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Junction Potentials Bias Measurements of Ion Exchange Membrane Permselectivity

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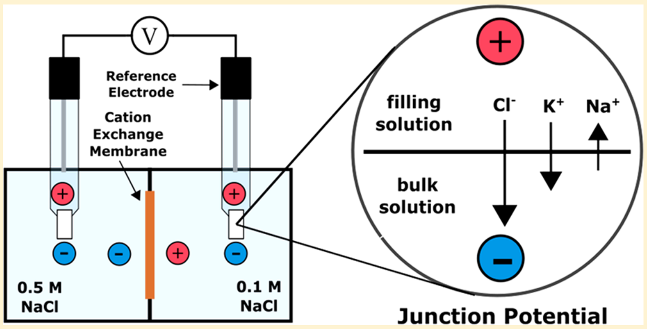
Supporting Information



ABSTRACT: Ion exchange membranes (IEMs) are versatile materials relevant to a variety of water and waste treatment, energy production, and industrial separation processes. The defining characteristic of IEMs is their ability to selectively allow positive or negative ions to permeate, which is referred to as permselectivity. Measured values of permselectivity that equal unity (corresponding to a perfectly selective membrane) or exceed unity (theoretically impossible) have been reported for cation exchange membranes (CEMs). Such nonphysical results call into question our ability to correctly measure this crucial membrane property. Because weighing errors, temperature, and measurement uncertainty have been shown to not explain these anomalous permselectivity results, we hypothesized that a possible explanation are junction potentials that occur at the tips of reference electrodes. In this work, we tested this hypothesis by comparing permselectivity values obtained from bare Ag/AgCl wire electrodes (which have no junction) to values obtained from single-junction reference electrodes containing two different electrolytes. We show that permselectivity values obtained using reference electrodes with junctions were greater than unity for CEMs. In contrast, electrodes without junctions always produced permselectivities lower than unity. Electrodes with junctions also resulted in artificially low permselectivity values for AEMs compared to electrodes without junctions. Thus, we conclude that junctions in reference electrodes introduce two biases into results in the IEM literature: (i) permselectivity values larger than unity for CEMs and (ii) lower permselectivity values for AEMs compared to those for CEMs. These biases can be avoided by using electrodes without a junction.

INTRODUCTION

Ion exchange membranes (IEMs) are versatile materials used in desalination, waste treatment, energy production, and industrial separation.[1−8] The IEM-based technologies used in these processes help mitigate human impacts to the environment in several ways. For example, diffusion dialysis (DD) enables recovery of acids and bases from industrial wastewaters,[9] electrodialysis (ED) can be used to produce drinking water from brackish groundwater with low energy input and high water recovery,[9−11] and reverse electrodialysis (RED) is an emerging technology for clean energy production and storage[9,12] that could satisfy the energy demand of many coastal communities.[13] As such, understanding IEM performance is essential for the continued development of many technologies relevant to environmental protection.

The defining characteristic of IEMs is their permselectivity, which refers to their ability to selectively allow ions of opposite charge to the membrane (counterions) to permeate.[4] Permselectivity ranges from 0 to 1, where 1 indicates perfect selectivity for counterions. Measured values of permselectivity that equal or slightly exceed unity (e.g., permselectivity = 1.00−1.04) have been reported for cation exchange membranes (CEMs) by several research groups (see Table S1).[14−16] These results do not make physical sense and call into question our ability to correctly measure this crucial membrane property. Moreover, the fact that CEM permselectivity measurements appear biased suggests that measurements of anion exchange membrane (AEM) permselectivity may also be inaccurate.

Ji et al.[16] determined that weighing errors, temperature, or measurement uncertainty in the membrane potential cannot explain these nonphysical values of permselectivity. Having ruled out these factors, we hypothesize that a possible explanation for the artificially high values of permselectivity for CEMs are junction potentials arising at the tips of reference electrodes used to measure membrane potential. Junction potentials occur due to differences in ion mobility and, in some cases, ionic selectivity of the separator (e.g., the tip of a

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$$\overbrace{\underbrace{\text{Ag / AgCl /}}_{E_{ref,C}}\text{ filling }\underbrace{\text{solution , 0.5 M}}_{E_{j,C}}\text{ NaCl }\underbrace{\text{/ membrane /}}_{E_{mem}}\text{ 0.1 M }\underbrace{\text{NaCl , filling}}_{E_{j,D}}\text{ solution }\underbrace{\text{/ AgCl / Ag}}_{E_{ref,D}}}^{E_{measured}}$$

Figure 1. Shorthand electrochemical notation for the cell commonly used to measure apparent membrane permselectivity. In the figure, "/" indicates a phase boundary, while "," indicates a boundary between components in the same phase, after Bard and Faulkner.[17] The cell reflects the use of single-junction Ag/AgCl reference electrodes. Subscripts C and D refer to the sides of the membrane containing the more concentrated and dilute salt solutions, respectively.

