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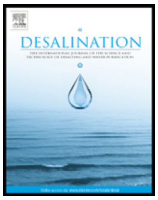

Transport coefficients in desalting processes by electrodialysis

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ABSTRACT

In this work a thermodynamic analysis on the transport equations in the processes of electrodiffusion (EF) and electrodialysis (ED) has been developed. The transport equations are classified in two sets according to the information they contain: *i*) fundamental and *ii*) complementary. We determine that there are four fundamental transport coefficients needed to characterize these membrane systems. We also conclude that this number is not reduced to three when the Onsager reciprocal relation (ORR) is assumed. I have also obtained a new expression for the concentration rate in EF and ED processes from the mass and volume balance. This relation provides a new way for evaluating the apparent transport number. This procedure has been applied to two membrane systems using data published in the literature.

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1. Introduction

One of the techniques used for desalting sea water is the electrodialysis (ED). An elemental ED stack is constituted by two ion-exchange membranes, one cationic and the other anionic, which separate three compartments filled with electrolyte solutions. The concentration of the central solution is reduced when an electric current is applied in the correct direction. These processes are characterized by transport equations with four coefficients [1].

The processes in an ED stack are a consequence of the constituents transport through the two membranes [2,3]. From the mass and volume balance we can relate the ED coefficients with those of electrodiffusion in membranes (EF). Since there are diverse EF formulations [4,5], there are also different ways of relating the coefficients of these two processes. A widely accepted EF formulation postulates the transport equations from the dissipation function [6].

In this paper I propose phenomenological transport equations for membrane processes without deriving them from the dissipation function [5,7]. The first step is to choose a set of independent fluxes and forces which characterizes the non-equilibrium states of the system. I postulate that any flux or force is linearly related to these independent quantities. The transport equations and the coefficients are classified as fundamental or complementary, according to the value of the information they provide. Finally, I deduce the relationships among the four overall ED coefficients and the four EF fundamental coefficients.

This approach has been satisfactorily used in the description of: *i*) electrodiffusion in bulk solutions [7], and *ii*) electrodiffusion in membranes [5]. These previous works have highlighted several advantages of this approach. The electric current characterizes better the electric equilibrium than the electric potential [5,7]. New relations between the fluxes and the observable quantities have been obtained from the mass and volume balance and it has been shown that these relations improve the results up to 25% in certain cases [5]. The solvent and ionic fluxes in bulk solution electrodiffusion are not independent quantities [7].

I study also the Onsager reciprocal relation (ORR). This one is proposed by the Statistical Mechanics for transport equations derived from dissipation function. In this paper I study the way in which the new EF approach is affected by the ORR. I discuss also the real meaning of the reduction in the number of independent transport coefficients due to the ORR.

2. Electrodiffusion in membranes (EF)

In this section I select firstly two observable quantities to be use in the study of EF. Then a mass and volume balance relates these observables to the membrane fluxes. I discuss also the best set of independent variables to describe the non-equilibrium states. And finally I postulate the phenomenological equations where four independent coefficients characterize the membrane.

Consider a system of uniform temperature and pressure formed by a membrane that separates two compartments (I and II) containing solutions of the same binary electrolyte $A_{\nu_+}B_{\nu_-}$ (component 2). The electrolyte dissociates into ν_+ cations A^{z_+} and ν_- anions B^{z_-}, with $z_+\nu_+ + z_-\nu_- = 0$. Stirrers in both compartments keep the solute concentrations uniform. The quantity $\Delta c_2 = c_2^{II} - c_2^{I}$ can be measured. An electric current I is driven through the solution by working electrodes B/B^{z_-}, where the electrode reaction $B^{z_-} \rightleftarrows B + |z_-|e^-$ is developed. Two horizontal capillaries at the same level ensure negligible pressure difference between the compartments. Fig. 1 shows a sketch of this cell.

