

Influence of temperature gradients on mono- and divalent ion transport in electro dialysis at limiting currents



Anne M. Benneker, Jasper Klomp, Rob G.H. Lammertink, Jeffery A. Wood*

Soft Matter, Fluidics and Interfaces, Faculty of Science and Technology, MESA+ Institute for Nanotechnology, University of Twente, Enschede, The Netherlands

ARTICLE INFO

Keywords:

Temperature gradients
Electrodialysis
Limiting current
Mono- and divalent ions

ABSTRACT

Temperature gradients in electro dialysis (ED) stacks can potentially enhance the efficiency of charge separation and the selective transport of ions. We have previously investigated temperature gradients in the Ohmic regime but not in the limiting current regime, where diffusion of ions towards the membrane determines the transport rate and temperature gradients potentially have the largest influence. In this research, commercial ion exchange membranes (FAS and FKS, FUMATECH, Germany) are used for the investigation of temperature gradients in the limiting current regime. In contrast to the Ohmic regime, we find that heating the diluted stream increases the current obtained (at a constant applied potential) when compared to heating the concentrate stream in systems containing monovalent KCl and NaCl solutions. For mixtures of mono- and divalent ions, the temperature gradient has a larger influence on the selectivity of the separation. If the desalinated stream is heated, divalent Mg^{2+} ions show a higher transport than the monovalent K^+ and Na^+ ions. This is due to the enhanced competitive transport of the mono- and divalent ions under the application of a temperature gradient. These results show the potential application and relevance of temperature gradients to enhance the selective separation of mono- and divalent ions.

1. Introduction

Electrodialysis (ED) is an established technique for the desalination of brackish water or the concentration of industrial streams [1]. An electric field is applied over a stack of alternating cation and anion exchange membranes to selectively transport ions, resulting in a concentrated and a diluted product stream. Counter-ions are transported through the oppositely charged polymeric membrane, while co-ions are mostly blocked by Donnan-exclusion. In industry, electro dialysis processes are mostly used for nitrate-removal, the desalination of brackish water and the deionization of whey [1].

The number of ions transported (indicated by the measured current) increases linearly (following Ohm's law) with increasing driving potential difference, until there is a mismatch between the supply and removal rates of ions at the membrane interface [2,3]. A depleted boundary layer at the membrane interface develops at elevated field strengths. Ion transport through this boundary layer, which is dictated by diffusion and electromigration, limits the total transport of ions in the system. As a result, a system specific so-called "limiting current density" is observed for all electro dialysis systems, in which the efficiency of the process is reduced since the required power ($P = VI$, where I is the current through and V is the potential over the stack) is

increasing while the ionic current is stable. To increase the process efficiency and to be able to operate at higher current densities, the enhancement of selective ion transport in electro dialysis has been of interest for many years [4]. Enhancing the membrane selectivity can be of interest, but nowadays commercial membranes have a permselectivity of over 90% [5] and enhancing this would only yield minor improvements on the overall process. Most research has focused on mixing the fluid in the stack by means of profiled membranes [6,7], non-conducting or ion conducting, turbulence promoting spacers [8–12] to increase the supply of ions towards the membrane interface.

The total flux of ions (J_i) through the boundary layer towards the membrane for dilute systems can be described by the Nernst-Planck equation (Eq. (1)). The ion transport consists of convection via the flow velocity \mathbf{u} , diffusion as a result of a concentration gradient ∇c_i and a molecular ion diffusivity D_i or similarly, through a temperature gradient ∇T with thermodiffusivity $D_{T,i}$, an electromigration flux resulting from the local electric potential gradient ∇V , the ionic mobility ν_i , charge z_i and Faraday's constant F .

$$\mathbf{J}_i = \mathbf{J}_{i,\text{conv}} + \mathbf{J}_{i,\text{migr}} + \mathbf{J}_{i,\text{diff}} = c_i \mathbf{u} - \nu_i z_i F c_i \nabla V - D_i \nabla c_i - D_{T,i} \nabla T \quad (1)$$

Temperature has a large influence on the physical properties of an ionic solution, and thus influences the total flux as described by Eq. (1).

* Corresponding author.

E-mail address: j.a.wood@utwente.nl (J.A. Wood).

For instance, the diffusivity D_i and mobility ν_i of ions in solution increase with increasing temperature, while the viscosity of the solution decreases with increasing temperature [13]. Since $D_i \sim T/\eta$ and $\nu_i \sim D_i/RT$, temperature generally has a larger influence on the diffusivity than on the electric mobility. If the temperature in electro dialysis systems is altered, the charge transport characteristics in the system will therefore be changed [14]. In general, at higher temperatures, an increased flux of ions is expected as a result of the enhanced ionic mobility and diffusivity of ions in the solution and the subsequent effect of this on the different terms of the Nernst-Planck equation [15,16]. Membrane resistance reduces as a function of increasing temperature, most pronounced at temperatures above 30 °C [17]. A thermodiffusive flux (known as the Soret effect) due to a temperature gradient ∇T and the thermodiffusion coefficient $D_{T,i}$ should be considered in non-isothermal systems [18]. While many studies have focused on the role of temperature in isothermal experiments, fewer have investigated the effect of temperature gradients on the charge transport in electro dialysis systems [19].

The combined effect of temperature gradients, (induced) potential gradients and developing concentration gradients in electro dialysis yields a complicated interplay of effects, opening up a rich field of investigation. Temperature gradients in the membrane directly influence the ion flux through the contribution of thermodiffusive transport yielding a thermoelectric potential difference [20–22] and can induce thermoosmotic water transport across ion exchange membranes [18,23–25]. The direction and magnitude of the thermoosmotic water transport are dependent on both membrane and system properties, and the thermoosmotic water transport number is different for all experimental systems [23]. Additionally, a temperature gradient can theoretically enhance the selectivity of the separation process as a result of reducing the non-desired co-ion transport through the membrane [26]. By heating the ion depleted stream, diffusive ion transport inside this stream can be enhanced compared to the transport in the enriched stream. This enhances the diffusive transport of counter-ions towards the membrane in the dilute stream, while the relative diffusive transport of co-ions in the concentrate stream is reduced. Since the diffusion boundary layer is most important in the limiting current regime, the effect of temperature and temperature gradients is expected to be most pronounced in this regime.