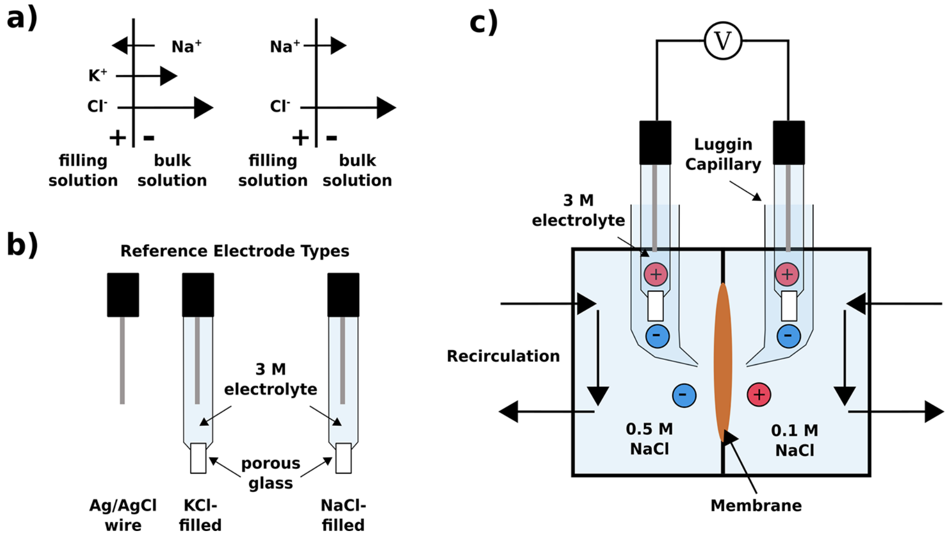

Figure 2. (a) Differences in ion mobility giving rise to liquid junction potentials in the filled electrodes immersed in NaCl solution. With KCl or NaCl filling solutions, the anion diffuses through the junction faster than the cation, making the filling solution positive with respect to the bulk solution. (b) Schematic illustration of the reference electrodes used in this work. (c) The two-compartment cell used for permselectivity measurements, illustrating the impact of junction potentials on the observed membrane potential, E_{mem}'. Due to the lower salt concentration, the junction potential is larger on the dilute side of the membrane and $\Delta E_j < 0$ (see eq 4). The sign of ΔE_j is independent of the type of membrane, but E_{mem} has an opposite sign for AEMs (+) and CEMs (−). Therefore, ΔE_j has an opposite effect on the magnitude of E_{mem}' for AEMs and CEMs. In panel (c), the sign of the membrane potential (resulting from diffusion of cations through the membrane) represents a CEM. Because both ΔE_j and the CEM membrane potential are negative, ΔE_j increases the magnitude of the observed membrane potential. For an AEM, the sign of the membrane potential would be reversed, but the sign of the junction potential would not change; therefore, the junction potential would decrease the magnitude of the observed membrane potential.

reference electrode)[17−19] wherever there is an interface between two electrolyte solutions of different concentration (e.g., the electrode filling solution and the bulk electrolyte).

Accordingly, toward determining how to correctly measure membrane permselectivity, our objective was to determine whether junction potentials affect permselectivity measurements of CEMs and AEMs. We tested our hypothesis by comparing permselectivity values obtained using bare Ag/AgCl wire electrodes (which have no junction) with values obtained from single-junction reference electrodes filled with either NaCl or KCl solutions. We show that measuring permselectivity using reference electrodes with junctions produces values of permselectivity greater than unity for CEMs and values that are artificially low for AEMs. These biases can be avoided by using electrodes without a junction.

■ THEORETICAL BACKGROUND

The apparent membrane permselectivity (α, dimensionless) is given by:[4,20]

$$\alpha = \frac{\frac{E_{\text{mem}}}{E_{\text{mem,ideal}}} + 1 - 2t_{\text{g}}}{2t_{\text{c}}} \tag{1}$$

where E_{mem} (V) is the potential across the IEM, $E_{\text{mem,ideal}}$ (V) is the potential of an ideally selective membrane, t_c and t_g (dimensionless) are the solution-phase transport numbers of coions and counterions, respectively, and the term "apparent" signifies that the permselectivity calculated in this way does not include the effects of water transport by osmosis and electro-osmosis.[4] $E_{\text{mem,ideal}}$ is given by the Nernst equation:[21,22]

$$E_{\text{mem,ideal}} = -\frac{RT}{z_{\text{g}}F}\ln\frac{a_{0.5}}{a_{0.1}} \tag{2}$$

where R (8.314 J·mol^{-1}·K^{-1}) is the ideal gas constant, T (K) is the temperature, F (96,485 C·mol^{-1}) is the Faraday constant, z_g is the charge on the counterion, a is the activity of the salt (NaCl in this case), and subscripts indicate the NaCl concentration in the respective solutions.

