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## Co-ion fluxes of simple inorganic ions in electro dialysis metathesis and conventional electro dialysis

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## ABSTRACT

The main functionality of ion-exchange membranes is to selectively permeate either cations or anions. However, co-ions may permeate as well to some extent through these membranes. For the production of chemicals with electro dialysis metathesis and conventional electro dialysis, these co-ion fluxes are a major source of impurities in the produced chemicals. The present paper studies the co-ion fluxes and the influence of operating parameters. The results clearly indicate that co-ion fluxes are predominately determined by the difference in ion concentration across the membrane. A more than linear increase in co-ion flux with respect to the ion concentration was observed. The current density has no significant influence on the co-ion fluxes. Therefore, a high current density leads to a smaller transport number of co-ions and improves the product purity in electro dialysis metathesis. Moreover, the co-ion flux can be decreased by the use of bulky counter-ions. In a conventional electro dialysis configuration, cation impurities are mainly caused by a diffusional flux. This flux is approximately three times larger than the co-ion flux. In contrast, the anion impurities are predominantly initiated by a co-ion flux and in magnitude smaller than the cation impurities.

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## 1. Introduction

Ion-exchange membranes are polymeric membranes with charged groups attached to the polymer matrix [1]. Depending on the charge of the fixed groups, two types of ion-exchange membranes are to be distinguished: cation-exchange membranes, with negatively charged groups, and anion-exchange membranes, with positively charged groups. In cation-exchange membranes, the fixed negatively charged groups and the negatively charged anions in the membrane phase are in electrical equilibrium with the positively charged cations. The mobile cations are referred to as counter-ions; ions with the same charge as the fixed groups are denoted as co-ions. These co-ions are largely excluded from the polymer matrix due to the electrical repulsion with the fixed groups. Therefore, cation-exchange membranes preferentially permeate cations and retain anions. This phenomenon is known as Donnan exclusion [1–6].

In ideal permselective ion-exchange membranes co-ions should be completely excluded from the polymer matrix. However, in real membranes small amounts of co-ions are absorbed in the membrane phase. According to the Donnan exclusion theory the

concentration of monovalent co-ions in ion-exchange membranes is inversely proportional to the concentration of fixed charged groups in the membrane [7] and proportional with the square of the ion concentration in the external solution [5]. The theory therefore predicts that a reduction in the concentration of the fixed charged groups should lead to a reduction in co-ion exclusion [8]. However, real ion-exchange membranes do not strictly obey the quadratic proportionality of the co-ion concentration with the external salt concentration. The Donnan exclusion theory assumes that the charge distribution in the membrane is homogeneous. Due to structural irregularities in actual membranes, small variations in the distribution of the charged groups result in a lower than calculated co-ion exclusion [8–12]. The local spatial variations increase with the volume fraction of water in the membrane. Membranes with a low water sorption therefore comply with the Donnan exclusion theory to a greater extent [8]. The co-ion concentration was found proportional to the external salt concentration with a power ranging from 1.2 to 1.5 [8,9], constituting an intermediate value between an ideal membrane (with a power of 2) and an uncharged membrane (with a power of 1).

The quantity of counter and co-ions in ion-exchange membranes has been widely studied in the literature [8,13–17]. For example, sorption of KCl and LiCl in three commercial available cation-exchange membranes was investigated by Nouri et al. over a concentration range from 0.1 to 3.0 M [15]. Diffusion coefficients

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of both counter and co-ions in cation-exchange membranes were determined. The authors found that the co-ion diffusion coefficient varied with the free water content of the membrane and is influenced by the internal interactions with the membrane. Geise et al. studied sorption of NaCl in sulfonated polymers and used the sorption data to develop a model predicting the overall salt uptake by the polymer [8]. Chakravarti studied the mobility and self-diffusion coefficient of the sulphate co-ion in a grafted cation-exchange membrane [16].

The permselectivity of an ion-exchange membrane is determined by the ratio of the transport of electrical charges by the counter-ions and the total electrical charges through the membrane [10]. A fast and simple method to determine the permselectivity is the determination of the membrane potential. In this case, the electrical potential difference is measured between two salt solutions with different concentrations and separated by a membrane. These measurements are conducted in absence of an electrical field; therefore, no concentration polarisation at the membrane-water interface occurs. Moreover, because water transport across the membrane is not taken into account, the measured permselectivity is referred to as the “apparent” permselectivity [18–20]. Furthermore, the co-ion flux varies with varying concentration. Therefore, this method yields a transport number which is an average of both salt concentrations [21]. The method is frequently used in the literature to determine transport and transference numbers of both counter and co-ions [22–28]. The transport number of an ion is the fraction of the current that is carried by the ion; the transference number indicates the number of moles transported per mole of electrons [10].