The separation of divalent from monovalent ions is of interest for industrial desalination [27–29], for instance in systems where heavy metals have to be selectively removed and in water softening by exchanging divalent ions with monovalent ions [30,31]. Electro dialysis is one of the techniques that is promising for this separation [32,33]. Competitive charge transport between mono- and divalent ions changes the ion flux through a membrane if a mixture is present versus a pure salt solution [34]. In a mixture, the relative flux of monovalent Na^+ was drastically reduced by the addition of divalent Mg^{2+} or Ca^{2+} ions, while the effect of adding Na^+ on the Mg^{2+} flux was minor. The temperature dependence of the diffusivity is slightly different for all ions and can influence the selectivity of the ED-process for di- or monovalent ions. In general, at higher temperatures, the relative differences between the diffusivity of the different ions are enhanced [35], resulting in altered transport characteristics. Unequal temperatures in the concentrate and dilute stream can, through these different relative diffusivities, theoretically yield more selective transport of these ions relative to one another. Temperature can also have an effect on the interaction between the different ions and the membrane. For example, the ion hydration radius affects the interaction with the membrane and this radius is dependent on temperature.

We have previously investigated the effect of temperature and temperature gradients in the industrially relevant Ohmic regime, where we found that increasing the temperature of (one of the) feed streams enhances the efficiency of ED processes [19]. However, at these lower currents the direction of the applied temperature gradient did not have a significant influence on the selectivity and the reduction in required

power for the ED process in the Ohmic regime. We expect this to be different for operation in the limiting regime, as in this regime the diffusion of ions plays a crucial role in the overall ion transport and the limiting current i_{lim} scales linear with D_i . In this research, we investigate the influence of temperature and temperature gradients on charge transport in electro dialysis systems in the limiting current regime. The effect of temperature gradients on the individual ion transport and overall currents is investigated in systems containing either or both mono- and divalent ions. It should be noted that the efficiency of the ED process in the limiting regime will be lower than the efficiency in the Ohmic regime, since the boundary layers present in the limiting regime increase the total resistance of the stack. An elevated temperature (or temperature gradient) can only shift the onset of the limiting current regime, allowing operation at higher potentials and current densities, but not increasing the efficiency of the separation. However, the fundamental investigation of ion transport in the limiting current regime is of interest as knowledge on this regime can be applied in the enhancement of ion separation and yields more insights in the physical background of electro dialysis processes.

2. Experimental details

A lab scale, commercially available electro dialysis stack with an active area of $10 \times 10 \text{ cm}^2$ (FUMATECH BWT GmbH, Germany) was used for all measurements. This is a different stack than the one used in our previous work [19]. The stack consists of three cell pairs, composed of three FAS-PET-100 (AEM) and four FKS-PET-100 (CEM) membranes spaced with ED-100-4CS PVC (600 μm) spacers, all obtained from FUMATECH BWT GmbH, Germany. Before composing the stack, membranes are pre-treated by placing them in 0.5 M KOH overnight and flushing them with 0.017 M KOH to ensure exchange of all native ions in the membrane for K^+ and OH^- , which are ions that are present in the experimental system. The membrane stack is assembled and secured by screwing the end-plates containing the electrodes in a metal framework. The stack is flushed overnight with the desired feed solution to equilibrate the ion composition in the membranes. The stack is operated in a vertical co-flow configuration, feeding the compartments from bottom to top to ensure a constant compartment fluid volume. In the co-flow configuration, there is less overall heat transfer than for experiments in cross-flow configuration, so we are able to maintain the temperature gradient over a larger part of the system.

To check if membrane permselectivity is affected by the increased temperature, we measured the membrane potential after the electro dialysis experiments, using a standard two compartment measurement [36] set-up at 0.1 M and 0.5 M KCl. By comparing the measured potential to the theoretical potential, $V_i = \frac{RT}{zF} \ln \frac{\gamma_c c_c}{\gamma_d c_d}$, the permselectivity of the membrane can be estimated. In this equation, γ_c and γ_d are the activity coefficients of the electrolyte in the different compartments.

Both IV-sweeps and chronoamperometric measurements are conducted in this work. IV-sweeps are performed to investigate the effect of temperature and temperature gradients on the characteristic shape of the IV-curve. The onset and magnitude of the limiting current regime can be determined by these measurements. For the investigation of the effect of temperature gradients on the charge transport through the boundary layer, and the effect of this on the desalination and selective transport of mono- and divalent ions, chronoamperometric measurements are conducted in the limiting current regime. In these measurements a constant potential is applied and the resulting current is measured. Ion concentrations of the dilute and concentrate streams are measured for the chronoamperometric measurements.

All measurements are done at a flow rate of 50 mL/min in both the dilute and concentrate stream, which corresponds to a linear flow speed of 0.46 cm/s and a residence time of ~ 22 s. Flow was pumped using peristaltic pumps (Cole-Palmer) and pulsations are suppressed by in-house built pulsation dampeners. The flow rate was controlled using an

Table 1

Actual feed cation concentrations, percentages of monovalent and divalent cations and amount of positive charge with their standard deviation for the different salt compositions.

Mixture	c_{F,Na^+} [mmol/L]	c_{F,K^+} [mmol/L]	$c_{F,Mg^{2+}}$ [mmol/L]	Monovalent cations [%]	Divalent cations [%]	$\Sigma z_i F c_j$ [C/L]
NaCl	5.53 ± 0.04	1.24 ± 0.02	-	100 ± 0.1	-	6.53 ± 0.06
MgCl ₂ ^a	0.60 ± 0.01	0.18 ± 0.001	2.82 ± 0.04	21.6 ± 0.04	78.4 ± 0.04	6.19 ± 0.01
Mix	2.93 ± 0.01	1.11 ± 0.01	1.41 ± 0.02	74.2 ± 0.3	25.8 ± 0.3	6.45 ± 0.04

^a Standard deviation is based on two measurements.

in-house built flow meter (TCO, University of Twente, The Netherlands), containing a McMillan Co. 101 flo-sen flow sensor. To ensure membrane packing, a 0.1 bar overpressure was applied to the electrolyte stream by adjusting the redox solution flow rate accordingly.

Different feed solutions are used for the different sets of measurements. Ionic strength is kept constant for all measurements, to be able to directly compare our measurement results. For measurements with NaCl, we use a model solution of 6.7 mM, which is corresponding to typical concentrations of river water in the Netherlands [37]. The electrode compartments are flushed with 6.7 mM K₂SO₄ as a redox solution for avoiding Cl₂ gas formation. We choose this relatively low electrolyte concentration to prevent osmotic water transport from the feed to the electrode rinse. For the measurements with MgCl₂, the concentration was 3.35 mM so that the ionic strength of the mono- and divalent solutions are equal. For the measurements with a mixture of mono- and divalent ions we use 3.35 mM NaCl and 1.68 mM MgCl₂, once again keeping the ionic strength of the solution constant and minimizing the osmotic pressure difference with the electrolyte solution. Outlet flows are recycled into a 20 L feed tank, which is continuously stirred using aquarium mixers (Wavereef® Auto Top Off System, Single Level Sensor WIC-01S, obtained from Aquaria Veldhuis BV, The Netherlands).