E_{mem} is typically measured using two reference electrodes placed on opposite sides of a membrane separating 0.5 and 0.1 M NaCl solutions.[15,16,20,21,23,24] Most measurements employ single- or double-junction Ag/AgCl reference electrodes containing a filling solution separated from the bulk salt solution by a porous frit.[14−16,20,24] This measurement apparatus is represented by the shorthand electrochemical cell notation given in Figure 1. Under these measurement conditions, $E_{\mathrm{mem,ideal}}$ is −37.8 mV for a CEM (see the Supporting Information), where E_{mem} is defined as the potential of the concentrated side of the cell with respect to the dilute side. Therefore, a measurement error of just ±0.4 mV in E_{mem} would cause 1% error in the permselectivity calculation.

As shown in Figure 1, the measured potential (E_{measured}) is composed of several additional potentials in addition to the membrane potential E_{mem}. First, there may be a difference in the potential of the two reference electrodes due to differences in the respective filling solution concentrations. This "offset potential" (ΔE_{ref}, V) can be expressed as:

$$\Delta E_{\mathrm{ref}} = E_{\mathrm{ref,C}} - E_{\mathrm{ref,D}} \tag{3}$$

where E_{ref} refers to the potential between the Ag/AgCl wire of the electrode and the corresponding filling solution, and the subscripts C and D indicate the electrodes immersed in the more concentrated and dilute electrolyte solutions, respectively. ΔE_{ref} can be measured directly by recording the potential difference between both electrodes placed in the same salt solution and is zero for ideal reference electrodes.

Second, when using single- or double-junction reference electrodes, there will be a potential due to the junction formed between the filling solution and the bulk solution in the cell, provided that their concentrations are different. In general, this junction potential consists of two components: (1) the liquid junction potential arising from differences in ion mobility[17,18,25] (see Figure 2a) and (2) a "tip potential" caused by the ionic selectivity of negatively charged porous glass frits.[19] Because the bulk salt concentrations on either side of the membrane are different, the junction potentials on the two sides will also be different. Thus, we define the difference in junction potential between the two sides (ΔE_{j}, V) as:

$$\Delta E_{\mathrm{j}} = E_{\mathrm{j,C}} - E_{\mathrm{j,D}} \tag{4}$$

where $E_{\mathrm{j,C}}$ and $E_{\mathrm{j,D}}$ are the junction potentials of the electrodes immersed in the concentrated and dilute electrolyte solutions, respectively (here, 0.5 and 0.1 M NaCl). We cannot calculate ΔE_{j} a priori because there is no way to quantitatively estimate the difference in tip potentials. However, Mousavi et al.[19] showed that the tip potential is reduced at higher ionic strengths (>0.1 M) due to charge screening. Considering that the ionic strengths of the solutions typically used for permselectivity measurement (0.5 and 0.1 M NaCl) are relatively high, we will estimate ΔE_{j} based only on the liquid junction potential, recognizing that this calculated value will represent a lower bound of the true junction potential. Accordingly, E_{j} is approximated as the liquid junction potential, which is given by:[17]

$$E_{\mathrm{j}} = -\frac{RT}{F}\sum_{\mathrm{i}}\int_{1}^{2}\frac{t_{\mathrm{i}}}{z_{\mathrm{i}}}d\ln a_{\mathrm{i}} \tag{5}$$

where t (dimensionless) is the transport number, z (dimensionless) is ion charge, a (dimensionless) is ion activity, the summation is performed over all ions (i) in solution, and the limits of integration represent the two liquid phases (fill and bulk solutions). In this study, we define phase 1 as the external solution and phase 2 as the electrode filling solution. Through the assumption of linear activity gradients through the junction, eq 5 can be solved analytically to give an activity-corrected form of the well-known Henderson equation:[26]

$$E_{\mathrm{j}} = \frac{\sum_{\mathrm{i}}\frac{|z_{\mathrm{i}}|u_{\mathrm{i}}}{z_{\mathrm{i}}}[a_{\mathrm{i}}(2) - a_{\mathrm{i}}(1)]}{\sum_{\mathrm{i}}|z_{\mathrm{i}}|u_{\mathrm{i}}[a_{\mathrm{i}}(2) - a_{\mathrm{i}}(1)]}\frac{RT}{F}\ln\frac{\sum_{\mathrm{i}}|z_{\mathrm{i}}|u_{\mathrm{i}}a_{\mathrm{i}}(1)}{\sum_{\mathrm{i}}|z_{\mathrm{i}}|u_{\mathrm{i}}a_{\mathrm{i}}(2)} \tag{6}$$

where u_{i} ($\mathrm{m^2 \cdot V^{-1} \cdot s^{-1}}$) is the mobility and of ion i.

