



# The permselectivity and water transference number of ion exchange membranes in reverse electrodialysis



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## ABSTRACT

Reverse electrodialysis of saline solutions (RED) is a renewable energy technology with large potential. Key components in the system are the ion exchange membranes. This work evaluates the efficiency of commercially available anion and cation selective membranes for RED. Their efficiency is often described with the apparent transport number for the ion in question, and this number depends on the salt concentration. It is known since long that the water transference coefficient contributes to the apparent transport number, but much of the recent literature on RED takes the permselectivity as defined by the apparent transport number as a direct measure of the membrane selectivity. The purpose of this paper is to clarify that situation with new data on Fumasep membranes. Concentration cell potentials were measured for anion- and cation exchange membranes from Fumasep (FAD and FKS, respectively, Fumatech, Germany) in the temperature range 12 – 45°C in salt solutions relevant for reverse electrodialysis. The results show that the anion exchange membrane is a perfectly selective ion exchange membrane, and has a water transference coefficient of  $-6 \pm 1$ . The cation selective membrane has a cation transport number of 0.93 and a water transference coefficient of  $8 \pm 7$ . We suggest that the developers of membranes should pay more attention to the water transference coefficient. To enhance the performance of ion selective membranes and RED, it is beneficial to have water transference coefficients as close to zero as possible.

## 1. Introduction

The Gibbs energy of mixing of seawater and freshwater can be converted into electrical energy in several ways [1–3], including in reverse electrodialysis (RED) [4–6]. This promising renewable energy technology is at focus here. The key components in the RED system are the ion exchange membranes (IEMs). IEMs are also widely used for separation purposes, including microfiltration [7,8], nanofiltration [9], reverse osmosis [8], evaporation [10] and separation from gas or liquid-phases [11,12]. Ion exchange membranes are also applied to waste water treatment in electrodialysis cells. Electrodialysis is a practical and most important technology for the treatment of unusable water; it is in general used for demineralization of solutions in a wide variety of industrial fluids encountered in the food industry [13–15], and in pharmaceutical industries [16]. It is therefore important for several reasons to have a precise understanding of the coupled transport processes that take place in the IEMs, in particular of how the ion and water transports interact. This work evaluates interaction in commercially available anion- and cation exchange membranes, for

application in reverse electrodialysis. In this context, their permselectivity is described with the apparent transport number, defined as the ratio between the measurable electromotive force (Emf) over the membrane and the ideal electric potential, which is the maximum achievable value [17]. When the apparent transport number is unity, the membrane has been said to be perfectly permselective. Alternatively, when the apparent transport number is below unity, it has been understood that the IEM is not perfectly selective to one ion, but allows more ions to pass.

It is well established experimentally that the water transference coefficient of a membrane decreases with increasing salt content in the solution [18–24], and that water transfer constitutes a major part of electroosmosis [24–27]. According to the literature [28], there is also a small temperature variation in these numbers. Values for the cation transport number in a cation exchange membrane,  $t_{\text{Na}^+}$ , is close to unity; 0.95 (Nafion 120) [29], 0.97–0.99 (MF-4SK) [30], 0.89 (FKD-Fumasep), 0.99 (CMX-Neosepta) [31,32], where the transport number in an anion exchange membrane is close to zero; 0.140 (FAD-Fumasep), 0.09 (AMX-Neosepta) [31,32]. The water transference

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coefficient,  $t_{w}$ , has a different sign in cation- and anion exchange membranes. For cation exchange membranes, reported values of  $t_{w}$  vary from 6.9 to 9.6 for  $\text{Na}^+$  salt solutions [26,33]. The membrane in the H-form (the fuel cell membrane) has an exceptionally high water content, but a low water transference coefficient ( $t_{w}=2.6$ ) [34–36]. The sign variation can be explained by a water transport which follows the main conducting ion. Protons are unable to carry much water along. The ion transport promotes simultaneous water transport in two ways. In the first place, there is an electrostatic drag on the water dipoles by the ion, which increases with increasing field strength. This effect is therefore larger for cations than for anions. The second effect is more of a bulk effect; clusters of water can be “pushed” along the membrane channel, forced by the ion transport [37]. Also this effect is larger for smaller ions. The transference coefficient is therefore not the same as the waters of hydration around the ion. Anion exchange membranes have accordingly relatively smaller values of  $t_{w}$ .

Direct measurement of the water transference coefficient is difficult, and is probably most accurately performed by using the streaming potential technique [38]. Few experimental values for  $t_{w}$  have been reported for anion exchange membranes. These observations are extended experimentally in this work. Emf measurements are done in the temperature range 12 – 45°C with Fumasep anion- and cation exchange membranes and electrolyte solutions varying in concentration between 2 and 30 g dm<sup>-3</sup> NaCl (similar to fresh- and seawater). Fumasep membranes have good electrochemical properties in terms of low membrane resistance and high selectivity [39], so they are good candidates for RED. It is perceived that imperfect membranes, having an apparent transport number different from unity, allows to some small degree a transport of the counter-ion. We shall see that this may not be the case.

Using a simple assumption about the concentration dependence of the various contributions to the apparent transport number, we shall see that it is possible to decompose the data to obtain information about the water transport, in addition to the ion transport. The theory of non-equilibrium thermodynamics is essential in this respect. Using this, we find that a membrane may appear not to have a supreme selectivity, while the deviation from an ideal selective membrane is caused by the transfer of water and not of any counter-ion. This leads us to suggest that membrane manufacturers and users should pay more attention to water transference coefficients. In the future, the performance of ion selective membranes can be enhanced by developing membranes that have water transference coefficients as close to zero as possible.