Experiments are carried out at four different temperature configurations; (1) isothermal at 5 °C, (2) dilute at 5 °C, concentrate at 25 °C, (3) dilute at 25 °C, concentrate at 5 °C and (4) isothermal at 25 °C. When we indicate the dilute or concentrate stream, this of course is an indicator of the stream leaving the stack, as the inlet concentrations of both streams are equal. Feed solutions are kept at the desired temperature by two Julabo F12-ED Refrigerated - Heating Circulators. Prior to all measurements, the system was allowed to reach thermal equilibrium. Both in- and outlet temperatures of both feed streams are constantly monitored using AMA-digit ad 15th thermometers (Amarell, Germany).

All electrical characterization of the system is done using a Metrohm Autolab PGSTAT302N (Metrohm, The Netherlands) which is controlled by NOVA 2.0 software. In the IV-sweeps, we first measure the open circuit potential of the system and afterwards apply currents between 0 and 0.2 A with steps of 0.01 A to the system. The system is allowed to settle for 30 s, which corresponds to ~1.5 residence times. After 30 s, the potential required to obtain the current is measured and the applied current is increased. At experimental times above 600 s the system becomes unstable due to gas formation. For the chronoamperometric measurements, a constant potential of 5 V is applied and the resulting current is measured for 500 s. This potential is confirmed to be in the limiting current regime based on the IV-sweeps.

During the chronoamperometric measurements, samples are collected for evaluating ion concentration by means of ion chromatography (IC). Anion concentrations were quantified with IC (Metrosep A Supp 16 - 150/4.0 column on a Metrohm 850 Professional IC). Cation concentrations were measured with IC as well (Metrosep C6 - 150/4.0 column on a Metrohm 850 Professional IC).

3. Results and discussion

The membrane permselectivity was found to be independent of

temperature in the range between 5 °C and 40 °C, with a value of 0.98 for all configurations for the cation exchange membrane. The selectivity of the anion exchange membrane dropped from 0.98 at a temperature of 25 °C to 0.93 at a temperature of 40 °C, but was constant in the range between 5 °C and 25 °C, in which we performed our ED experiments. We note that outside of the temperature range that was tested here, the permselectivity of the membrane may show larger changes [38]. No significant water transport was observed during the permselectivity measurements, indicating that the temperature has no influence on water transport through our commercial membranes.

After our measurements, we found K⁺ to be present in our in- and outlet streams. This is a result of leakage of K⁺ ions from the electrolyte solution in the electrode compartments towards the feed solution through the outer two cation exchange membranes. Na⁺ and Mg²⁺ are exchanged with K⁺. This also holds for the measurements with MgCl₂ as a feed, in which Na⁺ ions are present as a result of exchange with the membrane and the electrolyte. The cation composition of the feed (c_p) was measured for all configurations using additional IC measurements (Table 1). In the remainder of this work, we will focus on the measurements with only monovalent ions (NaCl feed in Table 1) and the intended mixture of mono- and divalent ions (Mix in Table 1). For the interpretation of the measurements we take the effect of both K⁺ and Na⁺ into account when discussing monovalent ions.

3.1. IV-characterization

For all systems and temperature configurations IV-sweeps were conducted, in order to determine the onset of the limiting current regime and investigate the influence of temperature/temperature gradients on the characteristics of the ED system. The highest current densities were measured for systems with the highest temperature and lowest current densities were measured for systems with the lowest temperatures, as was expected. The measurements for the NaCl and the mixed solution containing both Mg²⁺ and Na⁺ are shown in Fig. 1. The total current density was approximately 30% higher for the hot isothermal case (red line) when compared to the cold isothermal case (blue line) for the NaCl measurements. For the measurements of the mixture, the hot isothermal case also has an enhanced current density of 30% when compared to the cold isothermal case. This increase in current density between the two isothermal matches with the expected increase in ion diffusivity for a temperature increase of 20 °C [35]. The transition into the limiting current regime is shifted to a lower applied potential at higher temperatures and the limiting current density is higher, as is expected because of the enhanced transport of ions at a higher temperature [39].

As can be observed, at high field strengths for both cases slightly higher current densities are measured in the situation in which the concentrate stream is heated, which is in contrast to our expectations. We expected that heating the dilute stream would increase the overall current density since the transport main limitations for diffusive ion transport occur in this stream. However, the measured difference between the two different temperature gradient configurations is too small to be significant in these IV-sweeps, especially at low to moderate field strengths and for the measurement of the mixture. A possible explanation for this is the short times for which the current is measured

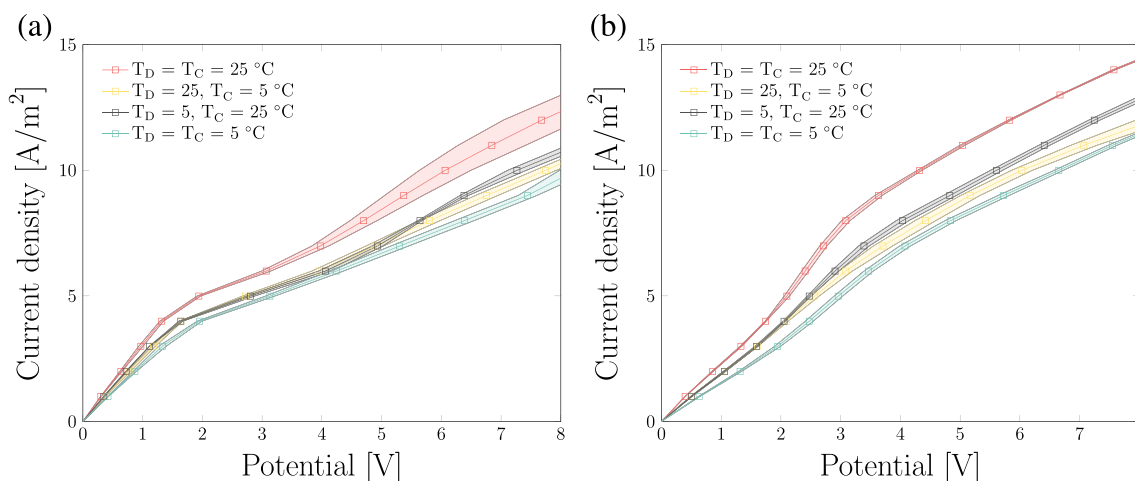


Fig. 1. IV-characterization of the ED stack. (a) for 6.7 mM NaCl as a feed solution and (b) for the mixed feed of 3.35 mM NaCl and 1.68 mM MgCl₂. The shaded area indicates the standard error between the measurements, lines are for visualization purposes only. (For interpretation of the references to color in this figure, the reader is referred to the web version of this article.)

