Mixed-Salt Effects on Water Uptake and Ion Selectivity in Commercial Anion Exchange Membranes

Abdulaziz Alharbi
Abdulaziz.s.alharbi.01@gmail.com

Prof. David Cheng
chi.cheng2@unsw.edu.au

King Abdullah University of Science and Technology · UNSW Sydney

Abstract

Anion exchange membranes are usually characterised in solutions containing a single salt, yet the water they treat contains several competing anions at once. This study measures water uptake and Donnan selectivity for three commercial membranes, Fumasep, PiperION and Sustainion, in solutions containing five competing anion pairs at three concentrations, giving 45 measurements. Membrane chemistry was the dominant factor: Sustainion absorbed approximately eight times more water than Fumasep, and this ordering held in every measurement without exception. Contrary to the expectation from hydration energy, sulfate-containing pairs did not give the highest water uptake. Ion chromatography showed that all three membranes preferentially absorb chloride over sulfate, with selectivity coefficients between 2.2 and 6.6, giving the sorption order $NO_3^- > Cl^- > SO_4^{2-}$. Wet mass was independent of external concentration over a fifty-fold range, varying by less than 1% for Sustainion. Selectivity showed an inverse trend with hydration for the chloride–sulfate pair but not for the nitrate–chloride pair, consistent with charge dilution affecting discrimination between ions of different valence more strongly than between ions of the same valence. The results indicate that single-salt characterisation does not transfer directly to mixed-ion conditions.

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1. Introduction

Anion exchange membranes (AEMs) are used in water treatment technologies including electrodialysis-based desalination and selective ion removal. Their performance rests on two properties. Water uptake determines how much water the membrane holds, which governs ionic conductivity and mechanical stability: too little water restricts ion transport and raises energy costs, while excessive uptake causes swelling that can compromise mechanical integrity and dilute the fixed-charge density [1]. Donnan selectivity describes how effectively the membrane distinguishes between competing anions, which matters wherever specific ions must be removed while others are retained.

These two properties are linked. Water uptake reflects how strongly the membrane interacts with the surrounding solution, and that interaction shapes the internal space available for ion transport. Selectivity reflects how the fixed charges partition ions between solution and membrane, a behaviour described by Donnan equilibrium [2]. Because both respond to the surrounding solution, neither can be treated as a fixed property of the material.

In practice, membranes are rarely exposed to a single anion. Industrial wastewater, brackish water and contaminated groundwater contain several anions simultaneously, all competing for the same fixed-charge sites. Despite this, most characterisation uses single-salt systems. The limitation is recognised: ion selectivity measured under single-salt conditions has been reported to differ from that measured in mixed-salt solutions [3]. What remains unclear is how the identity of the competing pair, the solution concentration and the membrane itself combine to determine behaviour under realistic multi-ion conditions.

This study addresses that gap. Three commercial AEMs, Fumasep, PiperION and Sustainion, were equilibrated in solutions containing five competing anion pairs (Cl^-/OH^-, SO_4^{2-}/Cl^-, NO_3^-/Cl^-, NO_3^-/OH^- and SO_4^{2-}/OH^-) at three concentrations (0.5, 0.1 and 0.01 M). Water uptake was determined gravimetrically and ion sorption by ion chromatography. Studying the same membranes across different pairs and concentrations allows the contribution of each factor to be separated, which a single measurement condition cannot achieve.

Several assumptions apply. The study covers three commercial membranes, so findings describe these materials rather than AEMs generally. Each solution contains two competing anions at equal molar concentration, a deliberate simplification of real water, which may contain a wider range of species at unequal ratios. The concentration range is limited to the

three levels examined. All salts were potassium salts, excluding cation effects by design, and temperature was held constant throughout.

2. Related Work

2.1 Donnan Equilibrium and Ion Partitioning

The theoretical basis for ion selectivity in charged membranes is Donnan equilibrium. When a membrane carrying fixed charges is equilibrated with an electrolyte solution, ions distribute unevenly between the two phases and an electrical potential develops at the interface, partially excluding co-ions and providing the basis of permselectivity [2].

For many years the Donnan potential could only be estimated indirectly. Aydogan Gokturk et al. [2] reported the first direct measurement for a commercial ion exchange membrane equilibrated with salt solutions across 0.001 to 1 M. Two findings are relevant here: the measured potential depended on both the external concentration and the counter-ion valence, and the measurements agreed reasonably with theoretical models that include ion activity coefficients. This supports treating concentration as a variable rather than a fixed background condition.

Theoretical descriptions have been extended beyond the ideal case. Wang et al. [4] extended Manning's counter-ion condensation model to mixed-salt systems and compared the resulting Donnan–Manning model against the ideal Donnan and Donnan-affinity models, finding improved prediction of partitioning with fewer fitting parameters. That work examined the same anion pairs of interest here, NO_3^-/Cl^- and SO_4^{2-}/Cl^-, as a function of external salt concentration. The difference is one of purpose: Wang et al. developed and validated a model against literature data, whereas the present study measures both properties directly for three specific commercial membranes.

Quantitative agreement between Donnan-based models and experiment has long been imperfect. Cwirko and Carbonell [5] found that the deviation from Donnan behaviour at low electrolyte concentrations is often attributed to a surface layer of bulk electrolyte, but that experiments designed to eliminate this effect still show the Donnan equation is not an adequate quantitative predictor of electrolyte sorption in many ion exchange materials. They attributed the residual discrepancy to non-uniform pore size and surface charge density within the membrane.

2.2 Selectivity in Mixed-Salt Systems

Descriptions of ion partitioning were developed for relatively simple systems, and extending Manning's framework to mixed-salt scenarios was necessary to describe selectivity between ions of the same charge [4]. This indicates that mixed-salt behaviour is not automatically captured by treatments developed for single-salt conditions.

Chen et al. [6] studied single and binary ion sorption in commercial Neosepta membranes across 0.01 to 1 M. Several of their findings bear directly on the present work. Water uptake in the anion exchange membranes was greatest in Na_2SO_4 solutions and lowest in $NaNO_3$ solutions, consistent with the hydrated radii of the anions. However, in binary mixtures with NaCl, sulfate sorption fell significantly at higher concentrations, while nitrate was absorbed more strongly than chloride. They also reported an order reversal on the cation side: potassium sorbed most strongly in single-salt solutions, while calcium dominated in binary mixtures due to Donnan exclusion at low concentrations.

Patel et al. [7] examined Cl^-/SO_4^{2-} separation under concentration-gradient-driven transport, holding total sodium concentration at 1 M while varying the chloride equivalent fraction from 0.1 to 0.9. High selectivity was maintained across a wide range of compositions. Their design is complementary to the present one: they held total concentration constant and varied composition, whereas this study holds the two anions at equal molarity and varies total concentration.

2.3 Concentration Dependence

AEM behaviour changes with the concentration of the surrounding solution. Sarapulova et al. [8] characterised commercial homogeneous AEMs in NaCl and Na_2SO_4 and reported that in relatively concentrated solutions, current tends to pass preferentially through well-conducting but non-selective macropores rather than the more selective gel phase, providing a structural mechanism by which increasing concentration reduces permselectivity.

Pismenskaya et al. [9] examined the concentration dependence of diffusion permeability and found that permeability increased on dilution for ampholyte solutions but decreased for a strong electrolyte, attributing part of this to increased pore size on dilution. The direction of the concentration effect can therefore depend on the ion involved.

Water content itself may be less concentration-dependent than transport properties. Elozeiri et al. [10] reported constant water content for high-capacity ion exchange membranes across 0.01

to 1 M NaCl, and largely constant water content below 0.5 M for other membranes. They attribute this to two opposing effects: higher ionic strength reduces the osmotic pressure difference and drives de-swelling of free water, while simultaneously promoting co-ion leakage that brings additional hydration water into the membrane.