Once ΔE_{ref} and ΔE_{j} are calculated, E_{mem} can be obtained from E_{measured} according to:

$$E_{\mathrm{mem}} = E_{\mathrm{measured}} - \Delta E_{\mathrm{ref}} - \Delta E_{\mathrm{j}} \tag{7}$$

Permselectivity measurements in the literature[15,16,20,23,27−29] have generally accounted for offset potentials (ΔE_{ref}) but neglected junction potentials (ΔE_{j}). Thus, previous studies are based on what we define as the observed membrane potential, E_{mem}', given by:

$$E_{\mathrm{mem}}' = E_{\mathrm{measured}} - \Delta E_{\mathrm{ref}} = E_{\mathrm{mem}} + \Delta E_{\mathrm{j}} \tag{8}$$

ΔE_{j} in eq 8 is usually neglected because it is difficult to measure directly and because electrode filling solutions are composed of salts in which the cation and the anion have similar mobilities. However, even for widely used filling solutions (e.g., KCl or $\mathrm{KNO_3}$), slight differences in cation and anion mobility can give rise to a small junction potential. Table 1 shows that the magnitude of ΔE_{j} for single-junction electrodes immersed in 0.5 and 0.1 M NaCl solution (estimated using eq 6) exceeds 0.4 mV for all commonly encountered filling solutions. While such small junction potentials may be negligible compared to the potentials measured in other electrochemical techniques, they are large enough to bias permselectivity measurements by 2−20% when using 0.5 M/0.1 M bulk solutions ($|E_{\mathrm{mem,ideal}}|$ = 37.8 mV).

Table 1. Predicted Liquid Junction Potentials (E_{j}) of Reference Electrodes Filled with Various Electrolyte Solutions

filling solution	cation transport number[a]	anion transport number[a]	E_{j} in 0.5 M NaCl[b] (mV)	E_{j} in 0.1 M NaCl[b] (mV)	ΔE_{j} (mV)[c]
NaCl	0.396	0.604	10.2	18.1	−7.9
KCl	0.491	0.509	−0.8	1.0	−1.8
$\mathrm{KNO_3}$	0.507	0.493	−2.3	−1.2	−1.1
CsCl	0.503	0.497	−4.2	−2.3	−1.9

[a] Calculated from ion diffusion coefficients at 25 °C and infinite dilution[30] as $\frac{D_+}{D_+ + D_-}$ for cations and $\frac{D_-}{D_+ + D_-}$ for anions. See the Supporting Information for discussion of the concentration dependence of transport numbers. [b] Calculated using the activity-corrected Henderson equation (eq 6), assuming a typical electrode filling concentration of 3 M. [c] Calculated as the difference between E_{j} in 0.5 M NaCl and E_{j} in 0.1 M NaCl. The tip potential is neglected.

As indicated by eq 6, ΔE_{j} depends only on the respective salt concentrations and is independent of the type of membrane under study (AEM or CEM). However, E_{mem} has an opposite sign for AEMs and CEMs, as shown by the Nernst equation (eq 2). In the case of CEMs, positive ions diffuse through the membrane, making the high-concentration compartment negative with respect to the low-concentration compartment, while the reverse is true for AEMs. Therefore, ΔE_{j} (which has the same sign regardless of membrane type) has an opposite effect on the magnitude of E_{mem}' for AEMs and CEMs (Figure 2c).

■ EXPERIMENTAL SECTION

Reference Electrodes. Reference electrodes in this work were based on the BaSi, Inc. RE-5B Ag/AgCl electrode (West Lafayette, IN), which is commonly used in the literature.[23,31−33] Single-junction reference electrodes were filled with either 3 M KCl or 3 M NaCl saturated with AgCl and contained CoralPor glass frits with a nominal pore size of 4−10 nm.[34] Bare Ag/AgCl wire electrodes (called "Ag/AgCl wire" hereafter) were constructed by removing the glass tubing and frit from RE-5B electrodes. The three electrode types are shown schematically in Figure 2b. We measured the potential of each type of electrode against a saturated calomel electrode (Fisher Scientific, Fair Lawn, NJ) with both electrodes immersed in 3 M KCl at room temperature (~23 °C). The resulting potentials were −20.6 ± 0.05, −26.0 ± 0.4, and −32.4 ± 0.6 mV for Ag/AgCl wire, KCl-filled, and NaCl-filled electrodes, respectively, and remained stable (±1.5 mV) throughout the course of the experiments reported here. A total of three pairs of each type of reference electrode were used simultaneously.

