Water Research 254 (2024) 121382

Contents lists available at ScienceDirect

Water Research

journal homepage: www.elsevier.com/locate/watres

Selective adsorption in ion exchange membranes: The effect of solution ion composition on ion partitioning

S. Ozkul [a], O. Arbabzadeh [a,c], R.J.M. Bisselink [b], N.J.M. Kuipers [b], H. Bruning [a], H.H.M. Rijnaarts [a], J.E. Dykstra [a,*]

[a] *Environmental Technology, Wageningen University & Research, Bornse Weilanden 9, Wageningen 6708 WG, the Netherlands*
[b] *Food and Biobased Research, Wageningen University & Research, Bornse Weilanden 9, Wageningen 6708 WG, the Netherlands*
[c] *Department of Civil, Environmental and Architectural Engineering, University of Padua, Via Marzolo 9, Padua 35131, Italy*

ARTICLE INFO

Keywords:
Electrodialysis
Membrane selectivity
Selective adsorption
Ion partitioning
Size exclusion
BMCSL theory

ABSTRACT

Electrodialysis is a water desalination technology that enables selective separation of ions, making it a promising solution for sustainable water reuse. The selectivity of the process is mainly determined by the properties of ion exchange membranes that can vary depending on the composition of ions in water, such as water uptake and charge density. In this work, we studied selective adsorption of Na^+ and K^+ ions in various ion exchange membranes considering the effect of solution ion composition on membrane water volume fraction. For that purpose, we conducted membrane adsorption experiments using solutions with Na^+ and K^+ ions with different ion compositions including Li^+, Ca^{2+} or Mg^{2+} ions at different concentrations (0.001 – 0.25 M). The experiments showed that with the total ion concentration and the amount of divalent ions in solution, the membrane water volume fraction decreases while the selective adsorption of the smaller (hydrated) K^+ ions over the Na^+ ions in the membrane increases. We developed a theoretical framework based on Boublik-Mansoori-Carnahan-Starling-Leland (BMCSL) theory to describe the effect of membrane water volume fraction on selective adsorption of the ions by including volumetric effects, such as size exclusion. The developed framework was used to describe ion partitioning results of the membrane adsorption experiments. In addition, the effect of solution ion composition on selective ion removal during electrodialysis operation was evaluated using experimental data and theoretical calculations. The results of this study show that considering volumetric effects can improve the ion partitioning description in ion exchange membranes for solutions with various ion compositions.

1. Introduction

Selective separation of ions in water is essential in many fields to achieve sustainable water reuse and resource recovery. This creates a rising interest for developing water treatment technologies that can selectively remove specific ions. Electrodialysis (ED) is a water treatment technology that is mainly applied to remove charged species from water using an electrical force and ion exchange membranes (IEMs) with high charge density (Sajjad et al., 2019; Ran et al., 2017). The ED process has shown a great potential to selectively remove ions based on their properties, such as valency, size, and hydration energy (Munchinger and Kreuer, 2019; Nagarale et al., 2006; Luo et al., 2018).

Physical-chemical characteristics of IEMs were reported to have a significant influence on the selectivity of membranes towards ions with different properties (Mubita et al., 2022; Sata et al., 1995; Mubita et al., 2020; Farrokhzad et al., 2015), which determines the selectivity of the ED process. Mubita et al. (2022) reported that increasing the membrane thickness and decreasing the membrane charge density increase the selectivity of NO_3^- over Cl^- for anion exchange membranes (AEMs). Sata et al. (1995) and Mubita et al. (2020) investigated the effect of AEM hydrophilicity on monovalent ion selectivity of the membranes; they concluded that decreasing hydrophilicity of the membranes can enhance selective removal of the ion with lower hydration energy. Farrokhzad et al. (2015) reported increasing selectivity of divalent ions over monovalent ions with higher water uptake for cation exchange membranes (CEMs); they explained their findings by the enhanced adsorption of the divalent ion provided by the higher water content in the membrane. Previous research showed that understanding the effect of membrane properties on ion selectivity is important to improve membrane selectivity, and therefore the selectivity of the ED process.

---

[*] Corresponding author.
E-mail address: jouke.dykstra@wur.nl (J.E. Dykstra).

https://doi.org/10.1016/j.watres.2024.121382
Received 22 November 2023; Received in revised form 23 February 2024; Accepted 24 February 2024

The water volume fraction of the membranes is one of the key parameters to consider when studying the selectivity of IEMs because it determines the membrane porosity, i.e., the volume available for solution to enter, and alters the thickness and the charge density of the membranes; hence influencing the selective adsorption of ions. However, defining the volume fraction of the membrane components, such as the water, the hydrated ions and the membrane polymer matrix, can be challenging since they do not only depend on the membrane structure, but also on the type and the concentration of ions in the bulk solution the membranes are in contact with (Geise et al., 2014; Strathmann, 2004). Improving the theoretical description of ion partitioning by considering the change in the membrane volume fractions with ion composition in solution can provide a better understanding of the selective adsorption of ions in the IEMs for a variety of water streams.

Various studies focused on the theoretical understanding and the definition of ion partitioning between a bulk solution and homogenous IEMs. Hannachi et al. (2009) and Miyoshi et al. (1992) studied the use of constant equilibrium coefficients between the ions and the membrane surface groups to describe selective ion adsorption in membranes for different two-cation systems. They reported that the obtained equilibrium coefficients are depending on the total ion concentration in solution for monovalent-monovalent (Hannachi et al., 2009), and monovalent-multivalent ion mixtures (Miyoshi et al., 1992), which could limit the use of the obtained values to describe ion partitioning for different water streams. The Donnan affinity theory that describes ion partitioning with the Boltzmann equation including a specific affinity term for each ion, and a membrane Donnan potential (the potential difference between the membrane and the bulk solution) was also used and validated for two-ion systems (Mubita et al., 2022; Ozkul et al., 2023). By including the Donnan potential, it is possible to improve ion partitioning predictions further for monovalent-multivalent ion mixtures based on the ion valency. However, the Donnan affinity theory does not evaluate the effect of membrane volume fractions on ion partitioning and describes all possible physical and chemical interactions between the counterions and the IEMs, such as volumetric interactions, using a single affinity term. The Boublik-Mansoori-Carnahan-Starling-Leland (BMCSL) theory was originally developed to describe ion partitioning for multi-component sphere mixtures based on the volume fractions. The theory has been modified and used to successfully describe ion partitioning for porous electrodes (Suss, 2017; Shocron et al., 2022), sediments (Spruijt and Biesheuvel, 2014) and polymer brushes (de Vos et al., 2009). The BMCSL theory can be used as a novel approach to describe the contribution of volumetric effects, such as size exclusion, on ion partitioning for IEMs (Biesheuvel and Dykstra, 2020).