(30 s), which, after the chronoamperometric measurements that will be presented in the next section, turned out to be a time at which the measured current was not yet stable. IV-sweeps with a longer waiting time per potential were done, but were found to be unstable at high measurement times.

The temperature increase from Joule heating as a result of the current through the system can be estimated using $\Delta T = P/(\phi_m c_p)$, in which $P = VI$ is the input power, $\phi_m = 50$ g/s is the mass flow rate through the system and $c_p = 4.2$ J/(gK) is the specific heat of the fluid. Joule heating is estimated to be negligible, as at the highest measured potentials ($V = 10$ V) and currents ($I = 0.2$ A), the temperature increase estimated in this way is 0.01 K. The different relative diffusivities of ions in the solution is also expected to have an influence on the total current density that is measured [34].

The transition towards the limiting current regime is sharpest in the pure NaCl measurements, occurring around a potential of 2 V with a corresponding current of 4 A/m², for the cold isothermal case. For the mixture, the onset of the limiting current regime is shifted to ~ 3 V, and a higher value of the current (~ 6 A/m²). The thickness of the diffusion boundary layer δ can be estimated through the Peers equation (Eq. (2)) [40], in which z_i is the charge number, F is the Faraday constant, D_i the diffusivity of the ions, $\bar{\tau}_i$ and τ_i are the relative ion transport numbers inside the membrane and the solution and c_b is the bulk ion concentration. We have $\bar{\tau}_i = 0.98$ for our commercial membranes at the low concentrations present in our system and we assume the relative transport of both cation and anion in the solution to be equal so that $\tau_i = 0.5$, although in reality the transport numbers of the different ions in solution are slightly different [41]. However, for our order of magnitude estimation of the boundary layer thickness, the effect of changing τ_i is minor.

$$i_{\text{lim}} = \frac{z_i F D_i c_b}{\bar{\tau}_i - \tau_i \delta} \quad (2)$$

By using our measured limiting current densities and taking $\bar{\tau}_i - \tau_i = 0.48$, we find a thickness in the order of hundreds of micrometers, which is in good comparison to boundary layer thicknesses found in similar systems [42, 43]. The thickness of the diffusion boundary can also be estimated based on the hydrodynamics of the system using the Leveque approximation [44] from which we find a similar value of 190 μm . The development of the concentration polarization in the diffusion boundary layer is not instantaneous, resulting in transient behaviour of the measured current.

For the measurements of the mixture (Fig. 1b), an inflection point can be observed in the Ohmic region (around 2 V), after which the slope

is increased and thus the resistance of the system decreases at these voltages. This inflection is attributed to the preferential transport of divalent ions at low current densities [33,45] resulting from an enhanced electrostatic interaction between divalent ions and the membrane. The transport of monovalent ions is reduced due to electrostatic repulsion between the Na⁺ and Mg²⁺. At higher current densities, the contribution of this additional attraction is of lesser influence and the transport of monovalent ions is enhanced by the larger electric driving force (higher ΔV) overcoming the electrostatic forces.

3.2. Chronoamperometric measurements

From the IV-sweeps we conclude that applying a potential of 5 V in the chronoamperometric measurements is sufficient to ensure operation in the limiting current regime, but to not be in the overlimiting regime. Samples are taken for all these measurements to be able to measure the ion concentrations in the dilute and concentrate streams and to investigate the influence of temperature gradients on the transport of the different ions in the system. In Fig. 2, the current is plotted as a function of time for (a) the NaCl and (b) the mixed MgCl₂ and NaCl. The system requires ~ 150 s (over five times the liquid residence time) to stabilize, after which a constant current is measured. This implies that when doing the IV-sweeps, the measured potential is not the equilibrium potential since for those experiments a hold time of 30 s per applied potential was used in order to avoid system instability at larger hold times (over the total IV-sweep). The measured current is highest (7.9 A/m² for NaCl, 10.7 A/m² for the mixture) for the isothermal case at 25 °C and lowest (5.7 A/m² and 8.4 A/m² respectively) for the isothermal case at 5 °C for all different feed compositions, as was expected. In contrast to our previous work, where measurements were done in the Ohmic regime [19] and the IV-sweeps in the current, here we are able to measure a difference between the two temperature gradient cases. In the limiting current regime the diffusion boundary layer is more developed compared to the Ohmic regime, resulting in a larger influence of temperature on the ion transport. Measurements for the monovalent salts are very reproducible, having a small standard error ($\sim 2\%$). For the measurements of the pure NaCl and MgCl₂ solutions (the latter is not shown here, the general trend is similar to NaCl) feed, the measured current is higher ($\sim 7\%$) for the case when the dilute stream is heated when compared to the concentrate stream and this is most pronounced for the NaCl case (Fig. 2a). For the mixture, the higher current is measured for the case in which the concentrate stream is heated, although the difference between these two temperature configurations is generally small (between 2 and 6%).

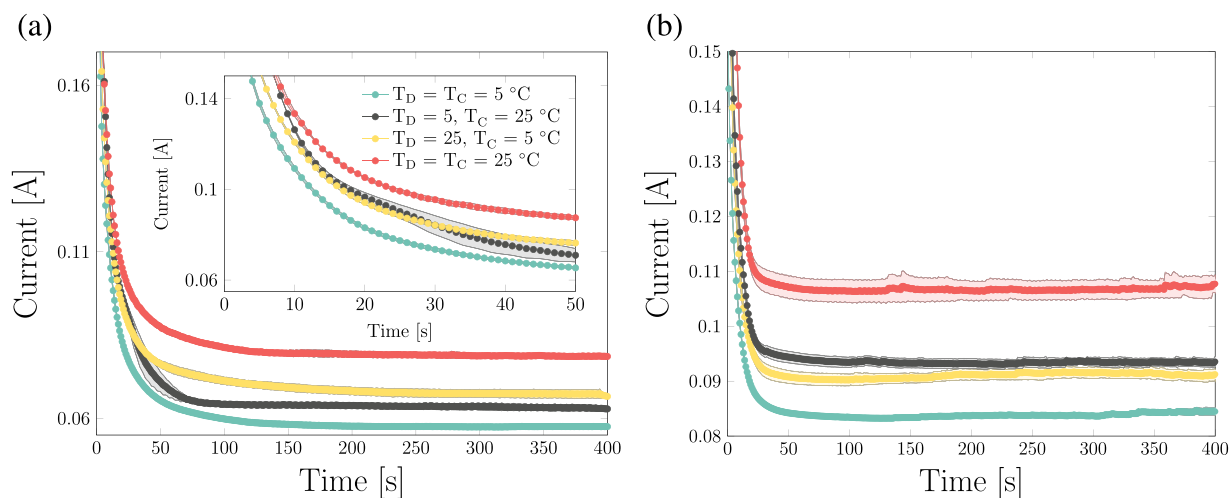


Fig. 2. It-characterization of the ED stack for all feed compositions. (a) Feed is 6.7 mM NaCl, with as inset a close-up of the first 50s. (c) Feed is 3.35 mM NaCl and 1.68 mM MgCl₂. Error bars are the standard error between the measurement runs.