2.4 Characterisation of the Membranes Studied

Cámaras-Miguel et al. [11] benchmarked nine commercial AEMs from five manufacturers, including the Fumasep, PiperION and Sustainion product families, measuring ion-exchange capacity, water uptake, swelling ratio and hydration number under consistent protocols. They concluded that performance is governed by a trade-off between ion-exchange capacity, hydration and dimensional stability. Their characterisation was carried out for alkaline water electrolysis, where the membranes are in hydroxide form, rather than for mixed-salt aqueous solutions.

The relationship between water content and selectivity has been treated quantitatively. Kitto and Kamcev [1] developed and validated a model for the conductivity–selectivity trade-off in which selectivity scales with the inverse square of water volume fraction through charge dilution: as the membrane takes up more water, the same number of fixed charges occupies a larger volume and the effective charge density falls. They note the empirical observation that membranes swollen excessively with water show high conductivity but reduced selectivity.

2.5 Research Gaps

Four gaps emerge. First, concentration dependence in AEMs has been examined mainly through transport properties such as conductivity and diffusion permeability [8], [9] rather than through equilibrium selectivity measured across several anion pairs. Second, work on mixed-salt selectivity has typically either varied composition at fixed total concentration [7] or focused on model development using literature data [4]. Third, pairs in which hydroxide competes directly with another anion have received comparatively little attention in a water treatment context; where hydroxide is studied it is usually in alkaline electrolysis, where conductivity rather than competitive selectivity is the property of interest [11]. Fourth, although comparative characterisation of the three membranes examined here exists [11], it was performed under alkaline electrolysis conditions. No published study was identified reporting water uptake and Donnan selectivity for these membrane families measured together across multiple competing anion pairs and multiple concentrations.

These observations rest on the literature identified during this review, and relevant work may exist that was not located. The contribution claimed here lies in the specific combination of membranes, anion pairs and concentrations examined rather than in the measurement techniques, which are well established.

3. Methodology

3.1 Method Details

3.1.1 Materials

Three commercial anion exchange membranes were used: Fumasep, PiperION and Sustainion. All salts were potassium salts (KCl, K_2SO_4, KNO_3 and KOH), so that differences between solutions could be attributed to the anions rather than to the accompanying cation. All solutions were prepared with deionised water.

3.1.2 Membrane Preparation

Membranes were cut into circular discs of 12 mm diameter, held constant across all samples so that results remain directly comparable. PiperION was pre-treated in 0.5 M KOH and Sustainion in 1 M KOH, each for 24 hours. This converts the membranes to a uniform hydroxide counter-ion form so that every sample begins from the same ionic baseline, and loosens the protective backing layer supplied with these membranes, which was removed after soaking. Fumasep required no pre-treatment.

3.1.3 Experimental Design

The study follows a three-factor design: three membranes, five competing anion pairs and three concentrations, giving 45 unique combinations.

Factor	Levels
Membrane	Fumasep, PiperION, Sustainion
Anion pair	Cl^-/OH^-, SO_4^{2-}/Cl^-, NO_3^-/Cl^-, NO_3^-/OH^-, SO_4^{2-}/OH^-
Concentration	0.5 M, 0.1 M, 0.01 M

Table 1. Three-factor experimental design.

In every solution the two competing anions were present at equal molar concentration. A 0.1 M SO_4^{2-}/Cl^- solution, for example, contained 0.1 M K_2SO_4 and 0.1 M KCl.

3.1.4 Paired Sample Design

Each equilibration vessel contained two membrane discs cut from the same sheet at the same time. One disc was used for gravimetric and dimensional measurement, the other for desorption and ion chromatography. Both discs therefore experienced identical solution composition, equilibration time and current treatment, and each ion chromatography measurement can be matched to the dry mass of its vessel partner. This removes the sample-to-sample variation that would otherwise limit any comparison between the two properties.

The equilibration volume was 50 mL per vessel, refreshed every 8 hours over the 48-hour equilibration period. This is large relative to the two discs, so depletion of the solution and competition between the two discs for the same ions are not expected to be significant.

3.1.5 Solution Preparation

For solutions containing both K_2SO_4 and KCl, the K_2SO_4 was dissolved first and stirred until fully dissolved before the KCl was added. Adding both salts together slows the dissolution of K_2SO_4, because the potassium supplied by KCl reduces its solubility through the common-ion effect. Dissolving the sulfate salt first avoids this.

3.1.6 Equilibration and Current Application

Each disc was immersed in its assigned mixed-salt solution for 48 hours to allow the competing anions to reach equilibrium partitioning. The solution was refreshed four times during this period, preventing depletion so that the membrane equilibrates against a solution of effectively constant composition. This matters here because concentration is one of the variables under study.

After equilibration, each membrane was mounted between the two compartments of a cell and a constant current density of 10 mA/cm² was applied for 5 minutes using a Keithley 2450 SourceMeter, with the same solution in both compartments. This drives ion redistribution under an applied electric field rather than relying on passive diffusion alone, giving a condition closer to practical operation. The same current density and duration were applied to every sample.

3.1.7 Desorption

Each membrane was then transferred to a desorption solution for 24 hours. The desorption solution was chosen to contain an anion that was not part of the equilibration pair, so that the absorbed anions are displaced without interfering with their measurement.

Equilibration pair	Desorption solution	Volume
SO_4^{2-}/Cl^-	0.1 M KOH	6 mL
NO_3^-/Cl^-	0.1 M KOH	6 mL
Cl^-/OH^-	0.1 M KNO_3	15 mL
NO_3^-/OH^-	0.1 M KCl	15 mL
SO_4^{2-}/OH^-	0.1 M KCl	15 mL

Table 2. Desorption conditions for each anion pair.

3.1.8 Dimensional and Mass Measurements

Diameter and thickness were measured with a micrometer at several points per sample and averaged. Dry dimensions were recorded on the as-cut disc before soaking; wet dimensions after equilibration, immediately before the wet mass was taken. The membrane surface was blotted with tissue before wet measurements. Membranes were then dried in a vacuum oven at 60 °C for 24 hours and the dry mass recorded.

3.1.9 Controlled Conditions

The following were held constant for all samples: disc diameter (12 mm), equilibration time (48 hours) and number of solution refreshes (four), applied current density (10 mA/cm²) and duration (5 minutes), desorption time (24 hours), drying conditions (vacuum oven, 60 °C, 24 hours) and laboratory temperature.

3.2 Evaluation Procedure

3.2.1 Water Uptake

Water uptake was calculated as the mass of water absorbed per unit mass of dry membrane:

$$WU\ (\%) \ = \ [\ (m_{wet} - m_{dry}) / m_{dry}\ ] \times 100$$

Because this is a ratio, it is independent of sample size and can be compared directly across all conditions.

3.2.2 Volume Fraction of Water

Mass-based uptake does not indicate how the absorbed water relates to membrane size. The hydrated disc was treated as a cylinder and its volume calculated from the measured wet dimensions:

$$V_{wet} \ = \ \pi\, r^2\, h$$

The volume fraction of water was then obtained as:

$$\varphi_w = (m_{wet} - m_{dry}) / V_{wet}$$

Taking the density of water as 1 g/cm³, the mass of absorbed water in grams equals its volume in cm³, so this gives the proportion of the hydrated membrane volume occupied by water.

3.2.3 Ion Concentrations in the Membrane Phase

The amount of each anion held in the membrane was obtained from the desorption solution:

$$q_i = (C_i \times V) / m_{dry}$$

where C_i is the concentration measured by ion chromatography, V the desorption volume, and m_{dry} the dry mass of the vessel partner disc. Normalising to dry mass is necessary because the three membranes differ in mass by a factor of approximately three at the same disc diameter; comparing total amounts would compare discs of different mass rather than capacities.

3.2.4 Donnan Selectivity

The selectivity coefficient compares the ratio of two anions inside the membrane with their ratio in the external solution:

$$K_{(A/B)} = (q_A / q_B) / (c_A / c_B)$$

Since the two anions were always prepared at equal molar concentration, c_A / c_B equals one and the expression reduces to the ratio of membrane-phase amounts. A value above one indicates preference for anion A. Selectivity coefficients were determined for the SO_4^{2-}/Cl^- and NO_3^-/Cl^- pairs, in which both competing anions are quantifiable by ion chromatography. Hydroxide is not detectable by this method, so for the three hydroxide-containing pairs only the partner anion could be measured and selectivity coefficients are not reported for those systems.

