A boundary layer analysis for determination of the limiting current density in an electrodialysis desalination

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HIGHLIGHTS

- A novel boundary layer analysis is proposed for an electrodialysis desalination.
- Asymptotic similarity solutions were obtained for electrodialysers with and without spacers.
- A volume average theory was introduced for analyzing electrodialysers with spacers.
- The present analysis agrees well with the experimental data of limiting current density.
- The model can be used to design practical electrodialysers with spacers.

ARTICLE INFO

ABSTRACT

A general ion-transport equation has been derived eliminating the electrophoresis term from the set of Nernst-Planck equations for cations and anions, under the local electro-neutrality assumption. Boundary layer solutions were obtained for the two asymptotic cases of sufficiently short and long channels, respectively, when the electric current is applied uniformly across the channels. A local volume averaging theory for porous media was also introduced to describe the cases of electrodialysis stacks with spacers. The results obtained for both with and without spacers are compared against available experimental data. The predicted limiting current density and stack voltage based on the asymptotic solutions for sufficiently short channels agree well with those of measurements for both cases with and without spacers, revealing the validity of the present analysis based on the local electro-neutrality assumption. It has been clearly shown that the spacers work to delay possible depletion of the ions on the dilute side of the membrane, thus increasing the limiting current density.

1. Introduction

Electrodialysis, which exploits an electrochemical separation process, is a quite effective means to treat brackish water, since it is versatile with respect to avoiding possible scaling and fouling. It has been a common practice to use an electrodialyser for water desalination, so as to remove dissolved minerals such as salts from seawater, wastewater or brackish water e.g. [1,2,3,4]. The electrodialysis process has advantages over conventional distillation techniques and other membrane based processes such as those using reverse osmosis [5], since, in this electrodialysis process, small quantity of dissolved species are removed away from large quantity of feed water rather than removing the large quantity of water from the small quantity of feed water, as in reverse osmosis.

The electrodialyser uses ion-exchange membranes e.g. [1] to transfer ions from dilute to concentrate chambers under the influence of an applied electric potential difference. The ion-exchange membrane electrodialysis stack, as shown in Fig. 1, consists of two electrodes, namely, anode and cathode. Between these electrodes, a number of dilute and concentrate channels are positioned to transfer ions through the ion-exchange membranes.

A unit cell in the stack refers to as a pair of adjacent dilute and concentrate channels formed by an anion exchange membrane (A. E. M.) and a cation exchange membrane (C. E. M.). These two kinds of membranes are placed alternately under the applied electric field. As the ions transfer through the membranes, the dilute cell loses the ions while the adjacent concentrate cell collects them. Thus, the bulk ion concentration in the dilute cell decreases while the that in the concentrate cell increases as the feed water, supplied from below, flows upward to the exit.

A substantial number of researchers attacked the Nernst-Planck equation, to investigate the ion transport from the dilute channel to

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Nomenclature

c	ion concentration [mol/m³]
D_i	diffusion coefficients of cation ($i = 1$) and anion ($i = 2$) [m²/s]
D_e	effective diffusion coefficient $D_e = (1 - \frac{z_1}{z_2})/(\frac{1}{D_1} - \frac{z_1}{z_2}\frac{1}{D_2})$ [m²/s]
F	Faraday constant [96,485 C/mol]
i_j	current density vector, $i_j = (0, i, 0)$ [A/m²]
i_{lim}	limiting current density [A/m²]
L	channel length [m]
n	coordinate outward normal to the membrane surface $n + y = W/2$
R	gas constant [8.314 J/mol K]
T	temperature [K]
u_j	velocity vector [m/s]
u	velocity component in x direction [m/s]
v	velocity component in y direction [m/s]
W	channel width [m]
x	vertical coordinate [m]
y	transverse coordinate measured from the axis of symmetry [m]
z	valency of an ion [−]
Greek symbols	
δ	concentration boundary thickness [m]
ε	porosity [−]
ς	ratio of the concentrate compartment width to the dilute channel width compartment [−]
η	similarity variable [−]
ν	kinematic viscosity [m²/s]
ξ	empirical coefficient for mechanical dispersion [−]
ρ	density [kg/m³]
φ	voltage [V]
Subscript	
c	concentrate
d	dilute
e	effective
dis	dispersion
m	membrane
Others	
$\langle \phi \rangle$	Darcain average
$\langle \phi \rangle^f$	intrinsic volume average
$\overline{\phi}$	Bulk mean