The molar fluxes through the membrane of solvent (component 1) J_1 and cation J_+ can be evaluated from the values measured in two

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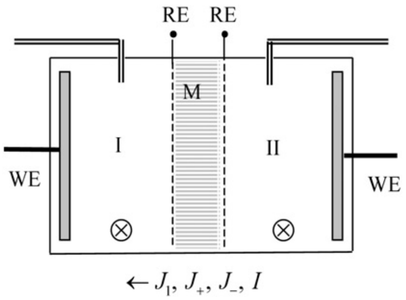

Fig. 1. Sketch of the cell: M: membrane; WE: working electrodes; RE: reversible electrodes; ⊗: stirrers; J_1, J_+, J_-: fluxes of solvent, cation, and anion, respectively; I: electric current; I, II: compartments.

observable quantities. These are the apparent volume flow rate that exits compartment I through the capillary $\mathrm{d}V^c/\mathrm{d}t$ and the electrolyte concentration rate $\mathrm{d}c_2/\mathrm{d}t$ in the same compartment. I consider as compartment I that in which a positive volume rate is measured, *i.e.* $\mathrm{d}V^c/\mathrm{d}t > 0$. In order to simplify the notation I have suppressed the superindex I. The fluxes J_1 and J_+ are defined as positive from compartment II to I.

In the control volume delimited by the walls, the membrane and the capillary, the mass balance is

$$\frac{\mathrm{d}n_1}{\mathrm{d}t} = J_1 - c_1\frac{\mathrm{d}V^c}{\mathrm{d}t} \tag{1}$$

$$\frac{\mathrm{d}n_+}{\mathrm{d}t} = J_+ - \nu_+ c_2\frac{\mathrm{d}V^c}{\mathrm{d}t} \tag{2}$$

where n_1 and n_+ are the amounts of solvent and cation, respectively.

The volume of the solution V^s inside this control volume changes due to the electrode reaction. This one proceeds at a rate $\mathrm{d}\xi/\mathrm{d}t = I/z_-F$ and therefore

$$\frac{\mathrm{d}V^s}{\mathrm{d}t} = -\frac{\bar{v}_B I}{z_- F} \tag{3}$$

where $\bar{v}_B$ is the partial molar volume of species B at the electrode and F is Faraday's constant.

Since $n_1 = c_1V^s$, $n_+ = \nu_+c_2V^s$, and $\bar{v}_1\,(\mathrm{d}c_1/\mathrm{d}t) + \bar{v}_2\,(\mathrm{d}c_2/\mathrm{d}t) = 0$, where $\bar{v}_i$ is the partial molar volume of constituents $i = 1,2$, Eqs. (1)–(3) lead to

$$J_1 = c_1\frac{\mathrm{d}V^c}{\mathrm{d}t} - V^s\frac{\bar{v}_2}{\bar{v}_1}\frac{\mathrm{d}c_2}{\mathrm{d}t} - c_1\frac{\bar{v}_B I}{z_- F} \tag{4}$$

$$\frac{J_+}{\nu_+} = c_2\frac{\mathrm{d}V^c}{\mathrm{d}t} + V^s\frac{\mathrm{d}c_2}{\mathrm{d}t} - c_2\frac{\bar{v}_B I}{z_- F} \tag{5}$$

which provide the fluxes J_1 and J_+ from the apparent volume flow rate $\mathrm{d}V^c/\mathrm{d}t$, the concentration rate $\mathrm{d}c_2/\mathrm{d}t$, and the electric current I.

In this system we found several typical quantities of non-equilibrium states. Among them I can mention: the fluxes through the membrane of solvent J_1, of cation J_+, of anion J_-, of electric current I, etc. And the differences in concentrations Δc_1, Δc_2, in chemical potentials $\Delta\mu_1$, $\Delta\mu_2$, in electrochemical potentials $\Delta\tilde{\mu}_+$, $\Delta\tilde{\mu}_-$, in observable electrical potentials $\Delta\psi_+$, $\Delta\psi_-$ [5,8], etc. I consider these differences as $\Delta X_i \equiv X_i^{II} - X_i^{I}$. The first ones are usually called thermodynamic fluxes and the latter thermodynamic forces. All these quantities vanish when the membrane system is at equilibrium. In order to analyze the irreversible processes, some of these fluxes and forces must be chosen as independent variables to characterize the non-equilibrium states. I select Δc_2 and I. Then I can postulate the following linear transport equations for the fluxes J_1 and J_+ [5]

$$J_1 = \frac{\tau_1}{F}I - AP_1\Delta c_2 \tag{6}$$

$$\frac{J_+}{\nu_+} = \frac{t_+}{\nu_+ z_+ F}I + AP_2\Delta c_2 \tag{7}$$

where A is the active membrane area, P_1 is the permeability of the membrane to the solvent, P_2 is the permeability of the membrane to the electrolyte, τ_1 is the solvent transference number in the membrane, and t_+ is the cation transport number in the membrane [5]. And for the anion flux we have $J_-/\nu_- = (t_-/\nu_-z_-F)I + AP_2\Delta c_2$ with $t_+ + t_- = 1$.