Junction Potentials. To obtain a direct measurement of the difference in junction potential, ΔE_j, for filled electrodes between the 0.5 and 0.1 M NaCl solutions, we measured the potential of each of the filled electrodes versus a bare Ag/AgCl wire electrode in each of 0.5 M NaCl ($E_{AgCl,0.5}$) and 0.1 M NaCl ($E_{AgCl,0.1}$) solutions. These two potentials were used to calculate $\Delta E_{AgCl} = E_{AgCl,0.5} - E_{AgCl,0.1}$, which corresponds to the total potential difference that a filled electrode would display between the two solutions. The ideal ΔE_{AgCl} when no difference in junction potentials exists between the 0.5 and 0.1 M NaCl solutions ($\Delta E_j = 0$) was calculated from the Nernst equation as:[17]

$$\Delta E_{AgCl,ideal} = -\frac{RT}{F}\ln\frac{a_{Cl,0.5}}{a_{Cl,0.1}} \tag{9}$$

where $a_{Cl,0.1}$ and $a_{Cl,0.5}$ are the activity of chloride in 0.1 and 0.5 M salt solutions, respectively, and activity coefficients were calculated using the Pitzer model[35] under the assumption that both cation and anion have equal activity coefficients. The experimental difference in junction potential between the two solutions was then obtained as:

$$\Delta E_j = \Delta E_{AgCl} - \Delta E_{AgCl,ideal} \tag{10}$$

Membranes. We selected one representative anion and cation exchange membrane (Neosepta AMX and CMX, respectively) for permselectivity measurements. Membrane coupons (area = 7.55 cm^2 per coupon) were equilibrated in 0.5 M NaCl for at least 24 h prior to each experiment then rinsed gently with deionized water and patted dry before being installed into measurement cells (described below). We tested four to six replicate coupons of each type of membrane.

Membrane Permselectivity. We measured permselectivity using 0.5 and 0.1 M NaCl solutions, corresponding to conditions for which permselectivity is most often reported. To minimize weighing errors, we prepared the salt solutions in 2 L batches, such that the smallest mass we had to weigh was 11.688 g. We also confirmed that the absorption of atmospheric water vapor by the crystalline NaCl did not significantly alter its weight (<0.05% difference between NaCl stored in ambient conditions and oven-dried NaCl).

Membrane coupons were installed into two-compartment cells (compartment volume = 17 mL, Figure 2c). Each compartment was connected to an external reservoir filled with 800 mL of freshly prepared salt solution, which was pumped through the compartment at approximately 50 mL·min^{-1}. The salt solutions flowed through each compartment in single-pass configuration for 1−2 min to remove any traces of 0.5 M NaCl from the dilute face of the membrane, and to remove any residual water or salt solution from inside the cell. After this initial rinse, the solutions were recirculated. We selected the volume and flow rate of the solutions to minimize concentration changes due to salt diffusion through the membranes (see the Supporting Information). We also reviewed our data carefully (see the Results and Discussion section) to confirm that the intended concentration difference was maintained, within experimental uncertainty, throughout the duration of our experiments.

To determine E_{mem}' for each pair of reference electrodes, we first measured the offset potential (ΔE_{ref}) between the pair of electrodes in each of 0.5 M NaCl and 0.1 M NaCl solutions using a multimeter (Fluke Co. 87). ΔE_{ref} was taken as the average of these two measurements, which differed by less than 0.3 mV on average. Next, the reference electrodes were inserted into glass Luggin capillaries in each cell compartment and connected to a potentiostat (VMP3, Bio-Logic Science Instruments). The Luggin capillaries were filled with the same electrolyte solution present in the cell compartments and had open tips. The primary function of the capillaries in these experiments was to provide a fixed location for installing the reference electrodes in the cell. We monitored the open-circuit voltage (OCV) between the reference electrodes until it stabilized to within 1.2 mV·h^{-1} (a criterion for stability used by other researchers)[15] and then recorded the OCV for 15 min. During this recording period, the OCV was stable within 0.4 mV·h^{-1} on average across all our experiments. We determined $E_{measured}$ as the mean of the 15 min time series of OCV data and obtained E_{mem}' according to eq 8 by subtracting the measured ΔE_{ref}. For Ag/AgCl wire electrodes, we also subtracted the difference in the potential of the electrode itself immersed in the concentrated and dilute solution ($\Delta E_{AgCl,ideal}$, calculated according to eq 9) from $E_{measured}$. By design, filled electrodes do not require this correction because the Ag/AgCl wires inside are exposed only to the filling solution. Example raw $E_{measured}$ data is provided in the Supporting Information. We calculated $E_{mem,ideal}$ for each experiment according to the Nernst equation (eq 2). After obtaining E_{mem}' and $E_{mem,ideal}$, we calculated the permselectivity according to eq 1 (substituting E_{mem}' for E_{mem}).