3.2.5 Comparison

Results were compared along the three factors of the design. Comparing across membranes at fixed pair and concentration isolates the effect of membrane type; comparing across pairs isolates the effect of anion identity; comparing across concentrations shows whether behaviour depends on the surrounding solution. The two properties were also examined together, since they describe different aspects of membrane behaviour. No predictive model was fitted; the aim is to characterise and compare measured behaviour.

4. Results

4.1 Water Uptake

4.1.1 Effect of Membrane Type

Membrane type had by far the largest influence. Averaged across all pairs and concentrations, Sustainion absorbed approximately eight times more water than Fumasep, with PiperION between them. This ordering held in every one of the 45 measurements without exception.

Membrane	Mean WU (%)	SD (%)	Range (%)	φ_w	Diameter swelling (%)
Fumasep	12.8	6.9	5.9 – 28.0	0.093	4.1
PiperION	35.8	7.7	24.0 – 47.8	0.183	5.3
Sustainion	101.8	18.8	72.6 – 131.0	0.430	7.7

Table 3. Water uptake and related properties by membrane, averaged over all pairs and concentrations (n = 15 each).

Volume fraction follows the same order. In Sustainion, water occupied on average 43% of the hydrated membrane volume against 9% in Fumasep. Diameter swelling also increased in the same sequence, but the differences between membranes were much smaller than the differences in water uptake: Sustainion absorbed eight times more water than Fumasep yet swelled only about twice as much in diameter. This indicates that a large part of the absorbed water is accommodated through thickness expansion rather than in-plane expansion, which is expected for reinforced membranes.

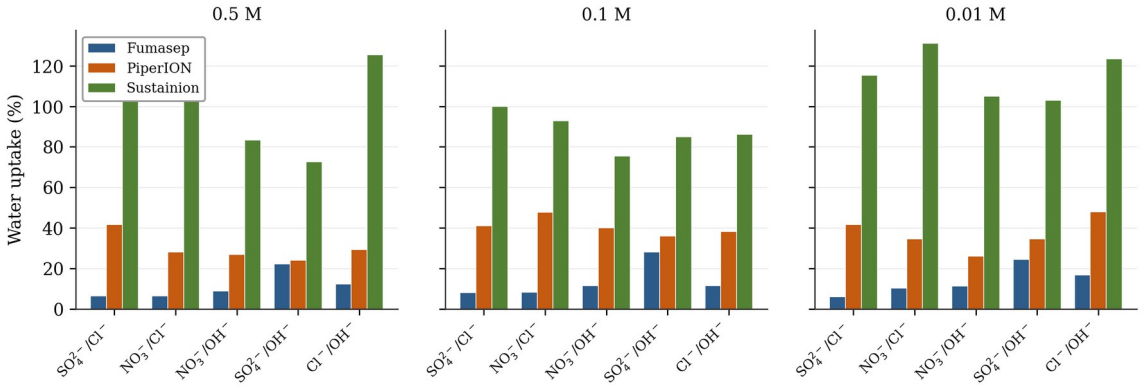


Figure 1. Water uptake for the three membranes across five anion pairs, shown separately at each concentration.

4.1.2 Effect of Anion Pair

Differences between anion pairs were much smaller than differences between membranes, spanning about 11 percentage points across the five pairs.

Anion pair	Mean WU (%)	Contains sulfate
Cl^- / OH^-	54.5	No
NO_3^- / Cl^-	53.2	No
SO_4^{2-} / Cl^-	52.2	Yes
SO_4^{2-} / OH^-	47.7	Yes
NO_3^- / OH^-	43.1	No

Table 4. Mean water uptake by anion pair, averaged over three membranes and three concentrations (n = 9 each).

Sulfate-containing pairs did not produce the highest water uptake. Averaged across all conditions, pairs containing sulfate gave 49.9% against 50.3% for pairs without sulfate, a difference of no practical significance. This is contrary to the expectation from hydration energy alone, since sulfate has the largest hydration energy of the three salt anions studied (SO_4^{2-} 1000 kJ/mol, Cl^- 370 kJ/mol, NO_3^- 270 kJ/mol) [6].

One membrane departed from the general pattern. In Fumasep, pairs containing hydroxide gave a mean water uptake of 16.3% against 7.5% for pairs without hydroxide, a ratio of 2.17, and the three hydroxide pairs occupied the top three positions for this membrane. PiperION and Sustainion both showed the opposite trend, with ratios of 0.86.

4.1.3 Effect of Concentration

Concentration had no consistent effect. This is clearest in the wet mass, which is a direct measurement requiring no normalisation.

Membrane	Wet mass 0.5 M (g)	0.1 M (g)	0.01 M (g)	Variation (%)
Fumasep	0.00886	0.00864	0.00906	4.7
PiperION	0.00322	0.00306	0.00334	8.7
Sustainion	0.01326	0.01326	0.01338	0.9

Table 5. Mean wet mass at each concentration. For Sustainion the total variation across a fifty-fold change in concentration was under 1%.

For Sustainion the wet mass varied by less than 1% across a fifty-fold change in external concentration. Dry mass, by contrast, varied by 4.6 to 12.7% between sample sets. Since water uptake is calculated as (m_wet − m_dry) / m_dry, this dry-mass variation propagates into the calculated percentage, and the apparent differences between concentration sets therefore originate largely from variation in dry mass rather than from differences in the amount of water absorbed.

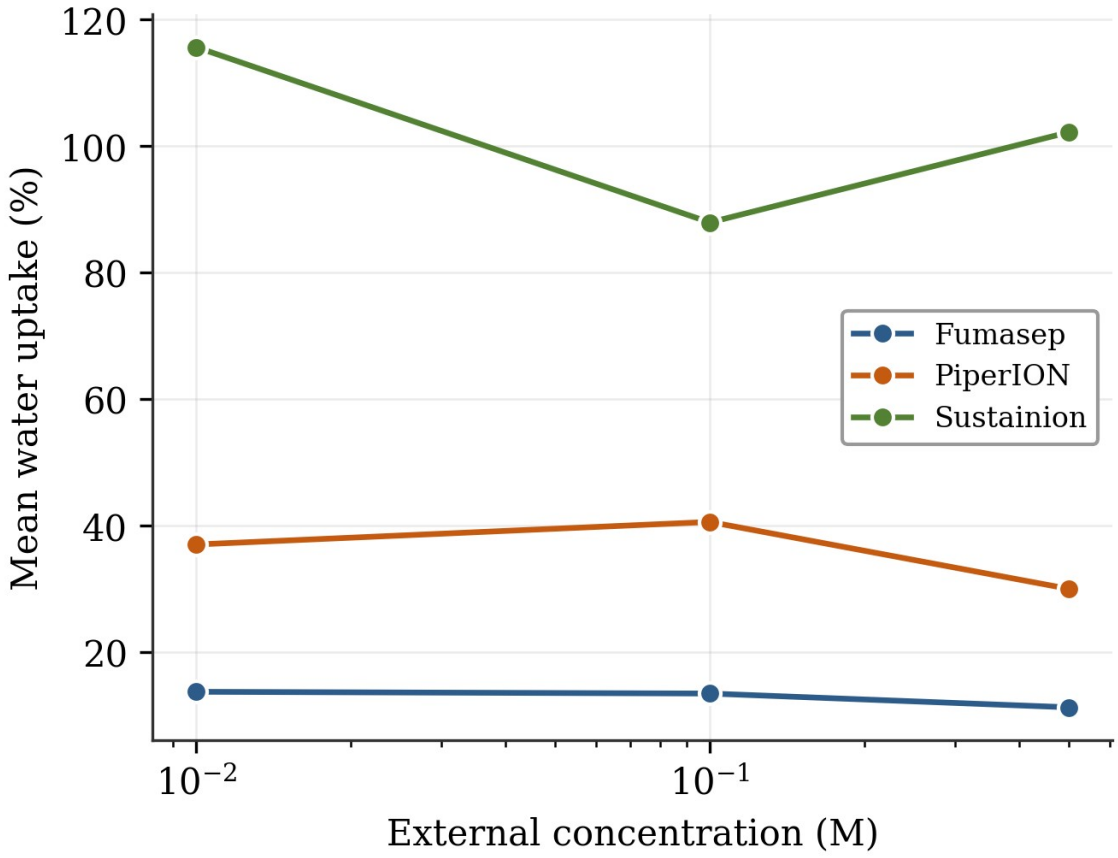


Figure 2. Mean water uptake against external concentration. No consistent trend is present for any membrane.

