, using the Donnan-Manning model (by assuming the membrane fixed charge concentration and dimensionless linear charge density values were 6.21 mol/L and 1.5, respectively, which is representative of the Selemion CMV membrane[104]).[111] The membrane phase counterion concentration, C_M^m, will be calculated using the electroneutrality requirement (i.e., $C_A^m + |z_X|C_X^m = |z_M|C_M^m$). Using the information described above, we will define and calculate the minimum counterion transport number, $t_{M,min}^m$, as

$$t_{M,min}^m = \frac{z_M{}^2 C_M^m D_M^s}{z_M{}^2 C_M^m D_M^s + z_X{}^2 C_X^m D_X^s} \quad (40)$$

Because the minimum counterion transport number describes the fraction of ionic current carried by the counterions, it can be used to estimate the extent to which the counterion diffusion coefficient is overestimated as a result of neglecting co-ion transport. This calculation can be done as

$$\text{max diffusivity overestimation (\%)} = \left(\frac{1}{t_{M,min}^m} - 1\right) \times 100\% \quad (41)$$

where $1/t_{M,min}^m$ reflects the overestimation (i.e., as $t_{M,min}^m$ decreases, the counterion diffusivity becomes increasingly overestimated). To highlight the effects of solution composition and membrane physicochemical properties on the co-ion sorption and migration, the minimum counterion transport number and the maximum diffusivity overestimation are plotted against the external salt concentration (Figure 5) and the fixed charge group concentration (Figure 6) used in the calculations.

The minimum counterion transport number (for this example that is representative of a Selemion CMV cation exchange membrane and all electrolytes considered) decreased

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by 0.2−16% as the solution salt concentration increased (Figure 5A), and the maximum diffusivity overestimation increased by 0.2% to 19% as the solution salt concentration increased (Figure 5B). These results show that co-ion transport becomes more important as the solution salt concentration increases, and they are consistent with Donnan theory.[116] When the external salt solution concentration increases, the difference between the fixed charge concentration and the ion concentration in solution deceases. This situation leads to a reduction in the Donnan potential (and therefore a reduction in Donnan exclusion effectiveness). Consequently, the values of C_X^m (and, thus, K_X) increase, and co-ion transport becomes more significant.

In addition to the salt solution concentration, the salt type also affects the minimum cation transport number and the maximum diffusivity overestimation. The effects of salt type are secondary, however, compared to the effects of salt solution concentration. In the following discussion, we will hold the salt solution concentration constant.

When the salt type is the same (e.g., NaCl vs KCl), the value of $\gamma_\pm^s$ is the only difference in the Donnan-Manning model,[112] and the salt with the lower value of $\gamma_\pm^s$ (i.e., KCl) will have lower co-ion sorption and transport compared to the salt with the greater value of $\gamma_\pm^s$. When the co-ion is the same in both electrolytes (e.g., NaCl and $CaCl_2$), several factors affect co-ion sorption. First, the Donnan potential that results from the divalent Ca^{2+} ion is lower compared to the monovalent Na^+ ion, and the lower Donnan potential directly translates into higher co-ion sorption.[116] Next, counterion condensation is more likely to occur with the divalent Ca^{2+} ion than with the monovalent Na^+ ion.[112] Counterion condensation reduces the Donnan potential and leads to an increase in co-ion sorption.[116] These two effects overpower the effect of the lower value of $\gamma_\pm^s$ for $CaCl_2$ compared to that of NaCl. As such, having a counterion with a greater valence will lead to greater co-ion sorption and transport. When the counterion is the same (e.g., KCl vs K_2SO_4), Donnan exclusion is more effective at excluding the co-ion with the higher valence.[116] Additionally, the value of $\gamma_\pm^s$ commonly is lower for higher valent co-ions (e.g., SO_4^{2-}) compared to monovalent co-ions. As such, both activity coefficient and Donnan exclusion effects lead to lower co-ion sorption and transport.

The minimum cation transport number increased by 0.2% to 16% as the fixed charge concentration increased (Figure 6A), and the maximum diffusivity overestimation decreased by 0.2% to 19% as the fixed charge concentration increased (Figure 6B). Similar to the results in Figure 5, the results in Figure 6 are consistent with Donnan theory.[116] If the solution composition is held constant and counterion condensation behavior does not change, increasing the value of the fixed charge concentration leads to an increase in the Donnan potential (and, therefore, an enhancement in Donnan exclusion effectiveness). Consequently, the values of C_X^m (and, thus, K_X) decrease, and the co-ion transport becomes less important.

This analysis could inform the design of conductivity measurements for diffusivity selectivity calculations. The assumption of negligible co-ion transport will be most applicable when the solution salt concentration is moderate (e.g., ∼0.5 M), the membrane fixed charge concentration is high (i.e., C_A^m > 6 mol/L), and the co-ion is chosen to be the sulfate ion. In situations where greater salt concentration is required, the membrane fixed charge concentration is low (e.g., a CR61 membrane with C_A^m < 3.5 mol/L), or the sulfate co-ion cannot be used, the Donnan-Manning analysis should be performed to estimate influence of co-ion transport on the counterion diffusion coefficient. Preferably, the ionic conductivity measurement should be coupled with the concentration-driven permeation measurement to determine the diffusivity selectivity without the need for an assumption about the contribution of the co-ion to the ionic conductivity.