## 2. Theory

The electrochemical cell we consider in this work is, with standard notation:



Here, MEM is a cation or anion exchange membrane. The purpose is now to find a more explicit expression for the permselectivity  $\alpha$  of the membranes as a function of the salt molality,  $m_s$ , where the permselectivity,  $\alpha$ , is defined as the ratio of the electrical potential difference  $E$  at open circuit conditions (the *Emf*), to the ideal potential difference,  $E_{ideal}$ :

$$\alpha = \frac{E}{E_{ideal}} \quad (1)$$

The ideal potential difference is taken as the maximum value obtainable from the difference in the chemical potential of the salt across the membrane,  $\Delta\mu_s$ :

$$E_{ideal} = -\frac{\Delta\mu_s}{F} \quad (2)$$

Here,  $F$  is Faraday's constant. An expression for  $E$  can be found from

the force-flux equations defined in irreversible thermodynamics [40,41]:

$$J_s = -L_{ss} \frac{\partial\mu_s}{\partial x} - L_{sw} \frac{\partial\mu_w}{\partial x} - L_{s\phi} \frac{\partial\phi}{\partial x} \quad (3)$$

$$J_w = -L_{ws} \frac{\partial\mu_s}{\partial x} - L_{ww} \frac{\partial\mu_w}{\partial x} - L_{w\phi} \frac{\partial\phi}{\partial x} \quad (4)$$

$$j = -L_{\phi s} \frac{\partial\mu_s}{\partial x} - L_{\phi w} \frac{\partial\mu_w}{\partial x} - L_{\phi\phi} \frac{\partial\phi}{\partial x} \quad (5)$$

Here,  $L_{ij}$  are Onsager coefficients,  $\mu_s$  is the chemical potential of the salt,  $\mu_w$  is the chemical potential of water,  $\phi$  is the electric potential, and  $j$  is the electric current density. The subscripts  $s$ ,  $w$  and  $\phi$  refer to salt, water and current respectively. We have considered transport in the  $x$ -direction only, i.e. the direction perpendicular to the membrane surface. In order to find the apparent transport number,  $t'$ , we solve the last equation for the gradient in electric potential with the condition,  $j \approx 0$ :

$$\left(\frac{d\phi}{dx}\right)_{j=0} = -\frac{L_{\phi s}}{L_{\phi\phi}} \frac{d\mu_s}{dx} - \frac{L_{\phi w}}{L_{\phi\phi}} \frac{d\mu_w}{dx} \quad (6)$$

The transport number for the salt is defined as:

$$t_s \equiv F \frac{L_{\phi s}}{L_{\phi\phi}} \quad (7)$$

In the present cell with Ag|AgCl-electrodes,  $t_s$  is equal to the transport number of  $\text{Na}^+$  or one minus the transport number of  $\text{Cl}^-$ :

$$t_s = t_{\text{Na}^+} = 1 - t_{\text{Cl}^-} \quad (8)$$

This identification depends on the electrodes and applies to cation as well as anion exchange membranes. A perfect cation exchange membrane has  $t_s=1$ , while a perfect anion exchange membrane has  $t_s=0$ . Similarly, the transference coefficient of water is defined as:

$$t_w \equiv F \frac{L_{\phi w}}{L_{\phi\phi}} \quad (9)$$

The transference coefficient measures how many moles of a component that is transported through the membrane from left to right per mole of electrons that are transferred between the electrodes in the external circuit. We introduce the definitions of the transference coefficients into Eq. (6):

$$\frac{d\phi}{dx} = -\frac{t_s}{F} \frac{d\mu_s}{dx} - \frac{t_w}{F} \frac{d\mu_w}{dx} \quad (10)$$

where the chemical potential  $\mu_s$  of an electrolyte (NaCl) in a solution is:

$$\mu_s = \mu_s^0 + 2RT \ln \left( \frac{m_s \gamma_s}{m^0} \right) \quad (11)$$

Here,  $\mu_s^0$  is the standard chemical potential for salt (a solution of 1 molal),  $R=8.314 \text{ J}/(\text{mol K})$  is the universal gas constant,  $m_s$  is the concentration of NaCl in mol/kg water and  $\gamma_s$  is the dimensionless activity coefficient of the salt. Eq. (11) gives that:

$$d\mu_s = 2RT \left( \frac{1}{m_s} + \frac{1}{\gamma_s} \left( \frac{\partial\gamma_s}{\partial m_s} \right) \right) dm_s \quad (12)$$

In the following, we omit the last term on the right hand side of Eq. (12) since we find numerically that  $m_s^{-1} \gg \gamma_s^{-1} (\partial\gamma/\partial m_s)$  in the range considered. Moreover, the Gibbs-Duhem equation relates the chemical potential of water to the chemical potential of the salt:

$$d\mu_w = -\frac{m_s}{m_w} d\mu_s \quad (13)$$

where  $m_w$  is the molality of water, which is the mole number of water in 1 kg, equal to  $1/M_w$ , where  $M_w$  is the molar mass,  $M_w = 18.015 \times 10^{-3} \text{ kg/mol}$ . The molality of water is expressed by

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