For the NaCl measurements, the IV-characterization and chronoamperometric measurements are seemingly contradictory. In the IV sweeps the case in which the concentrate stream was heated yielded the highest currents, but in the chronoamperometric measurements higher currents are observed when the dilute stream is heated. However, initially this was also the case for the chronoamperometric measurements (see inset of Fig. 2a). After ~30–40s, the current for the hot concentrate case drops below the current measured for the case with a hot dilute stream. We attribute this to the development of the diffusion boundary layer, which is not in equilibrium at shorter times. The boundary layer is calculated to be in the order of hundreds of micrometers in the channel of 600 μm, and the concentration profile in this boundary layer is not established at the start of the measurements. When the steady state concentration profile in the boundary layer is developed, the current through the system becomes stable. In the measurements with a mixed feed (Fig. 2b), higher current is measured when heating the concentrate stream, which is contrary to our expectations. This is possibly due to a different response of the mono- and divalent ions to the temperature [34]. Together with the competitive transport of these ions at different temperature configurations, this could lead to a higher current when the concentrate stream is heated when compared to the case in which the dilute stream is heated, most pronounced when the diffusivity of the divalent ions is less dependent on temperature than the diffusivity of the monovalent ions. This was confirmed by the measurements of ion concentrations of all outlet streams, as is described in the next sections.

From the measured currents and Eq. (2), we can identify the influence of different parameters on the current. The boundary layer thickness δ is dependent on the viscosity (and density) of the liquid, and can thus be influenced by the temperature of the stream. The flow rate and compartment geometry, have not changed between the measurements. The permselectivity of the membrane was found to be independent of temperature in the range applied in our measurements (5–25 °C). Apart from that, the diffusivity D_i changes with changing temperature. The difference in measured current (27 to 39%) can be compared with the difference in diffusivity of the different ions over the applied feed temperature range, which is roughly doubled for all ions (see Appendix A [35,46]). The ED system containing n cell pairs can be described as a series of electrical resistances, resulting in a total resistance $R_{tot} = 2 * R_{elec} + R_{CEM} + [R_{dil} + R_{AEM} + R_{conc} + R_{CEM}]_n$, which is dependent on the resistance of the electrolyte compartments (R_{elec}), the resistance of the membranes (R_{CEM} and R_{AEM}) and the resistance of the dilute and concentrate compartments (R_{dil} and R_{conc}). There is one additional CEM shielding the first cell pair from the electrolyte solution,

which shows up separately in the equation. The resistance of the membranes is typically in the order of $10^5 \Omega/m^2$ and the resistance of the electrolyte and salt solutions can be calculated using $R = \rho/(IA)$ in which $\rho = 1/\sigma$. The conductivity of the solution, $\sigma = F^2 \sum z_i^2 \nu_i c_i$, depends on the ion concentration c_i and charge z_i and the ionic mobility $\nu_i = D_i/RT$ which depends on the diffusivity D_i and temperature. If we take the difference in diffusivity at different temperatures into account we can calculate the change in resistance of the solution. For instance, considering Cl⁻ and K⁺, at $T = 298$ K and an inlet concentration of 6.7 mM the diffusivity of these ions is $\sim 2.0 \times 10^{-9} m^2/s$, yielding a resistance of $R = 1.65 \times 10^6 \Omega/m^2$. At a lower temperature of $T = 278$ K and the same feed concentration the diffusivity is $\sim 1.05 \times 10^{-9} m^2/s$ yielding a resistance of $R = 3.05 \times 10^6 \Omega/m^2$. The resistance of the solutions is higher than the resistance of the membranes and electrolyte and thus contribute most to the total resistance in the system. Decreasing the temperature of the solution by 20 °C increases the resistance of the electrolyte solution by 85%. From this, we can identify that the change in D_i is large enough to account for the change in measured current, even if the actual change in temperature is less than the inlet temperature differences due to heat transfer between the dilute and concentrate stream.

Cation concentrations have been measured for all different measurement configurations, and are shown in Fig. 3 for the NaCl and mixed feed. In this figure, the outlet concentrations for all ions are given relative to their inlet concentrations that were analyzed for all experiments as well (see Table 1). As was discussed previously, K⁺ ions are present in the system as a result of ion exchange with the electrolyte solution (K₂SO₄). In contrast to our previous results in the Ohmic regime, we do find differences in the relative outlet concentrations for the different temperature configurations. We can define an average relative separation based on the concentrate $c_{j,C}$ and dilute stream $c_{j,D}$ outlet concentrations when compared to the inlet concentrations $c_{j,F}$, as $\frac{1}{2}((1 - c_{j,D}/c_{j,F}) + (c_{j,C}/c_{j,F} - 1))$. For all measurements, the cold isothermal case yields the lowest degree of separation for all present ions (an average relative separation of ~26% in the NaCl measurements, ~40% for the mixture), while the hot isothermal case yields the highest degree of separation (average relative separation of ~43% in NaCl, ~56% for the mixture). This is in line with the currents that were measured, as higher currents imply a larger transport of ions. These measurements also indicate that there is no significant influence of temperature on water splitting in our system under these operating conditions, as the enhanced separation is in agreement with the increased current. For the cases with an applied temperature gradient, the difference in outlet concentrations is smaller. For the NaCl feed, the