4.2 Ion Sorption and Donnan Selectivity

4.2.1 Selectivity Coefficients

Selectivity coefficients were determined at 0.5 and 0.1 M for the two pairs in which both anions are quantifiable by ion chromatography.

Membrane	**K(Cl^-/SO_4^{2-}) 0.5 M**	**0.1 M**	**K(NO_3^-/Cl^-) 0.5 M**	**0.1 M**
Fumasep	6.63	4.93	1.75	2.08
PiperION	2.94	2.84	1.38	1.04
Sustainion	2.81	2.17	1.62	1.53

Table 6. Donnan selectivity coefficients. All values exceed unity, giving the sorption order NO_3^- > Cl^- > SO_4^{2-}.

Every value exceeds unity. Chloride is preferred over sulfate in all three membranes, and nitrate over chloride, giving a consistent sorption order of NO_3^- > Cl^- > SO_4^{2-} at both concentrations. Fumasep excluded sulfate most strongly at both concentrations.

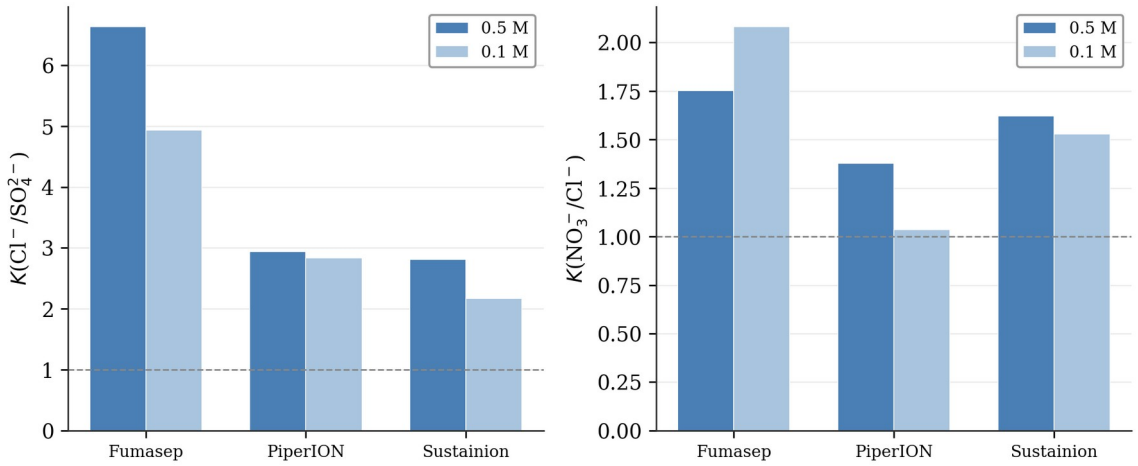


Figure 3. Selectivity coefficients at both concentrations. The dashed line marks unity, above which the first-named anion is preferred.

$K(Cl^-/SO_4^{2-})$ increased with concentration in all three membranes, by 34% for Fumasep, 30% for Sustainion and 4% for PiperION. $K(NO_3^-/Cl^-)$ showed no consistent direction, falling by 16% for Fumasep while rising by 33% for PiperION and 6% for Sustainion. Absolute ion uptake increased with concentration in every salt-pair sample, so the rise in $K(Cl^-/SO_4^{2-})$ reflects chloride increasing faster than sulfate rather than any absolute loss of sulfate.

4.2.2 Anion Uptake in Hydroxide-Containing Pairs

For the three hydroxide pairs, only the partner anion is quantifiable. Normalised to dry mass and averaged over both concentrations, uptake followed the order Cl^- (3.66×10^{-4}) > NO_3^- (2.63×10^{-4}) > SO_4^{2-} (1.33×10^{-4}) mol per gram of dry membrane. Sulfate was again the least readily partitioned, by a factor of 2.8 relative to chloride.

Comparing the amount of each anion absorbed when its partner was hydroxide against the amount absorbed when its partner was another salt anion gives ratios above unity in almost every case. For sulfate the ratios were 7.20, 1.88 and 1.91 at 0.5 M and 3.11, 7.97 and 4.51 at 0.1 M for Fumasep, PiperION and Sustainion respectively.

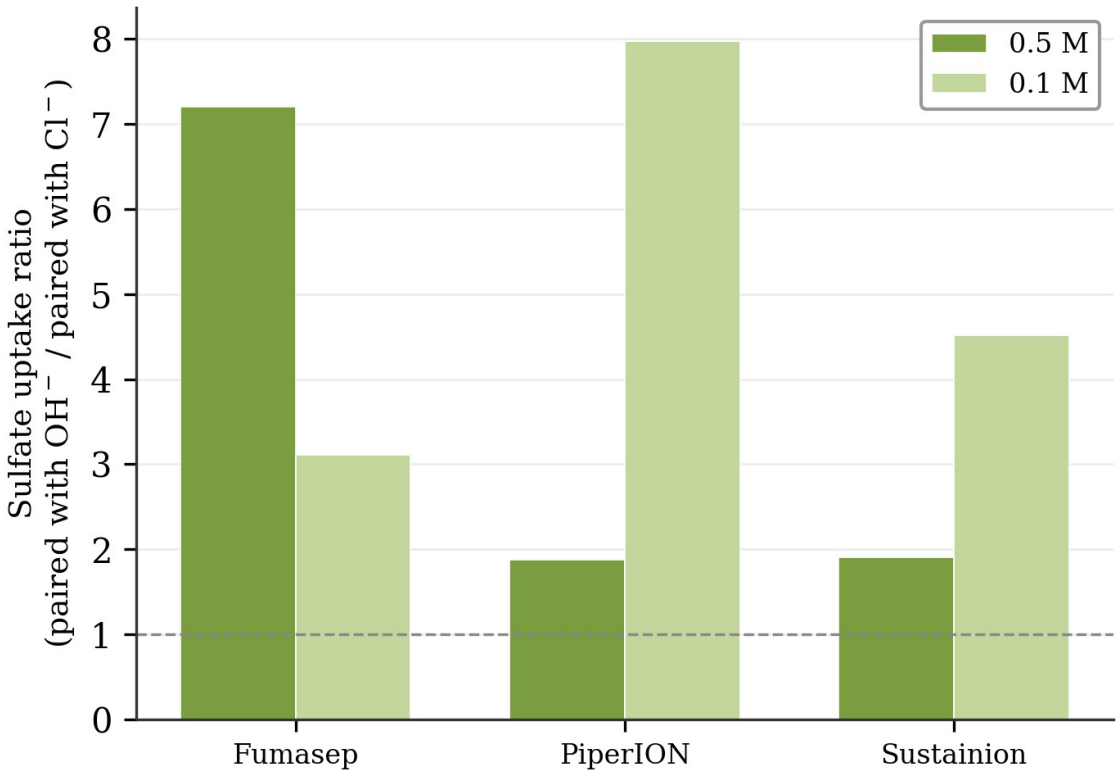


Figure 4. Sulfate uptake when paired with hydroxide relative to when paired with chloride. Values above unity indicate that more sulfate entered the membrane when hydroxide was the competing anion.