We previously developed a theoretical framework to describe the ion transport in the ED process using the extended Nernst-Planck equation, where we also successfully determined ion partitioning for Na^+ and K^+ mixtures using the Donnan theory (Ozkul et al., 2023). In the present study, we focus on improving the theoretical description of ion partitioning for solutions with different ionic compositions by including the volumetric effects. We investigated the selective adsorption of Na^+ and K^+ ions in the membranes submerged in solutions with Li^+, Ca^{2+} or Mg^{2+} ions at different concentrations. The effect of ion type and concentration in the bulk solution on the membrane volume fractions and the selective adsorption of ions was discussed. We evaluated the validity of the Donnan affinity theory and the BMCSL theory to describe experimental ion partitioning data. Additionally, we evaluated the effect of solution ion composition on ED process selectivity under operational conditions using experimental data and theoretical calculations.

2. Theory on ion partitioning in ion exchange membranes

The theoretical framework is developed to describe ion partitioning in IEMs for different solution ion compositions including volumetric effects. The theory domain is considered as the whole membrane volume comprised of three volume fractions: (i) rigid **membrane polymer matrix**, (ii) **hydrated ions** occupying volume, and (iii) **water** around the ions and the membrane matrix (Fig. 1). The partitioning of ions with different volumetric size is described based on the volume available inside the membrane for target ions to enter, i.e. the membrane porosity, which is defined by the membrane water volume fraction in this study.

We started defining ion partitioning with the chemical potential of the ions across the membrane-solution interface. At equilibrium, the electrochemical potential of an ion in the bulk solution outside the membrane is equal to that just inside the membrane, and can be expressed in non-dimensional form by

$$\ln c_{\mathrm{s},i} + \mu_{\mathrm{s},i} + z_i\phi_s = \ln c_{\mathrm{m},i} + \mu_{\mathrm{m},i} + z_i\phi_{\mathrm{m}} \tag{1}$$

where $c_{\mathrm{s},i}$ is the concentration of ions in the bulk solution ($\mathrm{mol\cdot L^{-1}}$), $c_{\mathrm{m},i}$ is the concentration of ions in the membrane ($\mathrm{mol\cdot L^{-1}}$), $\mu_{\mathrm{s},i}$ is the chemical potential of ions in the bulk solution, $\mu_{\mathrm{m},i}$ is the chemical potential of ions just inside the membrane, z_i is the valency of the ions, ϕ_{s} is the electrical potential in the bulk solution, and ϕ_{m} is the electrical potential just inside the membrane. Rearranging Eq. (1) gives

$$\ln c_{\mathrm{m},i} = \ln c_{\mathrm{s},i} + \Delta\mu_i + z_i\Delta\phi \tag{2}$$

where we evaluated the chemical potential difference for each counterion i, $\Delta\mu_i$, using the Boltzmann equation,

$$c_{\mathrm{m},i} = c_{\mathrm{s},i}\exp\left(-z_i\Delta\phi_{\mathrm{D}} + \Delta\mu_i^{\mathrm{aff}}\right) \tag{3}$$

where $\Delta\phi_{\mathrm{D}}$ is the dimensionless Donnan potential at the membrane-solution interface due to the fixed membrane surface groups, and $\Delta\mu_i^{\mathrm{aff}}$ is the ion affinity that describes the selective adsorption of specific ions in a membrane. In the Donnan theory extended with an affinity term, the **Donnan affinity theory**, the ion affinity value is assumed to be membrane or condition specific for each ion, which defines a certain selectivity for a type of membrane without describing its dependency on the parameters that can alter the selective adsorption of ions, such as the membrane volume fraction. Such parameters are depending on the ion composition in solution, hence, with the Donnan affinity theory, the affinity of the ions in the membrane should be defined for every ion for every condition. On the other hand, the **BMCSL theory** includes two phenomena to describe the chemical potential difference $\Delta\mu_i$: the chemical attraction of an ion towards the membrane surface groups, μ_i^{att}, and the excess term that relates to the exclusion of an ion by the membrane due to its volumetric size, μ_i^{exc}, both depending on the membrane water volume fraction. Using the BMCSL theory, ion partitioning can be described based on Eq. (3) as

$$c_{\mathrm{m},i} = c_{\mathrm{s},i}\exp\left(-z_i\Delta\phi_{\mathrm{D}} - \mu_i^{\mathrm{att}} - \mu_i^{\mathrm{exc}}\right) \tag{4}$$

where the total membrane affinity for ion i can be described as $\mu_i = -(\mu_i^{\mathrm{att}} + \mu_i^{\mathrm{exc}})$. Note that μ_i^{att}, μ_i^{exc} and $c_{\mathrm{m},i}$ in Eq. (4) are defined per unit of total wet membrane volume; $c_{\mathrm{m},i}$ can be defined as per unit of water volume inside the membrane by multiplying with the wet volume of the membrane divided by the water amount in the membrane. The chemical attraction term, μ_i^{att}, is defined using the specific interaction of an ion with the membrane surface groups (de Vos et al., 2009) as

$$\mu_i^{\mathrm{att}} = -V_i\chi_{\mathrm{m},i}\eta \tag{5}$$

where η is the packing degree of the membranes that relates to the membrane water volume fraction, p, as $\eta = 1 - p$ (Castaño Osorio et al., 2022), V_i is the hydrated volume of an ion i ($\mathrm{m^3}$) and $\chi_{\mathrm{m},i}$ is the non-electrostatic interaction between an ion i and the membrane surface groups ($\mathrm{m^{-3}}$). The size exclusion, μ_i^{exc}, is evaluated using the BMCSL equation developed for a mixture of species with different size using (Biesheuvel and Dykstra, 2020; Castaño Osorio et al., 2022),