Tests were carried out in three individual cells operated simultaneously, such that all three pairs of a given type of electrode were used at a given time. Then, without disassembling the cells, we repeated this test protocol using the other two types of reference electrodes, replacing the compartment solutions with fresh salt solutions before each experiment. For example, three coupons of one type of membrane (e.g., CMX) were tested simultaneously using NaCl-filled electrodes. Then, the compartment solutions were replaced, the electrodes changed to KCl-filled, and the test was repeated. Finally, the compartment solutions were replaced again, the electrodes changed to Ag/AgCl wire electrodes, and the test was repeated one last time. Thus, measurements of E_{mem}' with all electrode types were conducted on the same group of membranes.

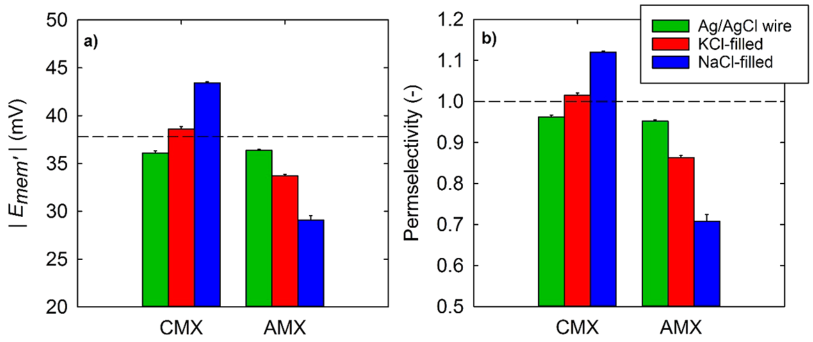

Figure 3. (a) $|E_{mem}'|$ and (b) apparent permselectivity of CMX (cation exchange) and AMX (anion exchange) membranes in 0.5 M/0.1 M NaCl, measured using three different types of reference electrodes, determined from eq 8. Ag/AgCl wire electrodes lacked a junction; KCl and NaCl-filled electrodes contained a porous glass frit that separated the filling solution (3 M salt) from the bulk salt solution. E_{mem}' was negative for CMX and positive for AMX. Dashed lines indicate the potential ($E_{mem,ideal}$) and permselectivity of ideally selective membranes. Error bars represent the standard error of four to six replicate measurements.

RESULTS AND DISCUSSION

Measurement Accuracy and Precision. Before calculating permselectivity, we first reviewed our data to confirm that the differences we obtained in results among the three different types of electrodes were real and not the result of lack of precision or accuracy. For this, we verified that (1) our measurements of E_{mem}' were sufficiently precise to distinguish differences on the order of ~0.4 mV, the measurement error that would produce α = 1.01, and (2) that concentration changes due to salt diffusion in our closed-loop experiments did not cause measurable decreases in E_{mem}'. With respect to the precision of our measurements, the standard error of the mean of $E_{measured}$ during the 15 min recording period was <0.03 mV in all experiments, well below the 0.4 mV discrepancy that would be required to cause $\alpha > 1$, and below the range of differences measured between any two different types of electrodes (2.6−7.3 mV; see detailed results in subsequent sections). Therefore, our method provided sufficient precision to distinguish differences in the value of E_{mem}' of the order of magnitude we sought to detect.

To confirm that salt diffusion did not meaningfully alter the value of E_{mem}' we obtained, we performed a single-pass experiment in which the solutions were not recirculated and compared the results to those using the closed-loop experimental protocol described in the Experimental section. For these tests, we used the same 5:1 concentration ratio but used 4 and 0.8 M NaCl to purposefully exacerbate salt diffusion. We found that E_{mem}' agreed within 1.1% between the single-pass and recirculation tests. As an additional check, we measured the conductivity of the dilute solution at the beginning and end of experiments with the AMX membrane in 0.5 and 0.1 M NaCl. The conductivity changed by <0.33% during the experiments. Thus, our results from the above checks show that any changes in $E_{measured}$ that occurred during our experiments due to salt diffusion were less than or comparable to the precision of our measurements and below the range of differences measured between any two different types of electrodes (2.6−7.3 mV). Moreover, if salt diffusion were significant, it would lower $E_{measured}$ and the corresponding calculated permselectivity (α) by reducing the concentration ratio across the membrane. Nevertheless, we still obtained values of E_{mem}' and α that exceeded theoretical expectations, as described in the following sections.