3.4. Determining the Counterion/Counterion Sorption Selectivity Using Conductivity Measurements. An attractive feature of conductivity measurements is that they can be used to determine the dimensionless composition of counterion j in the membrane (i.e., y_j) using eq 35. Coupled with eq 22, the value of K_j^i can be calculated. However, the applicability of eq 22 depends on the ion−polymer interactions and the solution compositions.

The linearity of eq 35 suggests that the ionic conductivity of the membrane exposed to a multielectrolyte system containing two different counterions is bounded by the separate ionic conductivity values of the membrane in contact with each of the two corresponding single-electrolyte systems. Furthermore, it suggests that the membrane ionic conductivity is expected to vary linearly with y_j (i.e., as the counterion composition in the membrane changes, the conductivity of the membrane will change accordingly between the two limiting cases (i.e., $y_j = 0$ and $y_j = 1$). Arriving at this linear relationship requires an assumption that the mobility of each ionic species is independent of the other ionic species in a solution of interest and that the conductivity of this solution is the weighted average of the conductivity of each ionic species (i.e., an assumption that Kohlrausch's law is valid).[167]

In a hydrated CEM, the value of C_M^m is often high (e.g., C_M^m > 3 mol/L), so the membrane cannot be treated as a dilute or ideal system. Furthermore, the presence of fixed charge groups prevents the ions from moving freely inside the membrane. Logette et al.[125] studied membrane ionic conductivity for a series of ion pairs and found that the membrane conductivity for monovalent/divalent and monovalent/trivalent ion pairs deviated more from the Kohlrausch's law predicted values than the conductivity for monovalent/monovalent ion pairs.

Nevertheless, if counterion condensation occurs in the membrane, as discussed earlier, the condensed counterions may have a greater mobility than the uncondensed counterions.[113] Hence, if two counterions, i and j, have different condensation behavior, the membrane ion conductivity might not vary linearly with y_j. Therefore, caution is warranted when using eq 35 with different multielectrolyte systems of interest. The validity of Kohlrausch's law for a particular electrolyte solution should be verified. If eq 35 does not describe the particular system, ion exchange experiments would be needed to obtain y_j and K_j^i.

If eq 35 does describe the system of interest, y_j can be determined by interpolation. The interpolation, however, requires that the difference in membrane ionic conductivity between the multielectrolyte system and each single-electrolyte system is measurable. This requirement might not always be met in practical ion separation processes. For example, in the Li^+/Mg^{2+} separation case discussed earlier,[76] the membrane counterions are mostly Mg^{2+}, so the contribution of Mg^{2+}, in the Li^+/Mg^{2+} mixture, to the membrane ion conductivity is nearly 100%. Consequently, it could be difficult to differentiate between the membrane ionic conductivity measured using the Li^+/Mg^{2+} solution and that measured using the pure Mg^{2+} salt

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solution, which would compromise this approach for characterizing K_j^i based on ionic conductivity measurements.

Equation 35 may be most suitable for systems where the difference between the dimensionless concentrations of counterions i and j in the solution is not dramatic (e.g., $0.2 < x_j < 0.6$), as this situation is likely to translate into a situation where the dimensionless compositions of counterions i and j in the membrane are not pushed toward the limiting values. For systems similar to the Li^+/Mg^{2+} case encountered in practical separations, an alternative method could be used. A model solution, where $0.2 < x_j < 0.6$, could be prepared for the conductivity measurements, and eq 35 could be applied to calculate y_j, which could be further translated into α_i^j using eq 19. The α_i^j value could then be used to calculate a new set of corresponding y_j values at x_j values of interest, and K_j^i could be calculated from this set of data using eq 22.

4. SUMMARY

In this review, definitions of the separation factor were discussed along with connections to the sorption and diffusivity selectivity properties of ion exchange membranes to provide insight into the use of IEMs in electric field-driven specific ion separation applications. The ion sorption selectivity can be determined from ion exchange isotherm or ionic conductivity measurements. When ion exchange isotherm measurements are used to determine the sorption selectivity, a dimensionless ion exchange affinity is used to connect the ion concentration in the membrane for a given solution composition and membrane fixed charge concentration. Alternatively, conductivity measurements can be used to determine the sorption selectivity when the counterion form of the membrane is not dominated by a single counterion and when ion specific interactions with the polymer are negligible. The diffusivity selectivity can be estimated using theory or be determined using ionic conductivity measurements. Free volume theory may be useful for connecting membrane water/salt selectivity, which is often measured for materials that are of interest for desalination, and the counterion/counterion diffusivity selectivity that is critical for specific ion separations. The influence of co-ion transport on diffusivity measurements made via conductivity measurements was estimated via sample calculations to highlight situations where neglecting co-ion transport is inappropriate. The discussion here is most applicable to homogeneous ion exchange membranes, but the connections between the ion separation factor and the sorption and diffusivity selectivity values could form the basis for understanding a wide range of membranes that are of interest for electric field-driven ion separation processes.

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Notes

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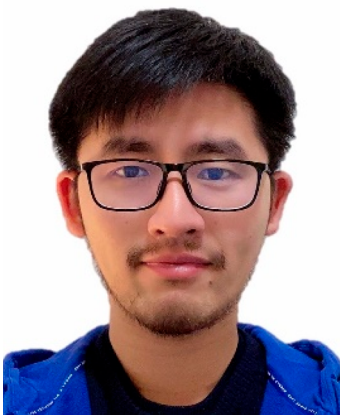

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