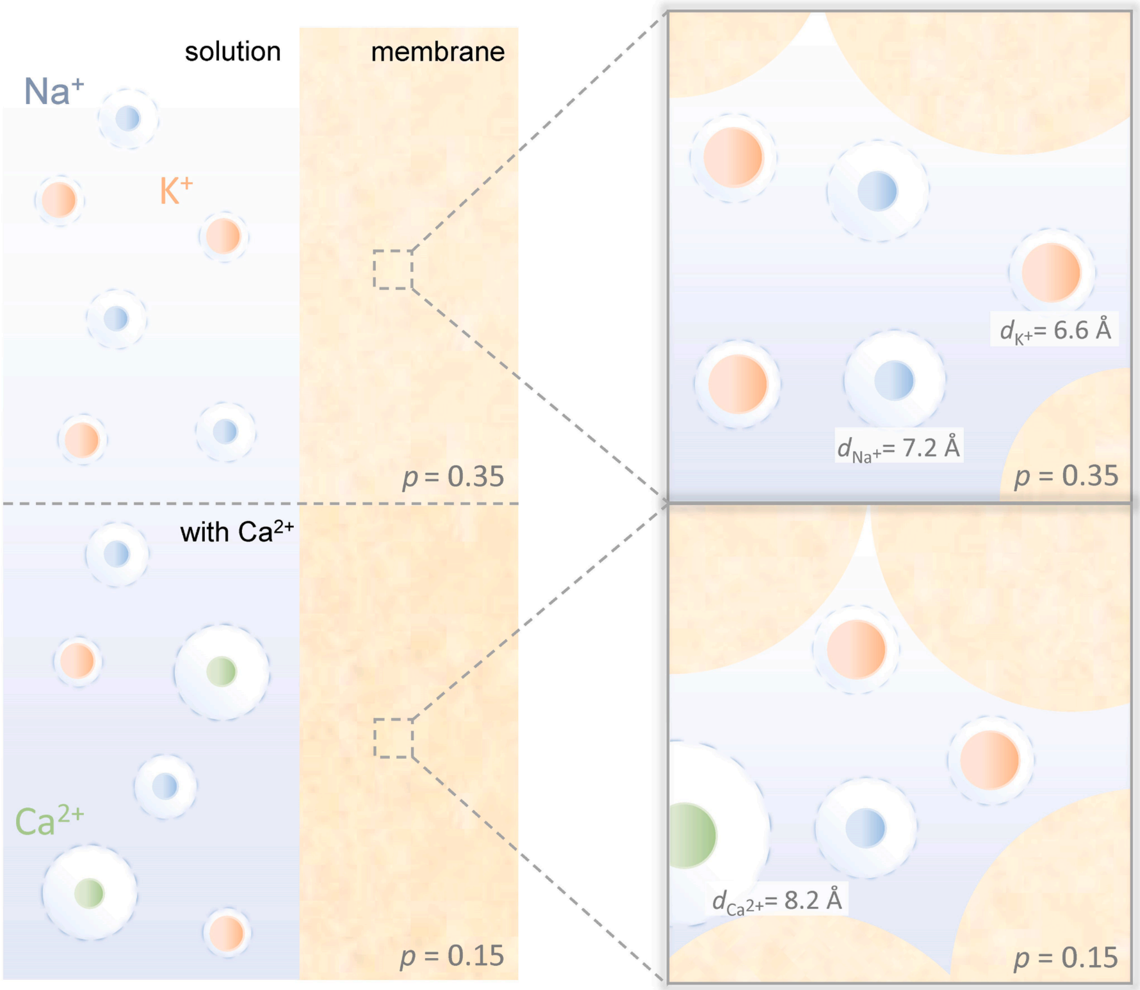

Fig. 1. Schematic description of selective ion adsorption in membranes depending on membrane water volume fraction. p: membrane water volume fraction, d_i: hydrated diameter of the ions.

$$\mu_i^{\text{exc}} = \frac{3\eta}{1-\eta}\alpha_i^{'} + 3\left(\ln(1-\eta) + \frac{\eta(2-\eta)}{(1-\eta)^2}\right)\alpha_i^{'2} - 2\left(\ln(1-\eta) + \frac{\eta(2\eta^2-4\eta+1)}{(1-\eta)^3}\right)\alpha_i^{'3} \tag{6}$$

where $\alpha_i^{'}$ defines the ratio of the ion size over the effective pore size of the membrane that can be defined by (Biesheuvel and Dykstra, 2020)

$$\alpha_i^{'} = \frac{6\eta}{1-\eta}\frac{d_i}{d_{\text{m}}} \tag{7}$$

where d_i is the hydrated diameter of an ion i (m) and d_{m} is the average diameter of the membrane spheres (m). The membrane sphere diameter in Eq. (7), d_{m}, and the specific interaction of ions with the membrane surface groups in Eq. (5), $\chi_{\text{m},i}$, are used as fitting parameters to describe ion partitioning. With the use of the BMCSL theory, the aim is to describe ion partitioning using a single value of d_{m} for the membranes, and for every ion i, a single value of parameter $\chi_{\text{m},i}$, independent of the ion composition of the solution.

Ion partitioning can be determined by solving Eq. (3) for the Donnan affinity theory or Eq. (4) for the BMCSL theory with the electroneutrality condition inside the membrane,

$$\sum_i z_i c_{\text{m},i} + \omega X = 0 \tag{8}$$

where ω is the sign of the membrane charge (−1 for CEM and +1 for AEM) and X is the fixed charge density of the membrane (mol·L^{-1}).

3. Materials and methods

The effect of type and concentration of ions in the bulk solution on the volume fractions in the membrane and the selective adsorption of Na^+ and K^+ ions was investigated by membrane adsorption experiments at equilibrium. Additionally, ED experiments were conducted to evaluate the effect of divalent ions in solution on selective ion removal by the ED process. The obtained data from the experiments were used to evaluate and validate the theoretical description of ion partitioning at equilibrium and during ED process operation. Solutions used in the experiments were prepared using demineralized water and reagent-grade NO_3^- salts.

3.1. Membrane adsorption experiments

Two types of cation exchange membranes were used for the adsorption experiments: Neosepta CMX-fg standard and Neosepta CMS monovalent selective membranes (Astom, Tokuyama Co., Japan). Both membranes have the same surface groups (-HSO_3^-) and the polymer structure (styrene and divinylbenzene copolymer structure reinforced with polyvinyl chloride) with different cross-linking degree and surface structure. Solutions with Li^+, Ca^{2+} or Mg^{2+} ions were used for the experiments due to their different properties, such as their valency, size, hydration energy (Table 1), and affinity to the membrane surface groups. The membrane adsorption experiments were performed at room temperature.

For the experiments, the membrane samples with a surface area of ~20 cm^2 were submerged into solutions with varying concentrations of Na^+ and K^+ (total of 0.1 M) in presence of Li^+ (0.05, 0.1 and 0.25 M), Mg^{2+} (0.01, 0.05 and 0.09 M) or Ca^{2+} (0.001, 0.0025, 0.01, 0.05 and 0.09 M). Solutions were renewed once after 2 h, and the membranes were left submerged in the solutions for 24 h to reach equilibrium. Thereafter, the surface water from the membrane samples was removed using a filter paper and the wet weight of the swollen membrane samples was determined. Afterwards, the membrane samples were briefly soaked into demineralised water to remove the excess solution, then the samples containing Mg^{2+} were submerged into 0.1 M $Ca(NO_3)_2$ solution, and the rest of the samples were submerged into 0.1 M $Mg(NO_3)_2$ solution to exchange all loaded ions in the membrane. Exchange solutions were collected once after 2 h for each membrane sample and renewed for another 22 h. Afterwards, the renewed solutions were collected and combined with the first solution collected for each membrane sample; the cation concentrations in the combined exchange solutions were measured using inductively coupled plasma spectrometry (ICP-OES, PerkinElmer Avio 500). Finally, the membrane samples were dried in a vacuum oven at 40 °C for 24 h to determine the dry weight of the membranes. The concentration of the target ions in the membrane, $c_{m,i}$, was calculated using

$$c_{m,i} = \frac{c_{a,i}\ V_{tot}}{M_i\ (m_{wet} -\ m_{dry})} \tag{9}$$

where $c_{a,i}$ is the concentration of ion i analysed using ICP-OES ($mg \cdot L^{-1}$), V_{tot} is the total volume of the combined exchange solutions (L), M_i is the molecular weight of ion i ($g \cdot mol^{-1}$), and m_{wet} and m_{dry} are the wet and dry membrane weight (g). Selective adsorption in the membrane is defined by a separation factor $\Delta\mu_{K^+ -\ Na^+}$ calculated as the affinity difference between the target ions K^+ and Na^+ ($\mu_{K^+} - \mu_{Na^+}$) based on Eq. (4) using

$$\Delta\mu_{K^+ -\ Na^+} = \ln\left(\frac{c_{m,K^+}\ c_{s,Na^+}}{c_{m,Na^+}\ c_{s,K^+}}\right). \tag{10}$$