Therefore, we conclude that both the accuracy and precision of our permselectivity measurement method were sufficiently high to resolve differences in $E_{measured}$ due to the presence of junction potentials among different types of reference electrodes.

Membrane Potential. The obtained values of E_{mem}' were distinctly different for the three types of reference electrodes we tested, as shown in Figure 3a. For each of the two types of filled electrodes, the membrane type (CMX versus AMX) did not play a role in the magnitude of the difference in potential ($\Delta E_{mem}'$) between E_{mem}' measured with filled electrodes and E_{mem}' measured with Ag/AgCl wire electrodes. Specifically, the magnitude of $\Delta E_{mem}'$ for KCl-filled electrodes and NaCl-filled electrodes was 2.49−2.66 mV and 7.29−7.32 mV, respectively. Thus, $\Delta E_{mem}'$ was sensitive to the filling solution inside the electrode but did not depend on the type of membrane tested. The observed $\Delta E_{mem}'$ values were consistent with the magnitude of the ΔE_j estimated for the filled electrodes using the Henderson equation (Table 2). For example, like our experimental results, the magnitude of the estimated ΔE_j for NaCl-filled electrodes was larger than that for KCl-filled electrodes, and ΔE_j did not depend on the type of membrane used. Thus, the observed differences in the magnitude of $\Delta E_{mem}'$ among electrode types were consistent with the hypothesis that junction potentials affect membrane potential measurements.

Table 2. Measured Junction Potentials of Filled Reference Electrodes

electrode	measured $\Delta E_{mem}'$[a] (mV)	calculated ΔE_j[b] (mV)	measured ΔE_j[c] (mV)
NaCl-filled	−7.3 ± 0.6	−7.9	−8.8 ± 0.8
KCl-filled	−2.6 ± 0.4	−1.8	−2.7 ± 0.4

[a] Difference between E_{mem}' measured with filled reference electrodes and E_{mem}' measured with Ag/AgCl wire electrodes. The reported $\Delta E_{mem}'$ is the average for both CMX and AMX membranes. Uncertainty represents the standard error of at least four replicate measurements. [b] Calculated as the difference between E_j in 0.5 M NaCl and E_j in 0.1 M NaCl using the activity-corrected Henderson equation (eq 6), assuming a typical electrode filling concentration of 3 M. The tip potential is neglected. See also Table 1. [c] Uncertainties represent the standard error of six individual electrodes.

Results also showed that the electrode type had an opposite impact on the magnitude of E_{mem}' for CMX and AMX membranes. For CMX, the magnitude of E_{mem}' increased along the sequence Ag/AgCl wire < KCl-filled < NaCl-filled, while for

AMX, the magnitude of E_{mem}' decreased along the same sequence. However, when we consider that E_{mem}' was positive for AMX but negative for CMX, we see that filled electrodes always lowered the value of E_{mem}' compared to Ag/AgCl wire electrodes. Thus, $\Delta E_{\text{mem}}'$ was always negative (Table 2). The fact that the electrode type had an opposite impact on the magnitude of E_{mem}' for AMX and CMX and always reduced the absolute value of E_{mem}' is also consistent with the expected impact of junction potentials. Junction potentials are expected to have an opposite impact on the magnitude of E_{mem}' for anion and cation exchange membranes (Figure 2c), and the calculated values of ΔE_{j} were all negative (Table 2).

As such, the observed variations in membrane potential across electrode types and membranes were entirely consistent with the hypothesis that junction potential in filled reference electrodes bias permselectivity measurements. In light of this conclusion, it is noteworthy that the values of E_{mem}' for the CMX membrane obtained with filled reference electrodes both exceeded $E_{\text{mem,ideal}}$ (Figure 3), while those obtained with Ag/AgCl wire electrodes did not. This result indicates that junction potentials may explain observed permselectivity values that exceed unity.

Permselectivity. We next turn our attention to permselectivity. The variations in E_{mem}' with electrode type gave rise to substantial corresponding differences in membrane permselectivity, as expected from eq 1. For CMX, the permselectivity obtained from Ag/AgCl wire, KCl-filled, and NaCl-filled electrodes was 0.962, 1.02, and 1.12, respectively. Only the permselectivity measured with Ag/AgCl wire electrodes was lower than unity (Figure 3b). For AMX, the permselectivity obtained from Ag/AgCl wire, KCl-filled, and NaCl-filled electrodes was 0.952, 0.863, and 0.709, respectively. In contrast with CMX and AMX having no substantial difference in the magnitude of $\Delta E_{\text{mem}}'$ among different types of reference electrodes, the corresponding differences in permselectivity among the different types of reference electrode were larger for AMX than for CMX. For example, there was a larger difference in permselectivity between Ag/AgCl wire and NaCl-filled electrodes for AMX (0.952 versus 0.709) than for CMX (0.962 versus 1.12). The larger permselectivity difference among reference electrodes for AMX over CMX was consistent with expectations from eq 1, considering that Na^+ has a lower transport number than Cl^- (t = 0.396 and 0.604 for Na^+ and Cl^-, respectively). As such, $t_g < t_c$ for CMX (in which Na^+ is the counterion), making α less sensitive to changes in E_{mem}'. The opposite is true for AMX (in which Cl^- is the counterion). Therefore, the bias introduced by junction potentials had a larger effect on the permselectivity of AEMs than on that of CEMs.