Every ratio exceeds unity, indicating that hydroxide competes less effectively than the other anions for the fixed-charge sites and leaves them more available to the partner ion. The distribution of this effect between membranes differed between the two concentrations, however: at 0.5 M it was concentrated in Fumasep, while at 0.1 M it was spread across all three.

4.3 Relationship Between Water Uptake and Selectivity

Because the two properties were measured on paired discs from the same vessel, they can be compared directly for each condition.

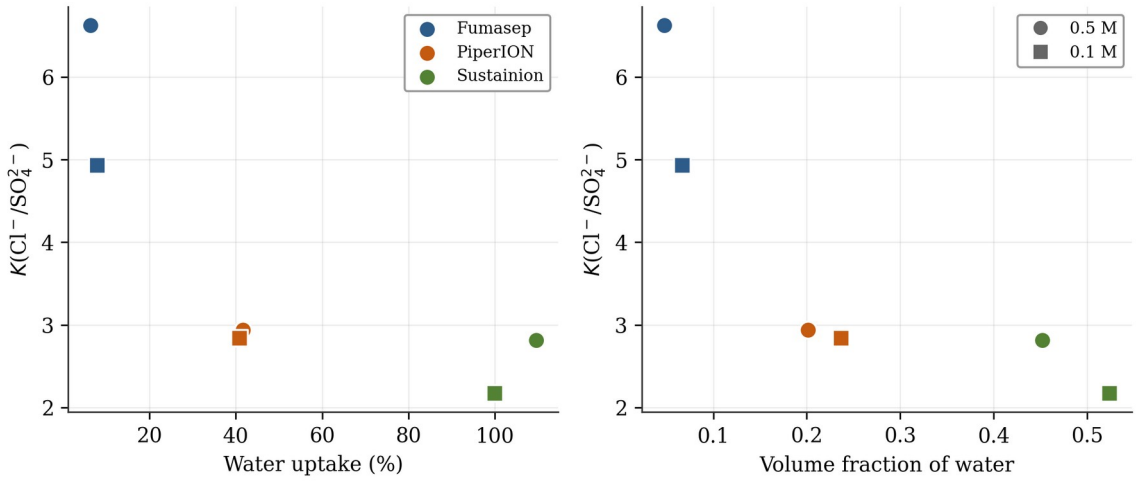


Figure 5. Selectivity coefficient $K(Cl^-/SO_4^{2-})$ against water uptake (left) and volume fraction of water (right), for both concentrations.

Selectivity decreased as hydration increased. $K(Cl^-/SO_4^{2-})$ fell from 6.63 in Fumasep, the least hydrated membrane at 6% water uptake, to 2.81 in Sustainion at 110%. The same direction was observed within each membrane between the two concentrations, giving six consistent cases out of six.

The nitrate–chloride pair showed no comparable trend. $K(NO_3^-/Cl^-)$ varied between 1.04 and 2.08 without systematic relation to hydration, and the least hydrated membrane did not give the highest value.

Absolute anion uptake in the hydroxide pairs showed no relationship with hydration either, across 18 measurements. This is consistent with expectation: absolute uptake is governed principally by ion exchange capacity, whereas the hydration effect concerns discrimination between ions rather than total amount absorbed.

5. Discussion

5.1 Membrane Chemistry Governs Water Content

The dominant result is that water uptake is determined primarily by which membrane is used, not by which anions are present or at what concentration. The eight-fold difference between Sustainion and Fumasep held under every condition tested, while the five anion pairs differed by only about 11 percentage points on average and concentration produced no consistent effect.

This has a practical consequence. Where hydration matters for an application, the choice of membrane material is the decision that governs the outcome. The composition of the feed water, at least within the range examined here, is secondary for water content, though as shown below it matters considerably for selectivity.

5.2 Sulfate Behaviour Departs From Single-Salt Expectation

Sulfate has the largest hydration energy of the salt anions studied, and in single-salt systems it gives the highest water uptake in anion exchange membranes [6]. That expectation was not met here: sulfate-containing pairs gave essentially the same average water uptake as pairs without sulfate.

The ion chromatography results explain why. All three membranes preferentially absorb chloride over sulfate under mixed conditions, with $K(Cl^-/SO_4^{2-})$ between 2.2 and 6.6. Sulfate is therefore largely excluded, and the water it would have carried does not enter with it. The ion that holds the most water is also the one the membrane admits least readily, and the two effects offset one another.

This reproduces the mixed-salt result of Chen et al. [6] rather than their single-salt result, despite substantial differences in membrane chemistry. In their study, water uptake was greatest in Na_2SO_4 solutions and sulfate sorption was strong in single salt, yet in binary mixtures with NaCl sulfate sorption fell markedly while nitrate was absorbed more strongly than chloride. The agreement across different membrane families suggests this is a general feature of mixed-salt systems rather than a property of a particular material.

Two mechanisms have been proposed for the reduced sulfate uptake in mixtures [6]. The first is that a hydrophobic polymer environment inhibits the entry of the strongly hydrated sulfate ion, whose Gibbs hydration energy is roughly three times that of chloride. The second is ion pairing: at higher concentrations, formation of $[MSO_4]^-$ converts sulfate into a monovalent species that competes less effectively with chloride. The second mechanism is consistent with the increase

in K(Cl^-/SO_4^{2-}) with concentration observed here, since ion pairing becomes more significant as concentration rises. Charge screening contributes to the same trend: increasing salinity reduces the effective range of electrostatic interactions between the membrane and solution ions, and divalent ions, which interact more strongly with the fixed charges, are more sensitive to this change than monovalent ions [3].

5.3 Effect of Hydroxide as the Competing Anion

Every anion measured was absorbed in greater amount when its partner was hydroxide rather than chloride or nitrate. This indicates that hydroxide competes least effectively of the four anions studied for the fixed-charge sites. Sulfate, the most strongly excluded anion in the salt-only pairs, showed the largest relative gain, which is consistent with an ion whose partitioning is limited primarily by competition rather than by the membrane structure itself.

Fumasep was the only membrane in which hydroxide-containing pairs also produced higher water uptake, at 16.3% against 7.5% for pairs without hydroxide. PiperION and Sustainion both showed the opposite trend. The pattern was consistent across all three concentrations and 45 measurements.

A mechanism specific to Fumasep, such as hydroxide-induced pore expansion, is not supported by the ion uptake data. Normalised to dry mass, PiperION absorbed the most sulfate at both concentrations, so Fumasep does not admit disproportionately more sulfate when hydroxide is present. A more plausible contributing factor is baseline hydration. Fumasep is by a wide margin the least hydrated membrane studied, at 12.8% against 35.8% and 101.8%. A given increment of additional water produces a proportionally larger change in a membrane that holds little water to begin with, whereas the same increment is a small fraction of the water already present in the other two. This remains unverified and is discussed further in Section 6.

5.4 Concentration Independence of Water Content

Wet mass was effectively independent of external concentration, varying by under 1% for Sustainion and under 9% for the other two membranes across a fifty-fold range. This is consistent with Elozeiri et al. [10], who reported constant water content for high-capacity ion exchange membranes across 0.01 to 1 M and largely constant water content below 0.5 M for others.

The accepted explanation involves two opposing effects. Increasing external concentration reduces the osmotic pressure difference across the membrane interface, which tends to drive

water out. At the same time, higher external concentration promotes co-ion leakage into the membrane, and those co-ions carry hydration water with them. Over the range examined here the two approximately cancel [10]. The concentration range of this study lies entirely within the region where this balance holds.

The practical implication is that within this range, a membrane's hydration state, and therefore its conductivity and mechanical behaviour, can be treated as stable even when feed concentration varies substantially.

5.5 Hydration and Selectivity

Selectivity for the chloride–sulfate pair decreased as hydration increased, falling from 6.63 in the least hydrated membrane to 2.81 in the most hydrated, with the same direction observed within each membrane between concentrations. This is directionally consistent with the charge-dilution mechanism described by Kitto and Kamcev [1], in which selectivity scales inversely with water content because the fixed charges become distributed over a larger volume and the effective charge density falls.