The water volume fraction of the membrane, p, is calculated for each membrane sample using

$$p = \frac{m_{wet} - m_{dry} - V_{m,j}}{m_{wet} - m_{dry} + \frac{m_{dry}}{\rho_m}} \tag{11}$$

$$V_{m,j} = c_{m,j}\left(m_{wet} - m_{dry}\right) N_A \frac{\pi d_j^3}{6} \tag{12}$$

where $V_{m,j}$ is the hydrated volume of additional ion j in the membrane, ρ_m is the density of the membrane material (1.3 $g \cdot cm^{-3}$), N_A is Avogadro's number ($6.02\ 10^{23}\ mol^{-1}$) and $c_{m,j}$ and d_j are the concentration and the hydrated diameter (Table 1) of ion j in the membrane, respectively.

Table 1
Properties of the ions investigated in the present study.

	Ion diameter (nm) (Nightingale, 1959)	Hydrated ion diameter, d_i (nm) (Nightingale, 1959)	Hydration (free) energy ($kJ \cdot mol^{-1}$) (Marcus, 2015)
Li^+	0.120	0.764	−489
Na^+	0.190	0.716	−383
K^+	0.266	0.662	−312
Mg^{2+}	0.130	0.856	−1837
Ca^{2+}	0.200	0.824	−1527

3.2. Electrodialysis experiments

A laboratory-scale ED setup (PCCell BED 1–3 Compact, PCA GmbH, Germany) including an ED stack and three tanks to store diluate, concentrate and electrolyte solutions was used for the ED experiments. The ED stack is equipped with a Pt-Ir coated titanium anode and a V4A steel cathode and is comprised of ten repeating cell pairs each consisting of one AEM (Neosepta AMX-fg) and one CEM (Neosepta CMX-fg) with a spacer between them to create the flow channels. The active surface area of each membrane in the ED stack was 8 cm x 8 cm. Experiments were performed using mixtures of 0.05 M Na^+ and 0.05 M K^+, in presence of 0.05 M Ca^{2+} or 0.05 M Mg^{2+}. Feed solutions were recirculated through the ED stack continuously at a flow rate of 70 $L \cdot h^{-1}$. A power supply (Voltcraft PPS-16,005) was used to apply a constant voltage of 10 V during the experiments. Samples were collected periodically from the diluate solution and analysed using ICP-OES (PerkinElmer Avio 500) to determine the concentration of cations. The temperature of the solutions was controlled at ~20 °C with a cooling system throughout the experiments. Conductivity of the solutions was measured and recorded continuously using a Hach SensION+ MM374 sensor, and the experiments continued until the diluate solution has reached a conductivity of 50 $\mu S \cdot cm^{-1}$. Selective removal of K^+ over Na^+ ions with the ED process during desalination is calculated by a separation factor expressed as (Mubita et al., 2022)

$$\beta_{K^+/Na^+} = \frac{J_{K^+}}{J_{Na^+}} \frac{c_{d,Na^+}}{c_{d,K^+}} \tag{13}$$

where $c_{d,i}$ is the concentration of ion i in the diluate channel ($mol \cdot L^{-1}$) and J_i is the flux of ion i from the diluate to the concentrate channel ($mol \cdot m^{-2} \cdot s^{-1}$), which is calculated by dividing the ion mass decrease in the diluate channel by the membrane area and the time interval between the measurements.

4. Results and discussion

4.1. Effect of solution ion composition on membrane properties

4.1.1. Membrane volume fractions

Volume fractions of the CMX-fg and the CMS membranes based on the solution ion composition are evaluated by the membrane adsorption experiments, and the results are presented in Fig. 2. The results of the two data sets for the CMX-fg membranes with 0.05 M Li^+ and 0.001 M Ca^{2+} ions are presented in Fig. S1 in the Supplementary Information (SI), Fig. 2. For each data set, CMS membranes showed lower water volume fraction than CMX-fg membranes (Fig. 2). The lower water volume fraction of the CMS membranes can be attributed to the more compact membrane structure due to their higher cross-linking degree (Tuan and Buess-Herman, 2007; Sarapulova et al., 2019). Also in general, the membrane water volume fraction is observed to be decreasing with the increasing total ion concentration in the bulk solution for both types of membrane, which is explained by reduced membrane water uptake due to a decreasing osmotic pressure difference between the bulk solution and the membrane (Strathmann, 2004; Fontananova et al., 2017).

The results also showed the membrane water volume fraction decreases when divalent Ca^{2+} and Mg^{2+} ions are present in the bulk solution; this effect is observed to be higher in the presence of Ca^{2+} than of Mg^{2+} ions at the same concentrations (Fig. 2). Multivalent ions can reduce the effective volume available inside the membranes for solution to enter by forming bridges between multiple membrane surface groups (Fontananova et al., 2017). Such effect is expected to be more significant for Ca^{2+} than for Mg^{2+} ions due to the higher affinity of Ca^{2+} ions to the membrane surface groups ($-HSO_3^-$) (Besha et al., 2020). In addition, the volume fraction of the Mg^{2+} ions in the membranes is higher than of the Ca^{2+} ions at the same concentration (Fig. 2), although the affinity of

