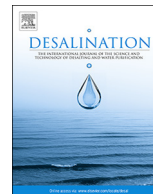




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# Influence of temperature gradients on mono- and divalent ion transport in electro dialysis at limiting currents

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## 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  $\nabla c_i$  and a molecular ion diffusivity  $D_i$  or similarly, through a temperature gradient  $\nabla T$  with thermodiffusivity  $D_{T,i}$ , an electromigration flux resulting from the local electric potential gradient  $\nabla V$ , the ionic mobility  $\nu_i$ , 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).

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For instance, the diffusivity  $D_i$  and mobility  $\nu_i$  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  $\nabla T$  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  $\text{Na}^+$  was drastically reduced by the addition of divalent  $\text{Mg}^{2+}$  or  $\text{Ca}^{2+}$  ions, while the effect of adding  $\text{Na}^+$  on the  $\text{Mg}^{2+}$  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  $i_{\text{lim}}$  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  $\mu\text{m}$ ) 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  $\text{K}^+$  and  $\text{OH}^-$ , 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,  $\gamma_c$  and  $\gamma_d$  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  $\sim 22$  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

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