Therefore the non-equilibrium state of this membrane system is characterized by the four following fundamental properties: *i*) mechanical equilibrium $\Delta p = 0$; *ii*) thermal equilibrium $\Delta T = 0$; *iii*) non-equilibrium in matter distribution expressed by the value of Δc_2; and *iv*) electric non-equilibrium given by I. When $\Delta c_2 = 0$ we have a process of "pure" electric conduction. And when $I = 0$ we have a solute–solvent diffusion process. In this last case the solute flux is given by $J_2 \equiv J_+/\nu_+$.

From the observable quantities $\mathrm{d}V^c/\mathrm{d}t$ and $\mathrm{d}c_2/\mathrm{d}t$ the four coefficients P_1, P_2, τ_1 and t_+ can be determined. And vice versa, from the values of the four coefficients P_1, P_2, τ_1 and t_+, and Eqs. (4)–(7), the two observable quantities

$$\frac{\mathrm{d}c_2}{\mathrm{d}t} = \frac{\bar{v}_1}{V^s}\left[A(c_1P_2 + c_2P_1)\Delta c_2 + \left(\frac{c_1t_+}{\nu_+z_+} - c_2\tau_1\right)\frac{I}{F}\right] \tag{8}$$

$$\frac{\mathrm{d}V^c}{\mathrm{d}t} = A(\bar{v}_2P_2 - \bar{v}_1P_1)\Delta c_2 + \left(\bar{v}_1\tau_1 + \frac{\bar{v}_2t_+}{\nu_+z_+} + \frac{\bar{v}_B}{z_-}\right)\frac{I}{F} \tag{9}$$

can be determined for a process $(\Delta c_2, I)$. In Eq. (8) I can substitute $(c_1t_+/\nu_+z_+ - c_2\tau_1)$ for $(c_1/\nu_+z_+)t_+^1$ where t_+^1 is the apparent transport number $t_+^1 \equiv t_+ - (\nu_+z_+c_2/c_1)\tau_1$. I emphasize the significant role which plays the apparent transport number in the EF processes.

I consider $\mathrm{d}V^c/\mathrm{d}t$ and $\mathrm{d}c_2/\mathrm{d}t$ as the fundamental observables of the process $(\Delta c_2, I)$, because they express the evolution of the membrane system, and from their values we can determine the matter flux through the membrane [see Eqs. (4), (5)]. But there are other observables which provide complementary information. Among these ones I emphasize the observable electric potential difference $\Delta\psi_-$, which is measured between the terminals of two reversible electrodes to the anions [5,8]. For this thermodynamic force I can also postulate a phenomenological equation

$$\Delta\psi_- = \alpha_-\Delta c_2 + RI \tag{10}$$

where α_- is a coefficient, and R is the electric resistance. The value of these two coefficients can be obtained from electric potential measurements $\alpha_- = (\Delta\psi_-)_{I=0}/\Delta c_2$ and $R = (\Delta\psi_-)_{\Delta c_2=0}/I$.

Then I can establish a classification of the coefficients in two kinds: *i*) fundamental, related with the fundamental observables, *e.g.* P_1, P_2, τ_1 and t_+; and *ii*) complementary, related with the complementary observables, *e.g.* α_- and R.

I discuss now whether the four coefficients P_1, P_2, τ_1 and t_+ are independent quantities. A doubt arises when we study the electrodiffusion processes in bulk solutions. I consider fluxes in the x direction. The processes are described by the flux equations [7]

$$J_1 = \frac{\tau_1}{F}I + AD_1\frac{\mathrm{d}c_2}{\mathrm{d}x} \tag{11}$$

$$\frac{J_+}{\nu_+} = \frac{t_+}{\nu_+z_+F}I - AD_2\frac{\mathrm{d}c_2}{\mathrm{d}x} \tag{12}$$

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