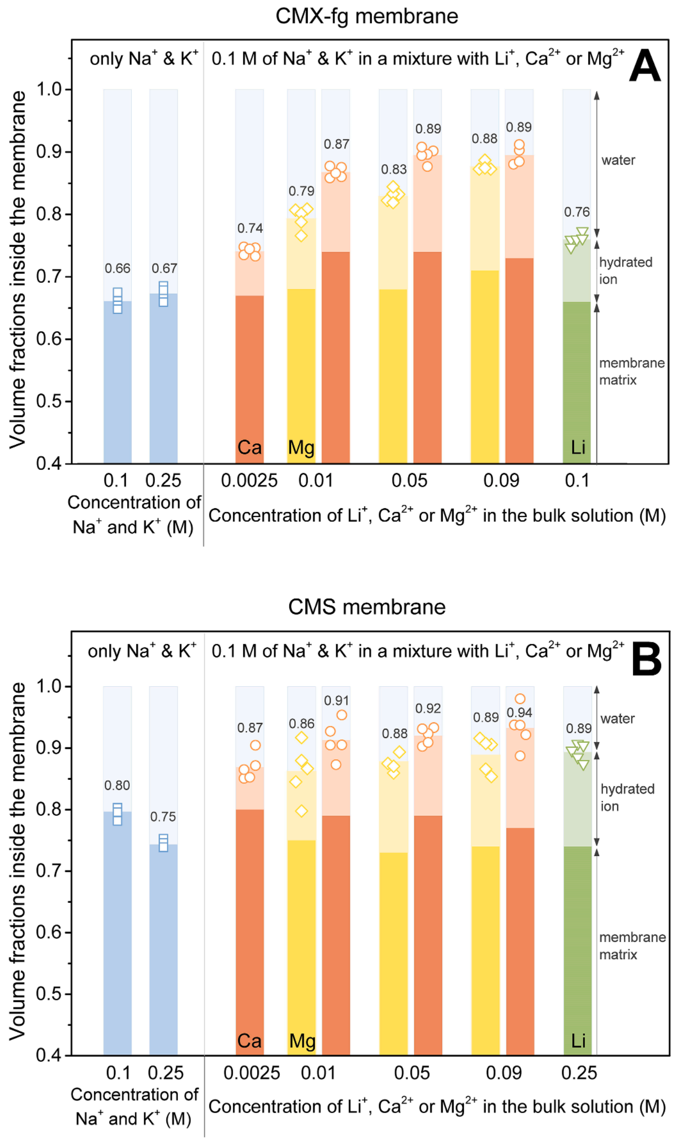

Fig. 2. Membrane volume fractions of CMX-fg (A) and CMS (B) membranes based on the ion type and concentration in the bulk solution. Markers: experimental data of the samples with varying Na^+/K^+ ratio, bars: average value of the samples with varying Na^+/K^+ ratio. For the experiments with Li^+, Ca^{2+} and Mg^{2+} ions, the total $Na^+ + K^+$ concentration in the bulk solution is set to 0.1 M.

Mg^{2+} to the membrane surface groups is lower, due to their bigger hydrated size (Table 1). As well, the bonded water molecules in the hydration shell of Mg^{2+} ions are more difficult to be detached than of the Ca^{2+} ions due to their higher hydration energy (Table 1) (Han et al., 2015; Richards et al., 2012) and weaker interactions with the membrane surface groups. As a result, the volume fraction of Mg^{2+} ions in the membrane is expected to contribute more to the decrease in the membrane water volume fraction than of Ca^{2+} ions, even though the concentration of Mg^{2+} ions in the membrane is lower.

On the other hand, the volume fraction of Li^+ ions in the membrane is lower compared to the divalent ions when the ions are present at a similar concentration in the bulk solution (Fig. 2A). The Li^+ ions have a relatively smaller hydration shell, lower hydration energy (Table 1) and weaker interactions with the membrane surface groups than the divalent ions due to their lower valency (Sahin et al., 2020). Therefore, the effect of Li^+ ions in the bulk solution on membrane water volume fraction is expected to be mainly limited to the decreasing osmotic pressure difference between the membrane and the bulk solution at low concentrations (0.1 M, Fig. 2A), rather than the nature of the ion in the solution.

4.1.2. *Selective adsorption of ions*

Selective adsorption of K^+ over Na^+ ions in the membrane, $\Delta\mu_{K^+-Na^+}$, is calculated using Eq. (10) for CMX-fg and CMS membranes based on the membrane water volume fraction. The data obtained from the experiments are presented in Fig. 3A. The experiments show that with decreasing water volume fraction in the membranes, dependent on the ion composition in the bulk solution, the selective adsorption

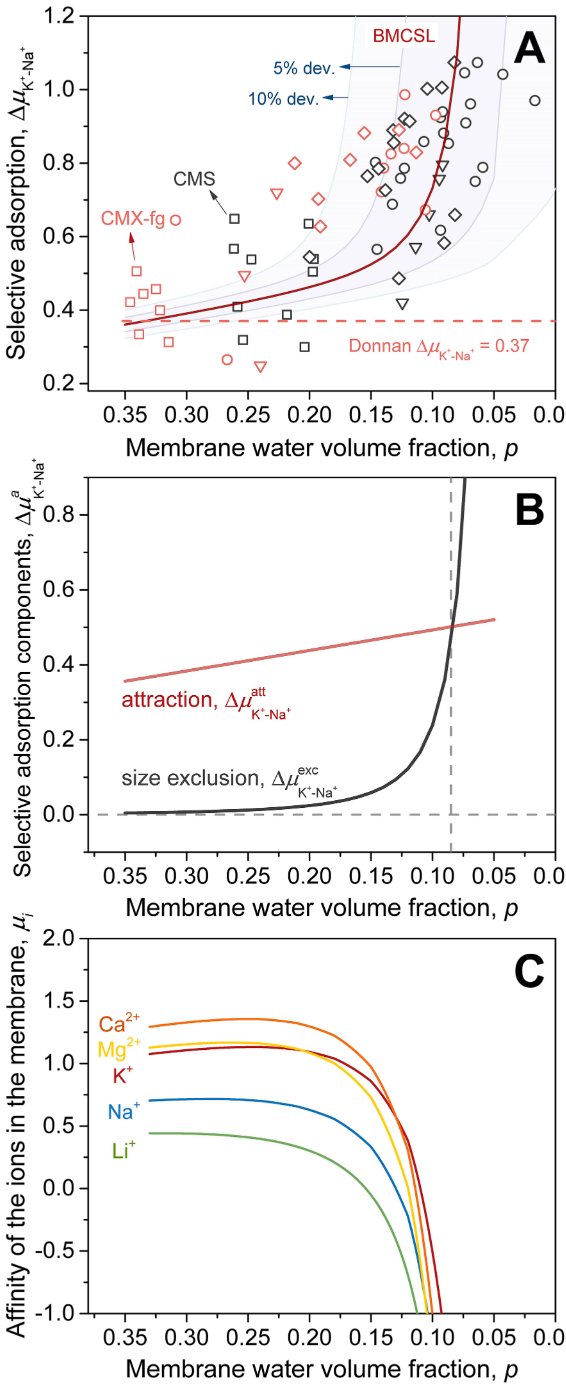

Fig. 3. Effect of membrane water volume fraction on the selective adsorption K^+ over Na^+ ions $\Delta\mu_{K^+-Na^+}$ (A), contributions of the chemical attraction and the size exclusion on the selective adsorption based on the membrane water volume fraction (B), and affinity of ions to the membranes based on membrane water volume fraction (C) according to the BMCSL theory.

