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Kinetic modeling and selectivity of anion exchange in Donnan dialysis

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ABSTRACT

The objective of this work was to compare selective sorption and transport behavior of a Selemion AMV membrane for different anions with a theoretically derived kinetic model describing the Donnan dialysis (DD) process. This analysis resulted in a suggested relation for the diffusivity of small ions through “nanochannels” of ion exchange membranes. Mass transfer through boundary layers and membrane diffusion were modeled on the basis of the Nernst–Planck equation by introducing constant diffusivity ratios between the exchanging counter ions. To indentify the kinetic and selectivity coefficients, DD batch experiments with sodium nitrate, sulfate or dihydrogen phosphate as feed electrolytes and sodium chloride as receiver electrolyte were conducted. The derived kinetic model simulated the measured concentration changes very precisely after fitting three concentration-independent parameters and the concentration-dependent permeability coefficient. The selectivity sequence was found to be nitrate>sulfate>dihydrogen phosphate>chloride, while this sequence is strongly connected to activity in solution and in the membrane. This influence was very significant for sulfate, which resulted in higher removal efficiency than expected. Regarding diffusivity the identified sequence was nitrate>sulfate>chloride>dihydrogen phosphate. These results led to a correlation that describes diffusivity of counter ions through nanochannels as a function of hydrated cross section area and valence.

1. Introduction

Donnan dialysis (DD) utilizes the properties of ion exchange membranes (IEMs) to exchange counter ions (opposite charge like the IEM surface) between a receiver and feed solution. To maintain electroneutrality in both solutions, the depleted feed ions are replaced by driving ions from the receiver and vice versa. The feed ions are enriched in the receiver solution by a factor which depends on the salinity and volume ratio between receiver and feed. Theoretically, the equimolar electrolyte concentration of both solutions should remain constant but co-ion (same charge like the IEM surface) leakage can lead to a salination of the feed and osmotic water flow can dilute the receiver. DD is a promising process since it uses a spontaneous “reaction” which offers the opportunity to replace and enrich troublesome or valuable ions with very low energy demand since no external driving forces are required except for feed and receiver pumping. However, the costs for IEMs are high (US $300–500 per m² in 2010) [1] which generates the necessity for a process optimization and a precise prediction of required membrane area.

Experimental investigations in the field of DD were presented in several studies. Especially those of Wisniewski et al. are relevant in the following. They conducted several studies aiming at the exchange of troublesome ions like nitrate, sulfate and bicarbonate [2–4], with emphasis on removing these troublesome ions prior to an electrodialytic desalination process. They observed a good removal of ions in single and multi component feed solutions and significant differences in co-ion leakage and counter ion flux for different IEMs. The latter observation was referred to differences in water content and porosity of the analyzed membranes. Recent work by Długołęcki et al. revealed that the electrical resistance of IEMs depends on the electrolyte concentration in solution, especially at low solution concentrations below 100 eq/m³ [5].

The DD exchange process can be theoretically simulated by combining the Navier–Stokes, Nernst–Planck and Poisson equation [6]. Although the results seem to be in good accordance with real behavior the numerical effort is immense and empirical determination of values like surface potential and mean pore diameter –which are usually not provided by the IEM manufacturer– is still required. A semi-empirical model can reduce the complexity by combining experimentally-calculated kinetic and selectivity coefficients with an electro kinetic model. Usually, the Nernst–Planck equation (NPE) is used to derive the functional dependency between concentration and exchange rate, like it was done in the following examples. Ho et al. studied the exchange behavior of sodium and hydronium ions by deriving a model which considers an unsteady state at the beginning of batch experiments due to saturation of the IEM with counter ions [7,8]. To reduce the numerical effort, Ho et al. assumed a constant diffusivity ratio between exchanging counter ions, calculated by using

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the respective diffusion coefficients in dilute aqueous solution. A significant increase of diffusion and mass transfer rate with rising feed ion concentration was observed. This connection between concentration and diffusivity was also observed by Miyoshi et al. They found that the diffusion coefficient is strongly affected by the counter ion concentration but scarcely affected by the co-ion species [9]. Their study, focused on the behavior of feed and driving ions of different valence, led to the result that monovalent driving ions are generating higher fluxes [10]. Preceding studies with Hasson et al., on modeling phosphate removal by assuming equal diffusion coefficients for both counter ions, led to a simple and applicable model which combines mass transfer through boundary layers on the IEM and diffusion resistance through the IEM within one equation [11].

The objective of the present study was to derive a kinetic model that considers different diffusivities and selectivities of involved counter ions for modeling the transport through the membrane and through boundary layers on the same. This was done with constant and concentration-independent parameters fitted with DD experiments. Two different diffusivity ratios were used, one for the transport through the boundary layer on the feed side and the other for the diffusion through the IEM matrix. Former were calculated using respective diffusion coefficients in dilute aqueous solution while latter were fitted with experimental DD data. The selective sorption process onto the IEM matrix was theoretically analyzed and selectivity was identified to depend on the total electrolyte concentration and ion activity in solution and in the membrane. The influence of ion activity and selectivity was determined experimentally and combined within an “effective separation factor”. The presented numerical fitting procedure allows identifying the following four important parameters by conducting simple bi-ionic DD batch experiments: mass transfer coefficients, effective separation factors, diffusivity ratios and permeability coefficients of analyzed counter ions. The main novelties of the present study can be manifested in three points:

1) Derivation of a mass transfer equation which can model counter ion exchange through boundary layers on the membrane.
2) Consideration of ion activity differences between feed and receiver phase as a parameter which influences the removal efficiencies in DD.
3) Identification of diffusivity ratios between involved counter ions as a method to understand transport processes through IEMs.