The permselectivity values that we obtained with Ag/AgCl wire electrodes were different from those reported in literature using single- or double-junction reference electrodes under similar conditions (see Table S3). For CMX, our value of 0.962 is lower than previous measurements of 0.992 reported in two studies[21,24] but higher than the value 0.938 reported in two other studies.[7,36] For AMX, our value of 0.952 is higher than the 0.883−0.886 range in previous reports.[7,21,24,36] To the best of our knowledge, all previously reported literature measurements were based on KCl-filled Ag/AgCl or saturated calomel electrodes. The permselectivity values we obtained with KCl-filled electrodes (1.02 and 0.863 for CMX and AMX, respectively) were substantially more similar to the values from the literature. With the exception of the anomalously low value of 0.938 for CMX reported by Długołęcki et al.,[7,36] the differences and similarities between our measurements and the literature values are consistent with the influence of electrode type shown in Figure 3: the use of reference electrodes with junctions results in higher and lower permselectivity for CEMs and AEMs, respectively, than the use of Ag/AgCl wire electrodes.

Overall, our observations were consistent with the hypothesis that junction potentials bias permselectivity measurements taken with filled reference electrodes. Further, the permselectivity measured with Ag/AgCl wire electrodes was the only value lower than unity for the CMX membrane. Thus, we conclude that the permselectivity measured with Ag/AgCl wire electrodes represents the true value and that the use of single- or double-junction reference electrodes exaggerates the difference in permselectivity between AEMs and CEMs.

Electrode Junction Potentials. To further confirm our hypothesis, we performed direct measurements of the difference in junction potentials, ΔE_{j}, between filled electrodes immersed in 0.5 and 0.1 M NaCl. Measured values of ΔE_{j} (Table 2) compared well with theoretical values calculated using the Henderson equation, assuming liquid junction potentials only (i.e., negligible tip potentials). The small deviations between the measured values and those calculated with the Henderson equation confirm that the difference in the tip potentials was negligible in our experiments, and that the measured ΔE_{j} was largely attributable to the liquid junction potential. The measured ΔE_{j} was also very close to the observed $\Delta E_{\text{mem}}'$, providing independent confirmation that the differences observed in E_{mem}' (and permselectivity) among different types of reference electrodes can be attributed to junction potentials.

Implications for Ion Exchange Membrane Research. By demonstrating how junction potentials encountered in single- or double-junction reference electrodes influence membrane permselectivity measurements, our results provide clear guidance for how to perform such measurements more accurately. Specifically, we have shown that junction potentials explain the reported values of membrane permselectivity that exceed unity and exaggerate the differences in permselectivity between AEMs and CEMs. Previous studies reported that the permselectivity of commercial AEMs (86−91%) is generally lower than that of CEMs (90−99+%).[21,24,37] Our findings indicate that this may not be the case. Based on measurements using electrodes without junctions (i.e., bare Ag/AgCl wires), the AMX and CMX membrane have very similar permselectivities, different by only 0.1 percentage points.

Accurate measurement of membrane permselectivity is essential for evaluating the effectiveness of strategies to improve membrane performance (e.g., new chemistries, coatings, and nanocomposites) and for the development and calibration of ion transport models. Future measurements of this important quantity should be performed in a way that minimizes or eliminates the influence of electrode junction potentials. At present, it is not possible to construct a single- or double-junction reference electrode immune to this influence; therefore, for chloride-containing electrolytes such as NaCl or KCl we recommend that membrane permselectivity measurements be performed using Ag/AgCl wire electrodes without junctions. The use of electrodes with junctions is likely unavoidable in cases in which the chosen electrolyte does not contain chloride. Regardless of the type of electrode selected, an increased awareness of how liquid junction potentials affect permselectivity measurements will facilitate more accurate interpretations of experimental membrane potential data.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.est.7b05317.

> Additional details regarding permselectivity values reported in literature that exceed unity, the calculation of $E_{\mathrm{mem,ideal}}$ under typical measurement conditions, the sensitivity of estimated ΔE_j to concentration dependence of ion transport number, the design of cells to minimize concentration changes, permselectivity data for AMX and CMX reported in literature, and example raw data. (PDF)

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Notes

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