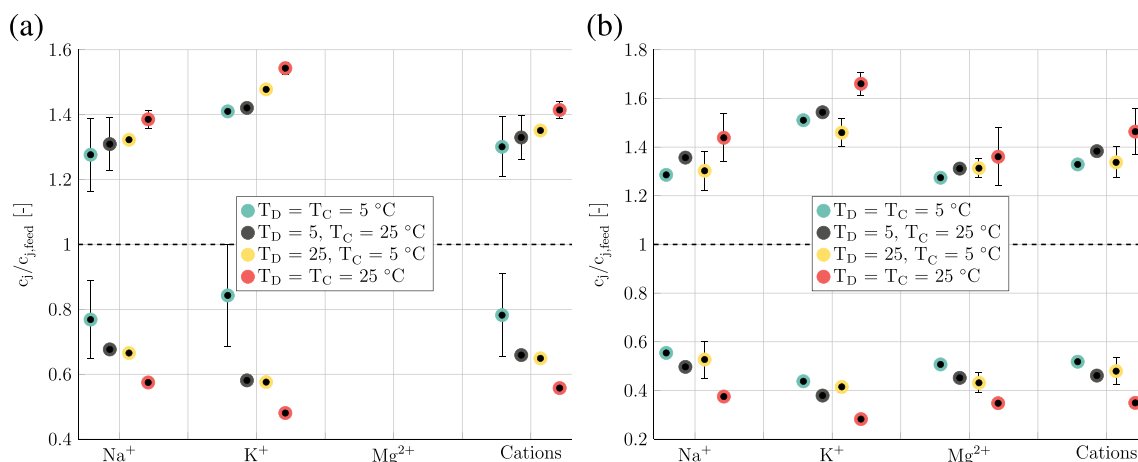


Fig. 3. Relative outlet concentrations (to feed concentrations) for all cations at the different temperature configurations, for the measurements with only NaCl (a) and the mixed NaCl and MgCl₂ feed (b). Relative concentrations of the individual cations as well as the total cation concentration are given. Concentrate concentrations are above the $c_i/c_{i,feed} = 1$ line, while dilute concentrations are below this line. The error is the standard deviation between the measurements. Note the different values on the y-axes.

case in which the dilute stream is heated has an average separation of 35%, while heating the concentrate stream yields a separation of 33%. For the mixture, the opposite is the case, here the case with the heated dilute stream yields a lower (43%) average separation than the case with a heated concentrate stream (46%). This again is consistent with the measured difference in currents for these different settings and can be explained by the increased competitive transport of ions in the case of the mixture.

Water transport as a result of an osmotic gradient is expected to be minor in our system since the commercial membranes have a high resistance to water transport and we have only small osmotic pressures (maximum of 0.17 bar for a concentration difference of 6.7 mM) in our system due to the low absolute salt concentrations in our system. In our set-up we cannot directly quantify the water transport, but based on the measured concentration differences we assume the role of osmotic, thermoosmotic and electroosmotic water transport to be minor. Taking typical total water transport numbers ($t_w \approx 10$) [47, 48], the water transport can be estimated as $\frac{t_w M_w}{F} \int Idt$, in which M_w is the molecular weight of water. For our system, taking an average current of 0.11 A and a chronoamperometric measurement time of 500 s this is estimated to be ~ 0.1 g. The maximum additional amount of NaCl ions transported as a result of this water transport is 6.7×10^{-7} mol (0.1 g of water at a maximum concentration of 6.7 mM) in total. This ion transport (corresponding to an additional current of 1.3×10^{-4} A, calculated using the Faraday constant) is negligible in comparison to the ionic transport as a result of the imposed electric field at which a total current of 0.11 A was measured (Fig. 2) indicating that the thermodiffusive contribution (the last term of Eq. (2)) is negligible.

From our ion concentration measurements (see Fig. 3), we find that in the case of temperature gradients the degree of separation of Na⁺ and K⁺ differs from the separation of Mg²⁺. In the mixture, the monovalent ions are separated to a lesser extent when the desalinated stream is heated when compared to the heating of the concentrated stream. This indicates that for the temperature configuration where the dilute stream is heated in a mixture of mono- and divalent ions there is competitive transport that reduces the transport of monovalent ions. For the Mg²⁺ ions, there is no reduced transport observed when changing the direction of the temperature gradient. This implies that the competitive transport of divalent ions [33] is more significant in the case of a hot diluted stream. The total charge transport is then reduced by the reduction in transport of monovalent ions, resulting in a lower current measured at this configuration.

With the measured current I , concentrations $c_{i,in}$ and $c_{i,out}$, Faraday's constant F and the dilute flow rate Q_f , the current efficiency η_{curr} of the

membrane stack containing N cell pairs can be calculated using Eq. (3) [49]. Based on our measurements we find the highest current efficiency for the hot isothermal cases, which means that apart from obtaining the highest current, the power in this case is also used most efficiently for the selective transport of ions.

$$\eta_{curr} = \frac{Q_f F \sum (z_i (c_{i,in} - c_{i,out}))}{NI} \quad (3)$$

The current efficiency is not significantly dependent on the direction of the temperature gradient. Current efficiency for the NaCl feed ranges from 69% (for the cold isothermal case) to 100% (for the hot isothermal case). This high efficiency indicates that for the high isothermal case there is no significant concentration polarization. This is a result of the increased diffusion of ions at the elevated temperature and is an indication that increasing the temperature is a useful strategy in enhancing the obtainable current in ED systems. For the mixture the efficiency is $\sim 83\%$ for all temperature configurations, except for the hot isothermal case, where the efficiency is 88%. The current efficiency of the mixture is therefore not dependent on the temperature configuration, but higher degrees of desalination can be obtained when working with a temperature gradient. This shows that the increased selective transport of ions is of more significance than the possibly increased water transport at elevated temperatures and temperature gradients.

The relative efficiency for the separation of Mg²⁺ when compared to the separation of Na⁺ and K⁺ is enhanced when the dilute stream is heated, albeit with a relatively small magnitude. The direction of the temperature gradient has an influence on the relative transport of Mg²⁺ when compared to the transport of K⁺ and Na⁺. If the dilute stream is heated the transport of monovalent ions is inhibited while the transport of the divalent ions is not impacted, resulting in a more selective transport of divalent ions for this temperature configuration. This is presumed to be a result of the competitive ion transport between the mono- and divalent ions [33,34,50], both in the solution and the membrane, inhibiting the transport of monovalent ions towards and through the membrane at this configuration. The flux of Na⁺ ions was found to decrease significantly when Mg²⁺ was also present in the feed stream [34], since Mg²⁺ can monopolize the transfer sites (yielding a possible partial charge inversion) in the membrane and thus suppress the transport of monovalent ions. The temperature gradient can enhance this, as the hydrated radii of the different ions are changing with temperature, yielding a different degree of polarization at different temperatures. Mg²⁺ ions are already relatively polarized when compared to the other ions in the system [34], yielding a higher affinity of

these ions with the cation exchange membrane. The hydration of Na^+ and K^+ ions increases more with temperature than the hydration of Mg^{2+} ions [51], meaning that at a higher temperature the relative polarization of the Mg^{2+} is increased, enhancing the transport of these ions over the monovalent ions. This effect is most pronounced for the case in which the dilute channel temperature is increased.

4. Conclusion

In this work, we investigated the influence of temperature gradients on charge transport in electro dialysis in the limiting current regime. It was found that temperature gradients can enhance the total ion transport in the system when operated in the limiting current regime. Higher currents, and thus an increased flux of ions, are measured when temperature in (one of) the streams is increased. For a feed of only monovalent ions, the efficiency of the ED-process is increased when the dilute stream is heated, since the main diffusive resistance is located in this compartment. This is in contrast to the application of temperature gradients in electro dialysis in the Ohmic regime, where the direction of the temperature gradient had no significant influence on the process efficiency [19]. The direction of the temperature gradient did not significantly enhance separation of monovalent ions.