A second method to determine the transport number of counter and co-ion is the use of the Hittorf cell [17,29,30]. In a Hittorf cell a membrane is placed between two electrodes. The ion flux through the membrane is measured by the increase or decrease in ion concentration. The permselectivity obtained with this method is referred to as the “true” transport number [10]. Bruce et al. used a Hittorf cell to determine actual transference numbers in amorphous poly(ethylene oxide)-based polymer electrolyte containing lithium perchlorate at 393 K [29]. The transport numbers of mobile ions in phenol-sulphonic cation-exchange membranes have been studied by Meares et al. [31]. The authors found that the transport number of chloride co-ions was much larger if bivalent counter-ions are used instead of monovalent counter-ions.

The use of electro dialysis for the production of chemicals, e.g., by electro dialysis metathesis [32], is restricted by the poor product purity. This is caused by the limited permselectivity of ion-exchange membranes. A profound understanding of the co-ion fluxes in electro dialysis metathesis and conventional electro dialysis is necessary for the exploitation of this technology. Experiments are performed in a metathesis stack and a conventional electro dialysis stack to achieve similar experimental conditions (e.g., concentration polarisation, linear flow velocity, etc.) as in a stack used for the production of chemicals. To the best of the authors' knowledge, a comparison between the magnitude of the unwanted fluxes and the influence of the stack configurations was not made earlier. Therefore, this paper offers new insights in the origin of impurities in the electro dialysis process. The first aim of this paper is to investigate the co-ion fluxes in detail and to find an optimal working range for the production of chemicals. Therefore, the influence of different operating parameters such as the salt concentration and the current density on the co-ion fluxes in an electro dialysis metathesis configuration is studied. As a consequence of electroneutrality, ion fluxes in a stack depend on all fluxes occurring in a stack. In the second part of this study, the two setups in which the production of chemicals is possible are compared. The co-ion flux in a conventional electro dialysis setup is compared with the fluxes found in a metathesis setup.

## 2. Materials and methods

### 2.1. Electro dialysis equipment

All experiments were carried out with a PCCell ED 64-002 stack manufactured by PCCell GmbH, Heusweiler, Germany. Each membrane has an active surface area of 0.0064 m<sup>2</sup>; all membranes are separated by spacers with a thickness of 0.5 mm. Membranes and spacers were supplied by PCA (PolymerChemie Altmeier GmbH, Heusweiler, Germany). An overview of the characteristics of the membranes, which was provided by the manufacturer, is given in Table 1. The transport of co-ions is investigated in the PC-SA and the PC-SK membranes. The PC-SC membrane is only used to separate the stack configuration from the electrode rinsing solution. Between the experiments membranes are stored in a 0.25 M NaCl solution.

The experimental setup was described in detail elsewhere [33]. In brief, the setup consists of three vessels for two salt streams and the electrode rinsing solution. All experiments are carried out in batch mode. The flow rate of the two salt streams was 6 L h<sup>-1</sup> per compartment, the flow rate of the electrode rinsing solution was 150 L h<sup>-1</sup>. The flow rates correspond with a linear flow velocity of 4.2 · 10<sup>-2</sup> m s<sup>-1</sup> for the two salt stream and 5.2 · 10<sup>-1</sup> m s<sup>-1</sup> for the electrode rinsing solution. The effects of osmosis and electro-osmosis were taken into account by measuring the change in volume height in the cylindrical vessels. During each experiment a constant current density is applied to achieve desalination. The current was set by using a DC adjustable power source (Delta Elektronika ES030-10, Zierikzee, The Netherlands).

### 2.2. Electro dialysis metathesis experiments

#### 2.2.1. Stack configuration

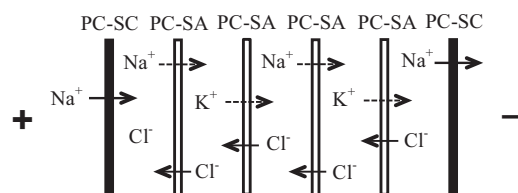
Fig. 1 shows the cell configuration used to determine the flux of co-ions through ion-exchange membranes. This figure specifies the configuration to test the permselectivity of anion-exchange membranes for cations. The permselectivity of cation-exchange membranes is tested in an analogous configuration where the anion-exchange membranes are replaced by cation-exchange membranes. For the investigation of anion-exchange membranes,

**Table 1**

Overview of the characteristics of PCA membranes, namely standard anion-exchange membranes (PC-SA), standard cation-exchange (PC-SK) and reinforced cation-exchange membranes (PC-SC).

Membrane	PC-SA	PC-SK	PC-SC
Thickness [μm]	90–130	90–130	90–130
Ion-exchange capacity [mequiv g <sup>-1</sup> ]			
Weak	ca 0.4	ca 1.2	ca 1.1
Strong	ca 1.1		
Chemical stability (pH)	0–9	0–9	0–12
Permselectivity <sup>a</sup>	> 0.93	> 0.95	> 0.92

<sup>a</sup> Determined as the membrane potential between a 0.1 and 0.5 M KCl solution.



**Fig. 1.** Cell configuration to determine the permselectivity of anion-exchange membranes (PC-SC: reinforced cation membrane, PC-SA: standard anion-exchange membrane, full arrows: transport of counter-ions, dotted arrows: transport of co-ions).

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