The dependence measured here is considerably weaker than the inverse-square scaling that model predicts. Quantitative deviations from Donnan-based predictions are long established. Cwirko and Carbonell [5] found the Donnan equation to be an inadequate quantitative predictor of electrolyte sorption in many ion exchange materials even after experimental artefacts are excluded, and attributed the residual discrepancy to non-uniform pore size and surface charge density within the membrane. Such structural non-uniformity is a plausible reason for the weaker scaling observed here.

The nitrate–chloride pair showed no comparable relationship. This difference is expected rather than anomalous. Charge dilution weakens the electrostatic field, and charge screening has been reported not to affect monovalent and divalent ions equally: divalent ions interact more strongly with fixed charges and are therefore more sensitive to changes in the electrostatic environment, a mechanism demonstrated for nanofiltration membranes and general to charged membranes [3]. Discrimination between two monovalent anions depends instead on hydrated size and hydration energy, properties not expected to scale with membrane water content. The trend therefore appears where theory predicts it and is absent where theory does not.

5.6 Consistency Between Measurement Contexts

Two independent datasets were available for comparing anion uptake. Selectivity coefficients came from the salt pairs, where the competing anions were present together in the same solution. Normalised partner-anion amounts came from the hydroxide pairs, where each anion competed only against hydroxide in a separate solution.

The two agree on sulfate, which was the least readily partitioned anion in both, with $K(Cl^-/SO_4^{2-})$ between 2.2 and 6.6 from the direct measurements and a chloride-to-sulfate amount ratio of 2.8 from the indirect comparison.

They differ on the relative positions of chloride and nitrate. The selectivity coefficients place nitrate above chloride, while the hydroxide-pair amounts place chloride above nitrate. Two factors account for this. First, the comparisons are not equivalent: selectivity coefficients describe direct competition in a shared solution, whereas the hydroxide-pair values compare measurements made in separate solutions with different desorption media. Second, the margin between chloride and nitrate is small, and errors in monovalent ion concentrations are amplified in selectivity coefficients by up to a factor of 500 [12], making this comparison far more sensitive to experimental variation than the larger sulfate margin.

Order reversals between measurement contexts are documented for this class of membrane. Chen et al. [6] reported that potassium sorbed most strongly into cation exchange membranes in single-salt solutions while calcium dominated the same membranes in binary mixtures, attributing the change to charge screening reducing Donnan exclusion as concentration rises.

Internal consistency of binary selectivity data can be assessed formally using the triangular rule, $K(A/C) = K(A/B) \times K(B/C)$, a test developed for analysing selectivity coefficient plots [13]. Applying this relation to the present data predicts $K(NO_3^-/SO_4^{2-})$ values of 11.6, 4.0 and 4.6 at 0.5 M and 10.3, 2.9 and 3.3 at 0.1 M for Fumasep, PiperION and Sustainion respectively. Direct measurement of the NO_3^-/SO_4^{2-} pair would provide an independent test of these predictions.

5.7 Implications for Membrane Selection

Taken together, the results indicate that water uptake and selectivity respond to different factors and should be assessed separately. Total hydration is governed principally by membrane chemistry and is stable across the concentration range examined. Selectivity depends on anion identity and, for pairs of differing valence, on the membrane's hydration state. A membrane

cannot therefore be chosen on a single property: the most hydrated membrane in this study was also the least selective toward sulfate, and the least hydrated the most selective.

The finding that single-salt expectations do not transfer to mixed conditions has direct consequences for design. A membrane characterised in single-salt sulfate solution would appear to be the highest water-uptake case; in a mixed chloride–sulfate feed it is not. Characterisation under conditions representative of the intended feed is therefore necessary rather than optional.

6. Limitations and Future Work

6.1 Limitations

Each of the 45 combinations was measured once. Without replicates the natural scatter of the measurement is unknown, so small differences between conditions cannot be reliably distinguished from noise. Only the larger differences reported here, particularly those between membranes, should be regarded as firmly established.

Selectivity coefficients rest on six measurements, two concentrations for each of three membranes. The inverse trend between hydration and selectivity is consistent in direction across all six, but six points indicate a trend rather than establish a quantitative relationship. Selectivity data at the third concentration would strengthen this considerably.

Hydroxide could not be quantified in the membrane phase. It is not detectable by the ion chromatography method used, which restricts selectivity coefficients to the two salt pairs and leaves three of the five pairs without a selectivity value. For those pairs only the partner anion could be measured.

Where selectivity coefficients were averaged across conditions, arithmetic averaging is known to overestimate the true value systematically, and a least-squares approach over a range of conditions has been recommended instead [12]. With only two concentrations available, that approach could not be applied here.

Volumetric swelling could not be calculated. Sustainion is supplied already hydrated and has no as-produced dry state, so no dry thickness exists for it. For the other two membranes only nominal manufacturer thicknesses were available, and these produced physically inconsistent results when used to compute volume change. Water content is therefore reported as the volume fraction in the hydrated membrane, which requires only wet dimensions.

Thickness measurements on PiperION are the least reliable in the dataset. The membrane is approximately 15 µm thick when dry, so a surface water film of a few micrometres represents a large relative error. Values derived from PiperION thickness, including its volume fraction, warrant more caution than those for the thicker membranes.

Hydrated discs of both PiperION and Fumasep curled during handling, which initially produced diameter readings at or below the dry cut size. Affected samples were re-measured with the discs flattened. Manufacturer documentation notes that membranes of this type may

vary by up to half a centimetre from cut dimensions and that wrinkling is expected, so this is a recognised handling difficulty rather than an isolated error.

Trace sulfate appeared in some NO_3^-/Cl^- samples where no sulfate was present in solution, at up to 1.85 mg/L. Measuring trace anions against a large background of another anion is a recognised analytical difficulty, and the desorption media used here contribute background concentrations of 400 to 1200 mg/L. These traces do not affect $K(NO_3^-/Cl^-)$, which uses only chloride and nitrate.

The scope was deliberately narrow in three respects. Temperature was held constant and not investigated. The two competing anions were always at equal molar concentration, so unequal ratios, which are common in real waters, were not examined. All salts were potassium salts, excluding cation effects by design.

6.2 Future Work

Measuring single-salt systems under the same protocol would be the most valuable addition. This study infers the difference between single-salt and mixed-salt behaviour from published data on different membranes; measuring both directly on the same membranes would make the comparison exact. Six samples would be sufficient to establish the principle.

Measuring the NO_3^-/SO_4^{2-} pair would allow the triangular-rule consistency test to be applied [13]. Three samples would test whether the two selectivity coefficients measured here are internally consistent, against the predicted values given in Section 5.6. This is a formal check on the existing data rather than simply an addition to it.

Selectivity data at 0.01 M would extend the dataset from two concentrations to three, raising the number of points from six to nine and allowing the hydration–selectivity trend to be assessed with more confidence. It would also test whether the concentration dependence of $K(Cl^-/SO_4^{2-})$ observed between two points is a genuine trend.

The behaviour of Fumasep with hydroxide-containing pairs deserves closer study. The effect was consistent across all three concentrations, but the proposed explanation based on baseline hydration remains unverified. Ion and water content measured on the same disc rather than on paired discs would establish directly whether the additional water enters with the additional counter-ion. Structural characterisation, for example by small-angle X-ray scattering, would test whether the hydroxide form of Fumasep differs in pore structure from the other membranes.

Unequal anion ratios would extend the work toward realistic conditions, since real water sources rarely contain two anions at equal concentration and the competitive behaviour observed here may change when one anion dominates.

Finally, replicate measurements throughout would allow proper statistical treatment and would make it possible to test which of the smaller differences observed here are real.

7. Conclusion

This study measured water uptake and Donnan selectivity for three commercial anion exchange membranes exposed to five competing anion pairs at three concentrations.

Membrane chemistry is the dominant factor governing water content. Sustainion absorbed approximately eight times more water than Fumasep, and this ordering held without exception across all 45 measurements. Neither anion identity nor concentration produced differences of comparable magnitude.