Experiments were also done for mixtures of mono- and divalent

cations. In this case, the influence of the direction of the temperature gradient on the measured current was lower. The selectivity favored the separation of divalent ions when the dilute stream was heated. This is attributed to competitive transport of the mono- and divalent ions that is influenced by their different response on temperature. Apart from an altered ratio in diffusivities in the solution, the polarization of the different ions has a different response to temperature. Increasing the temperature enhances the relative polarization of Mg^{2+} , resulting in a higher affinity of these ions towards the membrane and an enhanced transport of these multivalent ions. This work demonstrates that other gradients, such as temperature, can be applied in order to tune selectivity without having to change other operating parameters, such as the system geometry, spacers and flow rate. Our results can be of potential use in the improvement of separation of mono- and divalent ions by electro dialysis under temperature gradients.

Acknowledgments

This research was financially supported by the European Research Council, under the ERC starting grant 307342-TRAM awarded to R.G.H. Lammertink. The authors would like to thank Ehsan Reyhanitash for conducting the IC-measurements. Timon Rijnaarts and Harmen Zwijnenberg are thanked for the valuable discussions on the ED-system.

Appendix A. Diffusion coefficients for ions

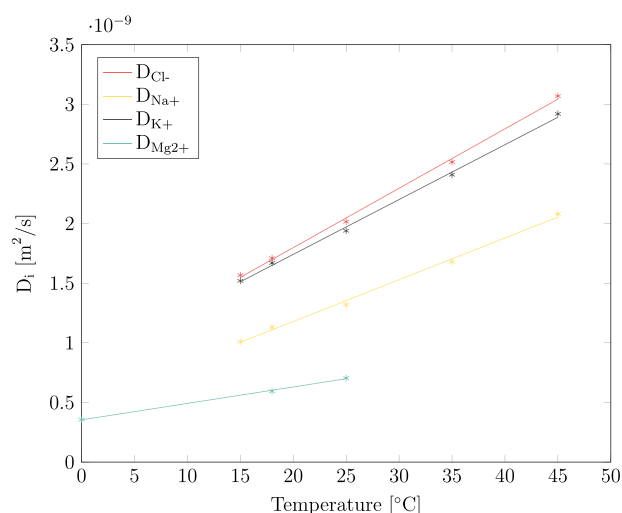


Fig. A.1. Temperature dependence of diffusivity of the different ions used in the experiments, extracted from experimental data reported elsewhere [35,46].

References

- [1] H. Strathmann, Electro dialysis, a mature technology with a multitude of new applications, *Desalination* 264 (3) (2010) 268–288.
- [2] C. Forgacs, N. Ishibashi, J. Leibovitz, J. Sinkovic, K.S. Spiegler, Polarization at ion-exchange membranes in electro dialysis, *Desalination* 10 (2) (1972) 181–214.
- [3] K.S. Spiegler, Polarization at ion exchange membrane-solution interfaces, *Desalination* 9 (4) (1971) 367–385.
- [4] H. Strathmann, A. Grabowski, G. Eigenberger, Ion-exchange membranes in the chemical process industry, *Ind. Eng. Chem. Res.* 52 (31) (2013) 10364–10379.
- [5] P. Długołęcki, A. Gambier, K. Nijmeijer, M. Wessling, Practical potential of reverse electro dialysis as process for sustainable energy generation, *Environ. Sci. Technol.* 43 (17) (2009) 6888–6894.
- [6] V.I. Zabolotskii, S.A. Loza, M.V. Sharafan, Physicochemical properties of profiled heterogeneous ion-exchange membranes, *Russ. J. Electrochem.* 41 (10) (2005) 1053–1060.
- [7] J. Balster, D.F. Stamatialis, M. Wessling, Membrane with integrated spacer, *J. Membr. Sci.* 360 (1-2) (2010) 185–189.
- [8] O. Kedem, Reduction of polarization in electro dialysis by ion-conducting spacers, *Desalination* 16 (1) (1975) 105–118.
- [9] O. Kedem, Y. Maoz, Ion conducting spacer for improved ed, *Desalination* 19 (1-3) (1976) 465–470.
- [10] J.M. Chiapello, M. Bernard, Improved spacer design and cost reduction in an electro dialysis system, *J. Membr. Sci.* 80 (1) (1993) 251–256.
- [11] F. Li, W. Meindersma, A.B. De Haan, T. Reith, Novel spacers for mass transfer enhancement in membrane separations, *J. Membr. Sci.* 253 (1-2) (2005) 1–12.
- [12] J. Balster, I. Pünt, D.F. Stamatialis, M. Wessling, Multi-layer spacer geometries with improved mass transport, *J. Membr. Sci.* 282 (1-2) (2006) 351–361.
- [13] D.R. Lide, *CRC Handbook of Chemistry and Physics*, eBook, (2003), p. 3485.
- [14] S. Tseng, Y.-M. Li, C.-Y. Lin, J.-P. Hsu, Salinity gradient power: influences of temperature and nanopore size. *Nanoscale* (2016) 2350–2357.
- [15] M. Tedesco, E. Brauns, A. Cipollina, G. Micale, P. Modica, G. Russo, J. Helsen, Reverse electro dialysis with saline waters and concentrated brines: a laboratory investigation towards technology scale-up, *J. Membr. Sci.* 492 (2015) 9–20.
- [16] A. Daniilidis, D.A. Vermaas, R. Herber, K. Nijmeijer, Experimentally obtainable energy from mixing river water, seawater or brines with reverse electro dialysis, *Renew. Energy* 64 (2014) 123–131.
- [17] E. Fontananova, W. Zhang, I. Nicotera, C. Simari, W. van Baak, G. Di Profio, E. Curcio, E. Drioli, Probing membrane and interface properties in concentrated electrolyte solutions, *J. Membr. Sci.* 459 (2014) 177–189.
- [18] Y. Kobatake, H. Fujita, Osmotic flows in charged membranes. II. Thermo-osmosis, *J. Chem. Phys.* 41 (10) (1964) 2963.
- [19] A.M. Benneker, T. Rijnaarts, R.G. Lammertink, J.A. Wood, Effect of temperature gradients in (reverse) electro dialysis in the Ohmic regime, *J. Membr. Sci.* 548