2. Theory

With the following theoretical approach it was intended to enable a clearer understanding of exchange processes through ion exchange membranes (IEM) by fitting four characteristic parameters on the basis of bi-ionic DD batch experiments. To model the DD process it is necessary to account for three different mechanisms. The exchange of counter ions is initiated in the respective bulk solution. The ions have to be transported from the bulk to the surface of the membrane which constitutes the first resistance; the mass transfer resistance. Prior to the transport through the membrane, the counter ions are adsorbed onto the IEM polymer structure and the resulting surface concentration depends on selectivities and concentrations in solution. Subsequent transport through the membrane constitutes the main – diffusive – transport resistance, before the ions are again desorbed and convectively transported to the opposite bulk solution. To simplify the modeling of DD, equimolar fractions (Eq. 1) were introduced, since electrokinetic transport and sorption processes in ion exchange materials rather depend on the regarded ion fraction than ion concentration [12]. They comprise the molar concentration of respective counter ion $c_i[\mathrm{mol}/m^3]$ with the valence z_i referred to the overall equimolar electrolyte concentration represented by the constant equimolar co-ion concentration $c_+[\mathrm{eq}/m^3]$.

$$X_i = \frac{c_i z_i}{c_+} \tag{1}$$

Electroneutrality conditions are summarized in Eq. (2). Electroneutrality appears in three different aspects. The first is the simple and well known additive variant (*left*), the second considers electroneutrality in the development of ionic fraction gradients (*middle*) and the third considers the fact that no net current flux can arise since no external electrical field is applied (*right*).

$$1 = \sum_i X_i \quad 0 = \sum_i \frac{dX_i}{dx} \quad 0 = \sum_i z_i \times J_i \tag{2}$$

The mass balance equation (Eq. 3) refers to a batch system with a concentration change solely attributed to the flux $J_i^{F/R}$ of the exchanging counter ions. The initial equilibration of the IEM with the surrounding solution is neglected since this saturation process is rather fast compared to the overall duration of the ion exchange between feed (F) and receiver (R) solution. The dependence between flux and concentration of respective counter ion is not linear and will be calculated numerically by combining the different transport processes described in the following. $V^{F/R}$ is the solution volume and A^m the IEM area, while the superscript m denotes properties of the membrane.

$$\frac{d(c_i^{F/R}\, V^{F/R})}{dt} = A^m \times J_i^{F/R}\,(c_i^F, c_i^R) \tag{3}$$

2.1. Membrane kinetics

The derivation of membrane kinetics is similar to other approaches [7–10,13]. They all base on the simplified Nernst–Planck equation (NPE) (Eq. 4) with D_i^m as membrane diffusion coefficient and c_A^m as counter ion concentration in the membrane. F is the Faraday constant, R_g the universal gas constant and T the absolute temperature. The simplifications of the general NPE are the negligence of pressure gradient, activity gradient and convective transport. Although these neglected terms may be present in DD (e.g. convective osmotic water flow and osmotic pressure difference), they are commonly disregarded because they are considered to be of minor importance in the calculation of the flux. Additionally, their negligence heavily simplifies the derivation of membrane kinetics and enables to model the kinetic behavior with an analytically derived equation. Hence, these simplifications will be also used in the following, while the negligence of activity gradients in the derived transport equation will be compensated by considering activity differences in the derivation of thermodynamic sorption equilibria (see Section 2.3).

$$\mathrm{J_i} = -D_i^m \left(\frac{dc_A^m}{dx} - c_A^m \frac{z_i F}{R_g T} \frac{d\varphi}{dx} \right) \tag{4}$$

Rearranging and combining Eq. (4) for feed and driving ion with the same electrical potential gradient for both ions lead to following flux equation after introducing the electroneutrality conditions:

$$J_A = -\frac{dc_A^m}{dx} \frac{\left[D_A^m D_{\mathrm{Cl}}^m (z_A^2 c_A^m + c_{\mathrm{Cl}}^m)\right]}{z_A^2 D_A^m c_A^m + D_{\mathrm{Cl}}^m c_{\mathrm{Cl}}^m} \tag{5}$$

As one can see in Eq. (5), the diffusion coefficient of respective counter ion is multiplied with its concentration in the membrane. This leads to a coupling effect of diffusivity and concentration in the membrane and represents the non linear part of Eq. (5), distinguishing this bi-ionic transport equation from the common Fick's law of diffusion. Nevertheless, it is shown in this and in other studies [5,7–11] that an additional dependence between