Sulfate did not produce the highest water uptake despite having the largest hydration energy of the anions studied. Ion chromatography showed that all three membranes preferentially absorb chloride over sulfate under mixed conditions, giving the sorption order $NO_3^- > Cl^- > SO_4^{2-}$. The ion that carries the most water is the least readily admitted, and the two effects offset.

Water uptake was independent of concentration over 0.01 to 0.5 M, with wet mass varying by less than 1% for Sustainion across a fifty-fold change. Within this range, membrane hydration can be treated as a property of the material rather than of the solution.

Selectivity showed an inverse trend with hydration for the chloride–sulfate pair but not for the nitrate–chloride pair, consistent with charge dilution affecting discrimination between ions of different valence more strongly than between ions of the same valence.

Taken together, these results indicate that characterising membranes in single-salt solutions does not reliably predict their behaviour in the multi-ion conditions encountered in practice, and that membrane selection requires water uptake and selectivity to be assessed as separate properties rather than inferred from one another.

Appendix A. Complete Water Uptake Dataset

All 45 gravimetric measurements. Water uptake is (m_wet − m_dry) / m_dry × 100. Volume fraction is the volume of absorbed water divided by the volume of the hydrated disc, taking the density of water as 1 g/cm³ and treating the disc as a cylinder. Diameter swelling is relative to the 12.0 mm dry cut size. Anion pair labels are abbreviated; all anions carry their usual charges.

Conc. (M)	Pair	Membrane	m_wet (g)	m_dry (g)	d_wet (mm)	t_wet (mm)	WU (%)	phi_w	Swell (%)
0.5	SO4/Cl	Fumasep	0.0083	0.0078	12.80	0.082	6.4	0.047	6.7
0.5	SO4/Cl	PiperION	0.0034	0.0024	12.90	0.038	41.7	0.201	7.5
0.5	SO4/Cl	Sustainion	0.0132	0.0063	13.00	0.115	109.5	0.452	8.3
0.5	NO3/Cl	Fumasep	0.0083	0.0078	12.75	0.079	6.4	0.050	6.2
0.5	NO3/Cl	PiperION	0.0032	0.0025	12.80	0.035	28.0	0.155	6.7
0.5	NO3/Cl	Sustainion	0.0134	0.0061	12.95	0.115	119.7	0.482	7.9
0.5	NO3/OH	Fumasep	0.0087	0.0080	12.40	0.084	8.7	0.069	3.3
0.5	NO3/OH	PiperION	0.0033	0.0026	12.60	0.039	26.9	0.144	5.0
0.5	NO3/OH	Sustainion	0.0110	0.0060	12.20	0.111	83.3	0.385	1.7
0.5	SO4/OH	Fumasep	0.0099	0.0081	12.95	0.097	22.2	0.141	7.9
0.5	SO4/OH	PiperION	0.0031	0.0025	12.20	0.046	24.0	0.112	1.7
0.5	SO4/OH	Sustainion	0.0145	0.0084	13.00	0.137	72.6	0.335	8.3
0.5	Cl/OH	Fumasep	0.0091	0.0081	12.30	0.093	12.3	0.090	2.5
0.5	Cl/OH	PiperION	0.0031	0.0024	12.50	0.043	29.2	0.133	4.2
0.5	Cl/OH	Sustainion	0.0142	0.0063	13.00	0.118	125.4	0.504	8.3
0.1	SO4/Cl	Fumasep	0.0081	0.0075	12.10	0.078	8.0	0.067	0.8
0.1	SO4/Cl	PiperION	0.0031	0.0022	12.70	0.030	40.9	0.237	5.8
0.1	SO4/Cl	Sustainion	0.0138	0.0069	12.40	0.109	100.0	0.524	3.3
0.1	NO3/Cl	Fumasep	0.0080	0.0074	12.40	0.076	8.1	0.065	3.3
0.1	NO3/Cl	PiperION	0.0031	0.0021	12.30	0.029	47.6	0.290	2.5
0.1	NO3/Cl	Sustainion	0.0135	0.0070	12.60	0.109	92.9	0.478	5.0
0.1	NO3/OH	Fumasep	0.0088	0.0079	12.20	0.089	11.4	0.087	1.7
0.1	NO3/OH	PiperION	0.0028	0.0020	12.10	0.032	40.0	0.217	0.8
0.1	NO3/OH	Sustainion	0.0121	0.0069	12.40	0.111	75.4	0.388	3.3
0.1	SO4/OH	Fumasep	0.0096	0.0075	12.40	0.098	28.0	0.177	3.3
0.1	SO4/OH	PiperION	0.0034	0.0025	12.50	0.039	36.0	0.188	4.2
0.1	SO4/OH	Sustainion	0.0135	0.0073	13.00	0.126	84.9	0.371	8.3
0.1	Cl/OH	Fumasep	0.0087	0.0078	12.50	0.091	11.5	0.081	4.2
0.1	Cl/OH	PiperION	0.0029	0.0021	12.20	0.040	38.1	0.171	1.7

Conc. (M)	Pair	Membrane	m_wet (g)	m_dry (g)	d_wet (mm)	t_wet (mm)	WU (%)	phi_w	Swell (%)
0.1	Cl/OH	Sustainion	0.0134	0.0072	12.80	0.113	86.1	0.426	6.7
0.01	SO4/Cl	Fumasep	0.0090	0.0085	12.90	0.089	5.9	0.043	7.5
0.01	SO4/Cl	PiperION	0.0034	0.0024	13.00	0.037	41.7	0.204	8.3
0.01	SO4/Cl	Sustainion	0.0140	0.0065	13.45	0.129	115.4	0.409	12.1
0.01	NO3/Cl	Fumasep	0.0086	0.0078	12.40	0.086	10.3	0.077	3.3
0.01	NO3/Cl	PiperION	0.0035	0.0026	13.40	0.039	34.6	0.164	11.7
0.01	NO3/Cl	Sustainion	0.0134	0.0058	13.50	0.111	131.0	0.478	12.5
0.01	NO3/OH	Fumasep	0.0089	0.0080	12.30	0.083	11.2	0.091	2.5
0.01	NO3/OH	PiperION	0.0029	0.0023	12.20	0.041	26.1	0.125	1.7
0.01	NO3/OH	Sustainion	0.0121	0.0059	13.05	0.120	105.1	0.386	8.8
0.01	SO4/OH	Fumasep	0.0097	0.0078	12.40	0.084	24.4	0.187	3.3
0.01	SO4/OH	PiperION	0.0035	0.0026	12.60	0.039	34.6	0.185	5.0
0.01	SO4/OH	Sustainion	0.0140	0.0069	12.60	0.132	102.9	0.431	5.0
0.01	Cl/OH	Fumasep	0.0091	0.0078	12.50	0.082	16.7	0.129	4.2
0.01	Cl/OH	PiperION	0.0034	0.0023	13.60	0.034	47.8	0.223	13.3
0.01	Cl/OH	Sustainion	0.0134	0.0060	14.00	0.120	123.3	0.401	16.7

Table A1. Complete water uptake dataset (n = 45).

Summary Statistics

Membrane	n	Mean WU (%)	SD (%)	Min (%)	Max (%)
Fumasep	15	12.8	6.9	5.9	28.0
PiperION	15	35.8	7.7	24.0	47.8
Sustainion	15	101.8	18.8	72.6	131.0

Table A2. Water uptake statistics by membrane, 15 conditions each.

Appendix B. Ion Chromatography Dataset

Measured anion concentrations in the desorption solution and derived membrane-phase amounts. Amounts are normalised to the dry mass of the paired disc from the same equilibration vessel. Salt pairs were desorbed in 6 mL, hydroxide pairs in 15 mL. Hydroxide is not detectable by ion chromatography, so for hydroxide-containing pairs only the partner anion is reported.