- (2018) 421–428.
- [20] G. Hills, P. Jacobs, N. Lakshminarayanaiah, Non-isothermal membrane potentials, *Nature* 179 (1957) 96–97.
- [21] T. Ikeda, Thermal membrane potential, *J. Chem. Phys.* 28 (1) (1958) 166.
- [22] M. Tasaka, Thermal membrane potential and thermoosmosis across charged membranes, *Pure Appl. Chem.* 58 (12) (1986) 1637–1646.
- [23] V.M. Barragán, S. Kjelstrup, Thermo-osmosis in membrane systems: a review, *J. Non Equilib. Thermodyn.* 42 (3) (2017) 217–236.
- [24] K.D. Sandbakk, A. Bentien, S. Kjelstrup, Thermoelectric effects in ion conducting membranes and perspectives for thermoelectric energy conversion, *J. Membr. Sci.* 434 (2013) 10–17.
- [25] M. Dariel, O. Kedem, Thermoosmosis in semipermeable membranes, *J. Phys. Chem.* (1975) 336–342.
- [26] J.A. Wood, A.M. Benneker, R.G. Lammertink, Temperature effects on the electrohydrodynamic and electrokinetic behaviour of ion-selective nanochannels, *J. Phys. Condens. Matter* 28 (11) (2016) 114002.
- [27] B. Van Der Bruggen, A. Koninckx, C. Vandecasteele, Separation of monovalent and divalent ions from aqueous solution by electrodialysis and nanofiltration, *Water Res.* 38 (5) (2004) 1347–1353.
- [28] M. Sadrzadeh, A. Razmi, T. Mohammadi, Separation of monovalent, divalent and trivalent ions from wastewater at various operating conditions using electrodialysis, *Desalination* 205 (1-3) (2007) 53–61.
- [29] N. Kabay, M. Arda, I. Kurucaovali, E. Ersoz, H. Kahveci, M. Can, S. Dal, S. Kopuzlu, M. Haner, M. Demircioglu, M. Yuksel, Effect of feed characteristics on the separation performances of monovalent and divalent salts by electrodialysis, *Desalination* 158 (1-3) (2003) 95–100.
- [30] R.K. Nagarale, G.S. Gohil, V.K. Shahi, Recent developments on ion-exchange membranes and electro-membrane processes, *Adv. Colloid Interf. Sci.* 119 (2-3) (2006) 97–130.
- [31] N. Kabay, M. Demircioglu, E. Ersöz, I. Kurucaovali, Removal of calcium and magnesium hardness of electrodialysis, *Desalination* 149 (1-3) (2002) 343–349.
- [32] N. Kabay, H. Kahveci, Ö. Ipek, M. Yüksel, Separation of monovalent and divalent ions from ternary mixtures by electrodialysis, *Desalination* 198 (1-3) (2006) 74–83.
- [33] A.H. Galama, G. Daubaras, O.S. Burheim, H.H. Rijnaarts, J.W. Post, Seawater electrodialysis with preferential removal of divalent ions, *J. Membr. Sci.* 452 (2014) 219–228.
- [34] L. Firdaous, J.P. Malériat, J.P. Schlumpf, F. Quéméneur, Transfer of monovalent and divalent cations in salt solutions by electrodialysis, *Sep. Sci. Technol.* 42 (5) (2007) 931–948.
- [35] Y.-H. Li, S. Gregory, Diffusion of ions in sea water and in deep sea sediments, *Geochim. Cosmochim. Acta* 1974 38 (2) (1973) 703–714.
- [36] P. Długołęcki, P. Ogonowski, S.J. Metz, M. Saakes, K. Nijmeijer, M. Wessling, On the resistances of membrane, diffusion boundary layer and double layer in ion exchange membrane transport, *J. Membr. Sci.* 349 (1-2) (2010) 369–379.
- [37] RIWA - Vereniging van Rivierwaterbedrijven, Jaarrapport 2015 De Rijn, Technical report, RIWA-Rijn, 2015.
- [38] Y. Ji, G.M. Geise, The role of experimental factors in membrane permselectivity measurements, *Ind. Eng. Chem. Res.* 56 (26) (2017) 7559–7566.
- [39] Y. Tanaka, Limiting Current Density, in: Y. Tanaka (Ed.), *Ion exchange membranes* (second edition), second, Elsevier, Amsterdam, 2015, pp. 199–214.
- [40] A.M. Peers, General discussion, *Discuss. Faraday Soc.* 21 (1956) 124–125.
- [41] J.J. Krol, M. Wessling, H. Strathmann, Concentration polarization with monopolar ion exchange membranes: current-voltage curves and water dissociation, *J. Membr. Sci.* 162 (1-2) (1999) 145–154.
- [42] P. Sizat, A. Kozmai, N. Pismenskaya, C. Larchet, G. Pourcelly, V. Nikonenko, Low-frequency impedance of an ion-exchange membrane system, *Electrochim. Acta* 53 (22) (2008) 6380–6390.
- [43] J.-H. Choi, J.-S. Park, S.-H. Moon, Direct measurement of concentration distribution within the boundary layer of an ion-exchange membrane, *J. Colloid Interface Sci.* 251 (2) (2002) 311–317.
- [44] A.A. Moya, A numerical comparison of optimal load and internal resistances in ion-exchange membrane systems under reverse electrodialysis conditions, *Desalination* 392 (2016) 25–33.
- [45] A. Chapotot, G. Pourcelly, C. Gavach, Transport competition between monovalent and divalent cations through cation-exchange membranes. Exchange isotherms and kinetic concepts.pdf, *J. Membr. Sci.* 96 (1994) 167–181.
- [46] G.C. Benson, A.R. Gordon, A reinvestigation of the conductance of aqueous solutions of potassium chloride, sodium chloride, and potassium bromide at temperatures from 15° to 45° C, *J. Chem. Phys.* 13 (11) (1945) 473–474.
- [47] A. Zlotorowicz, R.V. Strand, O.S. Burheim, Wilhelmsen, S. Kjelstrup, The permselectivity and water transference number of ion exchange membranes in reverse electrodialysis, *J. Membr. Sci.* 523 (September 2016) (2017) 402–408.
- [48] P. Długołęcki, B. Anet, S.J. Metz, K. Nijmeijer, M. Wessling, Transport limitations in ion exchange membranes at low salt concentrations, *J. Membr. Sci.* 346 (1) (2010) 163–171.
- [49] M. Sadrzadeh, T. Mohammadi, Treatment of sea water using electrodialysis: current efficiency evaluation, *Desalination* 249 (1) (2009) 279–285.
- [50] A. Chapotot, G. Pourcelly, C. Gavach, Transport competition between monovalent and divalent cations through cation-exchange membranes. Exchange isotherms and kinetic concepts, *J. Membr. Sci.* 96 (3) (1994) 167–181.
- [51] E.R. Nightingale, Phenomenological theory of ion solvation. Effective radii of hydrated ions, *J. Phys. Chem.* 63 (9) (1959) 1381–1387.