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Application of chronopotentiometry to determine the thickness of diffusion layer adjacent to an ion-exchange membrane under natural convection

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Abstract

A brief review of the evolution of the diffusion boundary layer (DBL) conception inspired by the works of Nernst, Levich and Amatore is presented. Experimental methods for studying the DBL in electrode and membrane systems are considered.

The electrochemical behaviour of a CM2 cation-exchange membrane in NaCl and KCl solutions is studied by chronopotentiometry at constant under-limiting current. Chronopotentiometric curves are described theoretically by applying the Kedem–Katchalsky equations in differential form to a three-layer system including the membrane and two adjoining DBLs. The conductance coefficients entering the equations are found by treating the results of membrane characterisation: the electrical conductivity, transport numbers of ions and water, electrolyte uptake, as functions of the equilibrium electrolyte solution. The two-phase microheterogeneous model is used for this treatment resulting in presentation of the conductance coefficients as functions of (virtual) electrolyte solution concentration in the membrane.

The steady-state DBL thickness (δ) is found by fitting experimental potential drop at sufficiently high times. It is found that δ is proportional to $(\Delta c)^{-0.2}$, where Δc is the difference between the electrolyte concentration in the solution bulk and at the interface. This result differs from the Levich equation, which gives the power equal to -0.25 for Δc. This deviation is explained by the fact that the theory of Levich does not take into account microscopic chaotic convection motion recently described by Amatore et al.

It is shown that the treatment of experimental chronopotentiometric curves with the model developed allows one to observe the role of streaming potential in the membrane. Different mechanisms of streaming potential and their effect on the shape of chronopotentiograms are discussed.

A simple analytical solution of Navier–Stokes equations applied to natural convection near an infinite vertical ion-exchange membrane is found. It is shown that the formation of DBL induced by electric current is quasi-stationary. This fact allows the empirical expression found earlier and linking δ with Δc under steady-state conditions to be used in transient regimes. The numerical solution of the non-stationary Kedem–Katchalsky equations together with this empirical expression results in quantitative description of the potential difference (pd) and δ as functions of time in chronopotentiometric experiments. The comparison of theoretical and experimental chronopotentiometric curves shows an excellent agreement, especially for the part after switching off the current. The reasons of a small deviation observed just before the curves attain steady state under a constant current applied are discussed.

Keywords: Ion-exchange membranes; Transport properties; Mathematical modelling; Concentration polarisation; Diffusion boundary layer

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1. Introduction

The diffusion boundary layer (DBL) arising at an electrode or an ion-exchange membrane affects significantly the mass transfer in electrochemical systems. There is a great interest in literature as regards the determination of DBL parameters and the development of the real meaning of this concept [1–19]. Following Nernst's approximation, the mass transfer within the diffusion layer (of thickness $\delta=\delta_N$) is controlled by diffusion, the convection here is negligible, which gives a concentration profile constituted of two straight lines (Fig. 1a).

Levich [1], improving Nernst's idea, has shown that taking into account the convective transport (induced by natural or forced convection) together with the diffusion near a conductive wall (e.g. an electrode) results in a smooth monotone concentration profile asymptotically approaching the value c_0 in the

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List of symbols

Abbreviations

DBL	diffusion boundary layer
pd	potential drop

Symbols

$a_\pm$	molar activity
c	molar electrolyte concentration
c_i	concentration of ion *i* in the solution
c_0	electrolyte concentration in the solution bulk
c_i^*	concentration of ion *i* related to a membrane unit volume
$c_s^{\mathrm{I}},c_s^{\mathrm{II}}$	electrolyte concentrations at the left-hand and right-hand membrane surfaces
D_0	diffusion coefficient at infinite dilution
f_1,f_2	volume fraction of gel and intergel regions in the membrane
F	Faraday constant
g	activity factor, Eq. (4); gravitational acceleration, Eq. (32)
i	current density
J_i	ionic flux density
J_v	volume flux density
K_D	Donnan constant
L_b	thickness of the space between a measuring electrode and the outer edge of DBL
L_e	distance between the measuring electrodes
L_p^*	membrane hydraulic permeability
p	pressure
P^*	membrane diffusion permeability
$\underline{Q}$	concentration of functional groups in the membrane (membrane exchange capacity, mequiv./cm^3 of wet membrane)
$\bar{Q}$	concentration of functional groups in the membrane gel regions (mequiv./cm^3 of gel)
R	universal gas constant
$Sc=\nu/D$	Schmidt number
t	time
t_{rel}	relaxation time needed to attain a steady-state velocity
t_+	counter-ion transport number
$t_{+\mathrm{app}}$	apparent counter-ion transport number
t_i^*	transport number of ion *i* in the membrane
t_w^*	water transport number
T	absolute temperature
T_{i}	effective transport number of ion *i* in the membrane (Eq. (17))
$U=\lvert\Delta\varphi\rvert$	absolute value of pd between two measuring electrodes
$V,\bar{V}$	velocity, average velocity
$\bar{V}_{\mathrm{s}}$	partial molal volume of electrolyte
$\bar{V}_{\mathrm{w}}$	partial molal volume of water
$y_\pm$	molar activity coefficient
Z	membrane (electrode) height

Greek symbols

β^*	electroosmotic permeability
δ	Nernst's diffusion layer thickness
δ_{cur}	thickness of the DBL related to current density *i*
δ_{lim}	thickness of the DBL related to the limiting current density i_{lim}.
κ	electric conductivity, S m^{-1}
λ	solution equivalent conductivity, cm^2 S mol^{-1}
ν	solution viscosity
σ^*	Staverman reflection coefficient
φ	electric potential
$\Delta\varphi_{\mathrm{Ohm}}$	ohmic potential drop