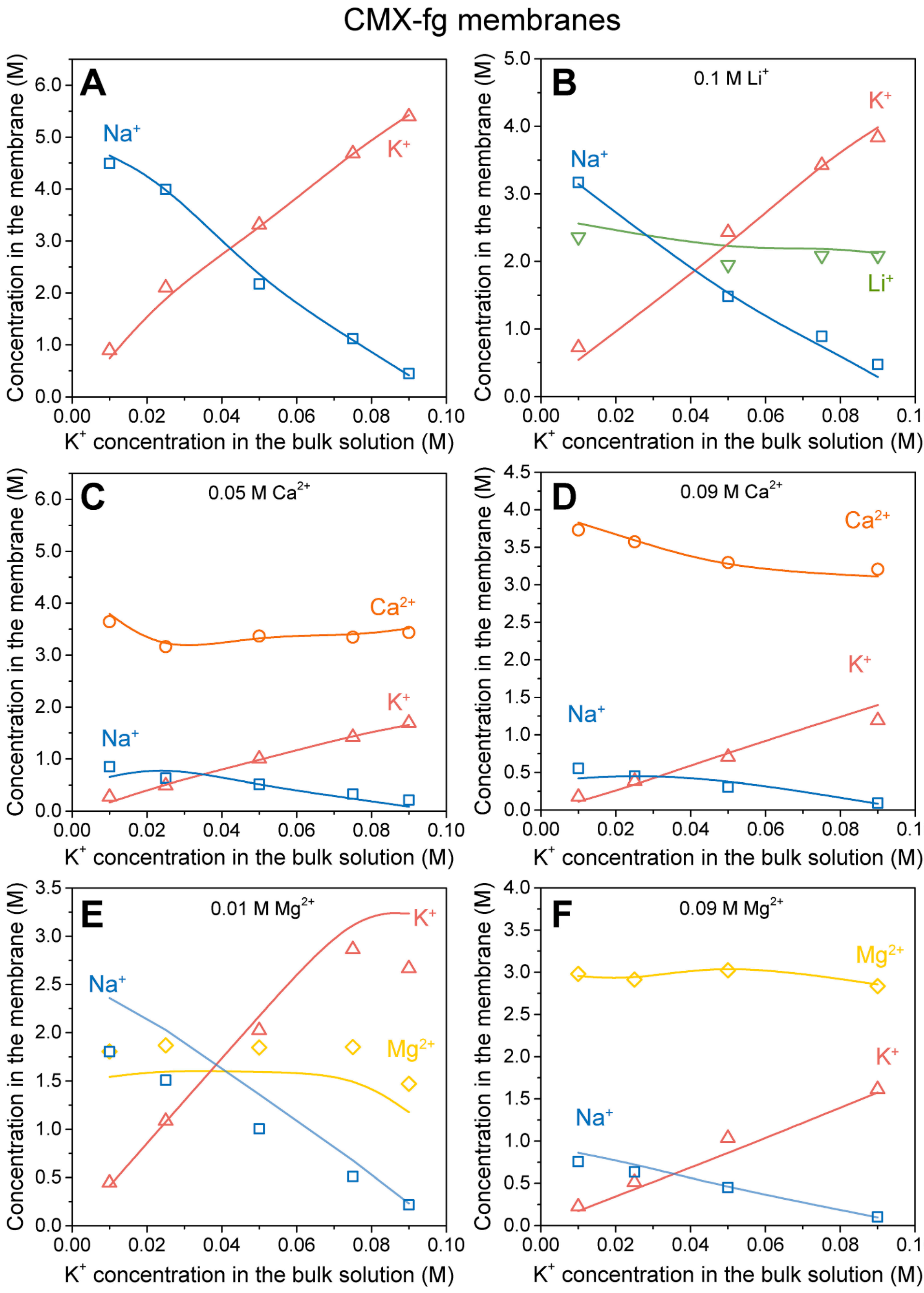

Fig. 4. Ion partitioning between the bulk solution and the CMX-fg membranes for solutions with different ionic compositions. Concentration of the ions inside the membranes for each condition is determined by the membrane adsorption experiments. Markers: experimental data, solid lines: BMCSL theory predictions. Membrane charge density values (X) used in Eq. (8) are individually calculated for each sample data point and used in the theory calculations. For all presented experiments, the total $Na^+ + K^+$ concentration in the bulk solution is set to 0.1 M.

towards K^+ ions increases for both types of membranes (from $\Delta\mu_{K^+-Na^+} \cong 0.35$ to $\Delta\mu_{K^+-Na^+} \cong 1.05$ for the complete data set, Fig. 3A) preferring the adsorption of the ion with smaller hydrated size (Table 1).

Two approaches, the Donnan affinity theory and the BMCSL theory, were used to describe the experimental ion adsorption data, the theoretical description of the experimental data by both theories are presented in Fig. 3A. For the Donnan affinity theory description, the affinity values obtained from the two-cation mixture experiments are used for the Na^+ and K^+ ions, and for the BMCSL theory the affinity values for the Na^+ and K^+ ions are calculated based on the membrane water volume fraction using a single $\chi_{m,i}$ for each ion i and a single d_m for the membranes in Eqs. (5) and (7), respectively. The values used for the theoretical calculations are given in Table S1 in the SI. In general, the affinity values obtained by the Donnan affinity theory for two-cation mixtures can describe the selective adsorption of ions only for solutions with specific ion compositions. However, the description for the complete data set for changing selective adsorption of K^+ over Na^+ ions, $\Delta\mu_{K^+-Na^+}$, is lacking. On the other hand, the BMCSL theory provides a good description of the selective adsorption of Na^+ and K^+ ions in the membranes for a wide range of experimental data based on the water volume fraction in the membrane. Although the sensitivity of the BMCSL theory increases significantly when the membrane water volume fraction approaches 0, more than 85 % of the experimental data can be explained within the 10% deviation for η used in Eq. (5).

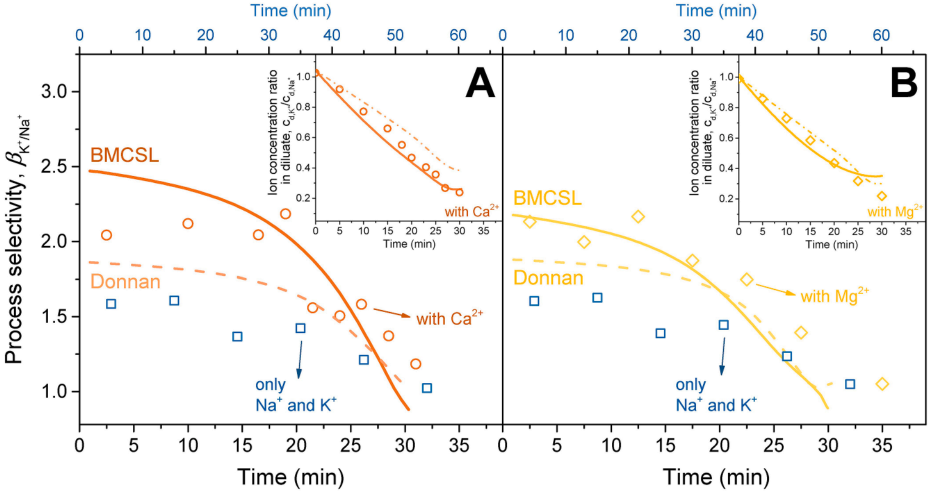

Fig. 5. Experimental data and model predictions of selective removal of Na^+ and K^+ ions during ED process operation in presence of 0.05 M Ca^{2+} (A) and 0.05 M Mg^{2+} (B) ions; both experiments were performed with a mixture of 0.05 M Na^+ and 0.05 M K^+ ions and at an applied voltage of 10 V. The experimental data for the only Na^+ and K^+ ion mixture is taken from our previous study, where $\Delta\mu_{K+-Na+}$ is calculated as ~0.27 for the same type of membrane from an older batch with different physical properties (Ozkul et al., 2023). Solid lines: model predictions with the BMCSL theory, dashed lines: model predictions using the Donnan affinity theory with $\Delta\mu_{K^+-Na^+} = 0.37$. The predictions are obtained using the theoretical model developed in our previous study (Ozkul et al., 2023) and the model input parameters can be found in Table S1 in the Supplementary Information.