concentrate channel through membranes e.g. [6,7,8]. Most of these investigations focus on one-directional ion transport across the channels and membranes. However, it is the role of thin concentration boundary
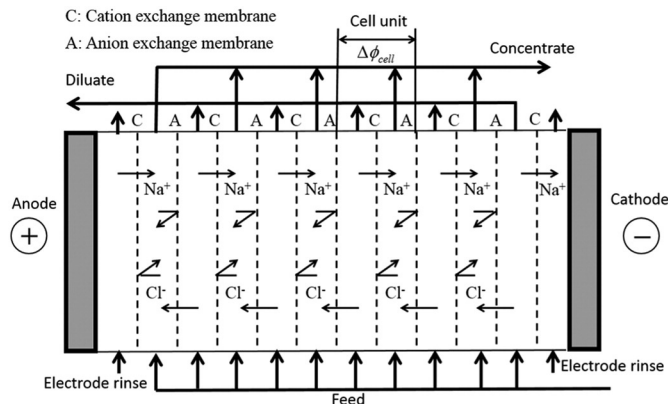

C: Cation exchange membrane
A: Anion exchange membrane

Fig. 1. Electrodialysis stack.

layer that determines the electrodialyser performance. Therefore, we must take full account of the boundary layer nature hidden in the Nernst-Planck equation.

In the dilute channel boundary layer, the ionic concentration deceases towards the C. E. M., whereas, in the concentrate channel, the ionic concentration, which is higher than that of the dilute channel, decreases away from the C. E. M., which is called "concentration polarization". A thinner boundary layer allows a steeper concentration at the membrane surfaces, thus, allowing a greater electric current to pass through the membrane. The electric current density that causes zero concentration on the ion exchange membranes as the result of excessive concentration polarization is termed as "limiting current density" e.g. [9,10]. This limiting current density is of great importance in practical applications, since, just under this limiting current density, the maximum ionic separation rate can be achieved in the electrodialyser without violating the electro-neutrality. When the limiting current density is exceeded, the electrical resistance in the dilute solution increases drastically due to the depletion of the ions within the boundary layer. The current above the limiting value is called "overlimiting current". Thus, any electrodialysis operations should be conducted below this limiting current to avoid water dissociation.

There are a number of theoretical and experimental investigations associated with ion concentration boundary layers, including those of Lee at al. [11] and Tanaka [12,13,14]. Tobias et al. [15] provides a review on diffusion and convection of ions in electrolysis and theoretical methods for predicting its diffusion layer. The ion film thickness was estimated for various cases appealing to mass, heat and momentum analogy and dimensional analysis. However, the boundary layer development in a multichannel system in electrodialysis has not been treated, perhaps, due to its complexity. Sonin and Probstein [16] proposed a hydrodynamic theory of desalination by electrodialysis. A classical integral method was used to obtain approximate solutions. An empirical matching formula for the limiting current density was introduced to cover a wide range of operating conditions.

Nevertheless, analytical boundary layer treatments based on the similarity transformations have not been reported in the literature. In this study, a general ion transport equation will be derived from the Nernst-Planck equation under the assumption of local electro-neutrality. The resulting ion transport equation is considered along with the prevailed velocity field. The classical boundary layer treatments established in viscous flows [17] are revisited to obtain possible similarity solutions for the two asymptotic cases of sufficiently short and long channels in the electrodialyser, when the electric current is applied uniformly across the channels.

A volume averaging theory will also be introduced for the first time to derive a volume averaged version of the Nernst-Planck equation, which is used to attack the case of electrodialysers with spacers [18]. It will be shown that the asymptotic solutions for sufficiently short channels agree well with that of measurement for both cases with and without spacers. This substantiates the validity of the present analysis based on the local electro-neutrality assumption.

2. General ion transport equation

The Nernst-Planck equation in a tensor form describing ion transport of species i in the solution runs as

$$\frac{\partial c_i}{\partial t} + u_j \frac{\partial c_i}{\partial x_j} = \frac{\partial}{\partial x_j}\left(D_i \frac{\partial c_i}{\partial x_j} + \frac{z_i F D_i c_i}{RT}\frac{\partial \varphi}{\partial x_j}\right) \tag{1}$$

where the species is either cation ($i = 1$) or anion ($i = 2$), such as Na⁺ or Cl⁻. The first term on the right hand side of Eq. (1) describes diffusion while the second term describes electrophoresis. D_i is the diffusion coefficient, φ, the voltage, $R(= 8.314$ J/mol K), gas constant, T, the temperature and $F(= 96,485$ C/mol), Faraday constant. z_i is the species charge