B.1 Salt Pairs

Conc. (M)	Membrane	Pair	Cl (mg/L)	NO3 (mg/L)	SO4 (mg/L)	m_dry (g)	K
0.5	Fumasep	SO4/Cl	5.7135	–	2.3356	0.0078	6.63
0.5	Fumasep	NO3/Cl	1.8616	5.7084	–	0.0078	1.75
0.5	PiperION	SO4/Cl	4.1034	–	3.7810	0.0024	2.94
0.5	PiperION	NO3/Cl	6.9819	16.8112	–	0.0025	1.38
0.5	Sustainion	SO4/Cl	7.0690	–	6.8108	0.0063	2.81
0.5	Sustainion	NO3/Cl	4.7841	13.5673	–	0.0061	1.62
0.1	Fumasep	SO4/Cl	3.5559	–	1.9540	0.0075	4.93
0.1	Fumasep	NO3/Cl	1.2669	4.6101	–	0.0074	2.08
0.1	PiperION	SO4/Cl	1.1403	–	1.0897	0.0022	2.84
0.1	PiperION	NO3/Cl	0.8636	1.5641	–	0.0021	1.04
0.1	Sustainion	SO4/Cl	2.5876	–	3.2341	0.0069	2.17
0.1	Sustainion	NO3/Cl	1.8983	5.0723	–	0.0070	1.53

Table B1. Salt-pair data. K is $K(Cl^-/SO_4^{2-})$ for sulfate pairs and $K(NO_3^-/Cl^-)$ for nitrate pairs. External concentrations were equal, so K reduces to the ratio of membrane-phase amounts.

B.2 Hydroxide Pairs

Conc. (M)	Membrane	Pair	Measured anion	Conc. (mg/L)	m_dry (g)	q (mol/g dry)
0.5	Fumasep	SO4/OH	SO4(2-)	6.7300	0.0081	1.297e-04
0.5	PiperION	SO4/OH	SO4(2-)	2.8385	0.0025	1.773e-04
0.5	Sustainion	SO4/OH	SO4(2-)	5.1984	0.0084	9.664e-05
0.5	Fumasep	NO3/OH	NO3(-)	9.5497	0.0080	2.888e-04
0.5	PiperION	NO3/OH	NO3(-)	2.8403	0.0026	2.643e-04
0.5	Sustainion	NO3/OH	NO3(-)	7.3420	0.0060	2.960e-04
0.5	Fumasep	Cl/OH	Cl(-)	6.8665	0.0081	3.587e-04
0.5	PiperION	Cl/OH	Cl(-)	4.1038	0.0024	7.235e-04

Conc. (M)	Membrane	Pair	Measured anion	Conc. (mg/L)	m_dry (g)	q (mol/g dry)
0.5	Sustainion	Cl/OH	Cl(-)	4.9011	0.0063	3.292e-04
0.1	Fumasep	SO4/OH	SO4(2-)	2.4306	0.0075	5.061e-05
0.1	PiperION	SO4/OH	SO4(2-)	3.4736	0.0025	2.170e-04
0.1	Sustainion	SO4/OH	SO4(2-)	5.8386	0.0073	1.249e-04
0.1	Fumasep	NO3/OH	NO3(-)	3.8806	0.0079	1.188e-04
0.1	PiperION	NO3/OH	NO3(-)	3.3308	0.0020	4.029e-04
0.1	Sustainion	NO3/OH	NO3(-)	5.8639	0.0069	2.056e-04
0.1	Fumasep	Cl/OH	Cl(-)	2.5173	0.0078	1.366e-04
0.1	PiperION	Cl/OH	Cl(-)	2.4013	0.0021	4.838e-04
0.1	Sustainion	Cl/OH	Cl(-)	2.8350	0.0072	1.666e-04

Table B2. Hydroxide-pair data. Only the partner anion is quantifiable; q is normalised to the dry mass of the paired disc.

B.3 Derived Comparisons

Membrane	SO4 ratio 0.5 M	SO4 ratio 0.1 M	Predicted K(NO3/SO4)
Fumasep	7.20	3.11	11.6
PiperION	1.88	7.97	4.0
Sustainion	1.91	4.51	4.6

Table B3. Sulfate uptake ratio when paired with hydroxide relative to chloride, and the $K(NO_3^-/SO_4^{2-})$ value predicted at 0.5 M by the triangular rule.

References

[1] D. Kitto and J. Kamcev, “Predicting the conductivity–selectivity trade-off and upper bound in ion-exchange membranes,” ACS Energy Letters, vol. 9, no. 4, pp. 1346–1352, 2024. doi: 10.1021/acsenergylett.4c00301

[2] P. Aydogan Gokturk, R. Sujanani, J. Qian, Y. Wang, L. E. Katz, B. D. Freeman, and E. J. Crumlin, “The Donnan potential revealed,” Nature Communications, vol. 13, art. 5880, 2022. doi: 10.1038/s41467-022-33592-3

[3] S. Pan, M. Levi, L. Birnhack, and R. Epsztein, “Regulating ionic composition to tune monovalent–divalent ion selectivity in nanofiltration membranes,” ACS ES&T Engineering, vol. 6, no. 5, pp. 1691–1704, 2026. doi: 10.1021/acsestengg.6c00239

[4] R. Wang, R. Duddu, and S. Lin, “Extended Donnan–Manning theory for selective ion partition and transport in ion exchange membrane,” Journal of Membrane Science, vol. 681, art. 121782, 2023. doi: 10.1016/j.memsci.2023.121782

[5] E. H. Cwirko and R. G. Carbonell, “Ionic equilibria in ion-exchange membranes: a comparison of pore model predictions with experimental results,” Journal of Membrane Science, vol. 61, pp. 211–226, 1992.

[6] G. Q. Chen, K. Wei, A. Hassanvand, B. D. Freeman, and S. E. Kentish, “Single and binary ion sorption equilibria of monovalent and divalent ions in commercial ion exchange membranes,” Water Research, vol. 175, art. 115681, 2020. doi: 10.1016/j.watres.2020.115681

[7] H. Patel, D. Roy, L. Santiago-Pagán, A. Bentley, and J. Kamcev, “Concentration gradient-driven transport in anion-exchange membranes enables highly selective Cl^{-}/SO_4^{2-} separation,” Journal of Membrane Science, vol. 754, art. 125647, 2026. doi: 10.1016/j.memsci.2026.125647

[8] V. Sarapulova, N. Pismenskaya, V. Titorova, M. Sharafan, Y. Wang, T. Xu, Y. Zhang, and V. Nikonenko, “Transport characteristics of CJMAED™ homogeneous anion exchange membranes in sodium chloride and sodium sulfate solutions,” International Journal of Molecular Sciences, vol. 22, no. 3, art. 1415, 2021. doi: 10.3390/ijms22031415

[9] N. Pismenskaya, V. Sarapulova, E. Nevakshenova, N. Kononenko, M. Fomenko, and V. Nikonenko, “Concentration dependencies of diffusion permeability of anion-exchange membranes in sodium hydrogen carbonate, monosodium phosphate, and potassium hydrogen tartrate solutions,” Membranes, vol. 9, no. 12, art. 170, 2019. doi: 10.3390/membranes9120170

[10] A. A. E. Elozeiri, R. G. H. Lammertink, H. H. M. Rijnaarts, and J. E. Dykstra, “Water content of ion-exchange membranes: measurement technique and influence on the ion mobility,” Journal of Membrane Science, vol. 698, art. 122538, 2024. doi: 10.1016/j.memsci.2024.122538

[11] M. Cámaras-Miguel, K. Van Daele, N. Daems, and T. Breugelmans, “Commercial anion exchange membranes for alkaline water electrolysis: linking performance, stability, and physicochemical properties,” International Journal of Hydrogen Energy, 2026. doi: 10.1016/j.ijhydene.2026.154225

[12] Y. Kim and D. F. Lawler, “Selectivity coefficients of cation-exchange membranes: maximizing consistency and minimizing error amplification,” Separation and Purification Technology, vol. 81, pp. 357–362, 2011.

[13] S. Ioannidis, A. Anderko, and S. J. Sanders, “Internally consistent representation of binary ion exchange equilibria,” Chemical Engineering Science, vol. 55, pp. 2687–2698, 2000.