Based on the BMCSL theory, individual contributions of the chemical attraction ($\Delta\mu^{att}_{K^+-\ Na^+}$) and the size exclusion ($\Delta\mu^{exc}_{K^+-\ Na^+}$) on the selective adsorption of K^+ over Na^+ ions with the membrane water volume fraction is also evaluated. The values are defined as the difference between the affinities of K^+ and Na^+ ions calculated using Eqs. (5) and (6); the results are presented in Fig. 3B. The results show that both affinity factors contribute to the increasing selective adsorption of K^+ ions, $\Delta\mu_{K^+-\ Na^+}$, with decreasing membrane water volume fraction due to the smaller size and stronger interaction of the K^+ ions to the membrane surface groups. Yet, the contribution of size exclusion on the selective adsorption stays limited ($\Delta\mu^{exc}_{K^+-\ Na^+} \cong 0$) for the membrane water volume fraction values higher than 0.2, where the selective adsorption is mainly defined by the chemical attraction of the ions. The influence of the size exclusion on selective adsorption is shown to be more significant when the membrane water volume fraction is lower than 0.15, i.e. when the divalent ion concentration in the bulk solution is more than 0.05 M.

In addition, the total affinity of Na^+, K^+, Li^+, Ca^{2+} and Mg^{2+} ions to the membrane ($\mu_i = \mu_i^{att} + \mu_i^{exc}$) is determined based on the membrane water volume fraction by theoretical calculations using the BMCSL theory; the results are presented in Fig. 3C. The divalent ions (Ca^{2+} and Mg^{2+}) show higher affinity to the membranes than the monovalent ions (Na^+, K^+ and Li^+) when the membrane water volume fraction is high as a result of their higher chemical attraction to the membranes. However, with decreasing membrane water volume fraction, affinity of the divalent ions drops significantly due to their greater size exclusion. The obtained findings are in line with the results of Louati et al. (2016) for AEMs. They reported that the affinity of the divalent ion, SO_4^{2-}, in the membranes is higher than the monovalent ions, NO_3^- and Cl^-, when the total ion concentration of the bulk solution is relatively low (Louati et al., 2016). With increasing ion concentration in the bulk solution, the affinity order of the ions in the membranes switches towards the smaller monovalent ions, first to NO_3^- and then to Cl^- (Louati et al., 2016). These results also support that when the membrane water volume fraction becomes smaller as a result of the change in the solution ion composition, the volumetric size of an ion becomes more significant than the valency of an ion for defining the selective ion adsorption in the membrane.

4.1.3. Ion partitioning

Ion partitioning between the bulk solutions and the membranes is also evaluated at equilibrium for the Na^+, K^+, Li^+, Ca^{2+} and Mg^{2+} ions by the membrane adsorption experiments performed using solutions with different ion compositions. The obtained data of ion concentrations in the membrane based on the ion concentrations in the bulk solution are presented in Fig. 4 for the CMX-fg membranes and in Fig. S2 in the SI for the CMS membranes, including the BMCSL theory predictions. The theoretical calculations are obtained using Eq. (4) for each ion with the affinity values determined based on the membrane water volume fraction and the electroneutrality condition in the membranes, Eq. (8); the values used for the theoretical calculations are given in Table S1 in the SI. The results show that the BMCSL theory can be used to describe the experimental ion partitioning data for all the ions in different two-cation or three-cation mixtures at different concentrations.

4.2. Effect of solution ion composition on ion removal with ED

The effect of divalent ions, Ca^{2+} or Mg^{2+}, in solution on the selective removal of Na^+ and K^+ ions was evaluated by the ED experiments. The results for the separation factor β_{K^+/Na^+} calculated using Eq. (13) and the ion concentration ratio in the diluate channel during operation are presented in Fig. 5. The theoretical predictions were obtained using the ED process model developed in our previous study based on extended Nernst-Planck equation and Boltzmann equation (Ozkul et al., 2023). In order to define the concentration of individual ions inside the membrane, we used Eq. (3) for the Donnan affinity theory, and Eqs. (4)–(6) for the BMCSL theory. Input values of the model for given equations are reported in Table S1 in the SI.

For both ED experiments including 0.05 M Ca^{2+}or 0.05 M Mg^{2+} in solution, the selective removal of K^+ over Na^+ ions increases in the presence of Ca^{2+} (Fig. 5A) and Mg^{2+} (Fig. 5B) in the solution due to increasing selective adsorption of K^+ ions with decreasing membrane water volume fraction. For the overall process operation, a good description of the experimental data is obtained using the BMCSL theory to define the selective adsorption of the ions in the membrane for both solutions. On the other hand, the Donnan affinity theory with a membrane specific affinity for Na^+ and K^+ ions showed a similar trend to the experimental data collected for the experiments including only Na^+ and K^+ ions (Fig. 5A and 5B), underestimating the removal of K^+ ions in presence of divalent ions. The results show that considering volumetric effects based on the solution ion composition in the definition of ion partitioning can improve the predictions of the selective ion removal by an ED process for different water streams.

5. Conclusions

In the present study, we investigated the effects of Li^+, Ca^{2+} and Mg^{2+} ions in the bulk solution at different concentrations on the membrane water volume fraction and the selective adsorption of Na^+ and K^+ ions in two types of cation exchange membranes (Neosepta CMX-fg and Neosepta CMS). The results show that the membrane water volume fraction decreases with increasing total ion concentration and amount of divalent ions in the bulk solution for both types of membranes. In addition, the selective adsorption in the membrane is found to be increasing for K^+ over Na^+ ions with decreasing membrane water volume fraction, preferring the adsorption of the smaller ion. A theoretical framework is developed using Boublik-Mansoori-Carnahan-Starling-Leland (BMCSL) theory to describe selective ion adsorption and ion partitioning in the membranes based on the membrane water volume fraction by including the volumetric effects; the results are compared with the commonly used Donnan theory extended with an affinity term. The results show that, with the BMCSL theory the description of selective ion adsorption in ion exchange membranes can be improved for solutions with a variety of ion types and concentrations.

CRediT authorship contribution statement

S. Ozkul: Investigation, Methodology, Resources, Software, Supervision, Validation, Visualization, Writing – original draft, Writing – review & editing. **O. Arbabzadeh:** Conceptualization, Investigation, Methodology, Resources, Software, Supervision, Validation, Visualization, Writing – original draft, Writing – review & editing. **R.J.M. Bisselink:** Conceptualization, Investigation, Methodology, Resources, Software, Supervision, Validation, Visualization, Writing – original draft, Writing – review & editing. **N.J.M. Kuipers:** Conceptualization, Investigation, Methodology, Resources, Software, Supervision, Validation, Visualization, Writing – original draft, Writing – review & editing. **H. Bruning:** Conceptualization, Investigation, Methodology, Resources, Software, Supervision, Validation, Visualization, Writing – original draft, Writing – review & editing. **H.H.M. Rijnaarts:** Conceptualization, Investigation, Methodology, Resources, Software, Supervision, Validation, Visualization, Writing – original draft, Writing – review & editing. **J.E. Dykstra:** Conceptualization, Investigation, Methodology, Resources, Software, Supervision, Validation, Visualization, Writing – original draft, Writing – review & editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

Acknowledgements

This project was funded by the Dutch Topsector AgriFood “Natte Stromen” (DFI-AF-18003).

Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.watres.2024.121382.

References

Besha, A.T., Tsehaye, M.T., Aili, D., Zhang, W.J., Tufa, R.A., 2020. Design of monovalent ion selective membranes for reducing the impacts of multivalent ions in reverse electrodialysis. Membranes 10, 7.

Biesheuvel, P.M., Dykstra, J.E., 2020. Physics of electrochemical processes.

Castaño Osorio, S., Biesheuvel, P.M., Spruijt, E., Dykstra, J.E., van der Wal, A., 2022. Modeling micropollutant removal by nanofiltration and reverse osmosis membranes: considerations and challenges. Water Res. 225, 119130.

de Vos, W.M., Biesheuvel, P.M., de Keizer, A., Kleijn, J.M., Stuart, M.A.C., 2009. Adsorption of anionic surfactants in a nonionic polymer brush: experiments, comparison with mean-field theory, and implications for brush-particle interaction. Langmuir 25, 9252–9261.

Farrokhzad, H., Moghbeli, M.R., Van Gerven, T., Van der Bruggen, B., 2015. Surface modification of composite ion exchange membranes by polyaniline. React. Funct. Polym. 86, 161–167.

Fontananova, E., Messana, D., Tufa, R.A., Nicotera, I., Kosma, V., Curcio, E., van Baak, W., Drioli, E., Di Profio, G., 2017. Effect of solution concentration and composition on the electrochemical properties of ion exchange membranes for energy conversion. J. Power Sources 340, 282–293.

Geise, G.M., Cassady, H.J., Paul, D.R., Logan, B.E., Hickner, M.A., 2014. Specific ion effects on membrane potential and the permselectivity of ion exchange membranes. Phys. Chem. Chem. Phys. 16, 21673–21681.

Han, L., Galier, S., Roux-de Balmann, H., 2015. Ion hydration number and electro-osmosis during electrodialysis of mixed salt solution. Desalination 373, 38–46.

Hannachi, C., Ali, M.B., Hamrouni, B., 2009. Determination of the selectivity coefficient of the CMX cationic membrane at various ionic strengths. Desalin. Water Treat. 10, 47–52.

Louati, I., Guesmi, F., Chaabouni, A., Hannachi, C., Hamrouni, B., 2016. Effect of ionic strength on the ion exchange equilibrium between AMX membrane and electrolyte solutions. Water Qual. Res. J. Can. 51, 60–68.

Luo, T., Abdu, S., Wessling, M., 2018. Selectivity of ion exchange membranes: a review. J. Membr. Sci. 555, 429–454.

Marcus, Y., 2015. Ions in Solution and their Solvation. John Wiley & Sons, New Jersey.

Miyoshi, H., Chubachi, M., Yamagami, M., Kataoka, T., 1992. Characteristic coefficients for equilibrium between solution and neosepta or selemion cation-exchange membranes. J. Chem. Eng. Data 37, 120–124.

Mubita, T., Porada, S., Aerts, P., van der Wal, A., 2020. Heterogeneous anion exchange membranes with nitrate selectivity and low electrical resistance. J. Membr. Sci. 607, 118000.

Mubita, T.M., Porada, S., Biesheuvel, P.M., van der Wal, A., Dykstra, J.E., 2022. Strategies to increase ion selectivity in electrodialysis. Sep. Purif. Technol. 292, 120944.

Munchinger, A., Kreuer, K.D., 2019. Selective ion transport through hydrated cation and anion exchange membranes I. The effect of specific interactions. J. Membr. Sci. 592, 117372.

Nagarale, R.K., Gohil, G.S., Shahi, V.K., 2006. Recent developments on ion-exchange membranes and electro-membrane processes. Adv. Colloid Interface Sci. 119, 97–130.

Nightingale, E.R., 1959. Phenomenological theory of ion solvation - effective radii of hydrated ions. J. Phys. Chem. 63, 1381–1387.

Ozkul, S., van Daal, J.J., Kuipers, N.J.M., Bisselink, R.J.M., Bruning, H., Dykstra, J.E., Rijnaarts, H.H.M., 2023. Transport mechanisms in electrodialysis: the effect on selective ion transport in multi-ionic solutions. J. Membr. Sci. 665, 121114.

Ran, J., Wu, L., He, Y.B., Yang, Z.J., Wang, Y.M., Jiang, C.X., Ge, L., Bakangura, E., Xu, T. W., 2017. Ion exchange membranes: new developments and applications. J. Membr. Sci. 522, 267–291.

Richards, L.A., Schafer, A.I., Richards, B.S., Corry, B., 2012. The importance of dehydration in determining ion transport in narrow pores. Small 8, 1701–1709.

Sahin, S., Dykstra, J.E., Zuilhof, H., Zornitta, R.L., de Smet, L.C.P.M., 2020. Modification of cation-exchange membranes with polyelectrolyte multilayers to tune ion selectivity in capacitive deionization. ACS Appl. Mater. Interfaces 12, 34746–34754.

Sajjad, A.A., Yunus, M.Y.B.M., Azoddein, A.A.M., Hassell, D.G., Dakhil, I.H., Hasan, H.A., 2019. Electrodialysis desalination for water and wastewater: a review. Chem. Eng. J. 380, 122231.

Sarapulova, V., Shkorkina, I., Mareev, S., Pismenskaya, N., Kononenko, N., Larchet, C., Dammak, L., Nikonenko, V., 2019. Transport characteristics of fujifilm ion-exchange membranes as compared to homogeneous membranes AMX and CMX and to heterogeneous membranes MK-40 and MA-41. Membranes 9, 84.

Sata, T., Yamaguchi, T., Matsusaki, K., 1995. Effect of hydrophobicity of ion-exchange groups of anion-exchange membranes on permselectivity between two anions. J. Phys. Chem. 99, 12875–12882.

Shocron, A.N., Atlas, I., Suss, M.E., 2022. Predicting ion selectivity in water purification by capacitive deionization: electric double layer models. Curr. Opin. Colloid Interface Sci. 60, 101602.

Spruijt, E., Biesheuvel, P.M., 2014. Sedimentation dynamics and equilibrium profiles in multicomponent mixtures of colloidal particles. J. Phys. Condens. Matter 26, 075101.

Strathmann, H., 2004. Ion-Exchange Membrane Separation Processes, 1st ed. Elsevier, Amsterdam; Boston.

Suss, M.E., 2017. Size-based ion selectivity of micropore electric double layers in capacitive deionization electrodes. J. Electrochem. Soc. 164, E270–E275.

Tuan, L.X., Buess-Herman, C., 2007. Study of water content and microheterogeneity of CMS cation exchange membrane. Chem. Phys. Lett. 434, 49–55.