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Competition between diffusion and electroconvection at an ion-selective surface in intensive current regimes

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ABSTRACT

Considering diffusion near a solid surface and simplifying the shape of concentration profile in diffusion-dominated layer allowed Nernst and Brunner to propose their famous equation for calculating the solute diffusion flux. Intensive (overlimiting) currents generate electroconvection (EC), which is a recently discovered interfacial phenomenon produced by the action of an external electric field on the electric space charge formed near an ion-selective interface. EC microscale vortices effectively mix the depleted solution layer that allows the reduction of diffusion transport limitations. Enhancement of ion transport by EC is important in membrane separation, nano-microfluidics, analytical chemistry, electrode kinetics and some other fields. This paper presents a review of the actual understanding of the transport mechanisms in intensive current regimes, where the role of diffusion declines in the profit of EC. We analyse recent publications devoted to explore the properties of different zones of the diffusion layer. Visualization of concentration profile and fluid current lines are considered as well as mathematical modelling of the overlimiting transfer.

1. Introduction

1.1. Overlimiting transport: role of electroconvection

For a long time, the use of intensive current regimes in electromembrane processes was avoided, as it was believed that the overlimiting current is mainly due to water splitting [1], which reduces current efficiency and produces undesirable pH changes in solutions [2,3].

The study of Frilette [4] and relatively recent researches [5–8] have shown that in intensive current regimes not only the total current density surpasses the limiting current density, $i_{\lim}$, but also the partial current density of salt counterion is higher than $i_{\lim}$. The use of currents $i > i_{\lim}$ allows to overcome diffusion transport limitations [9], to diminish the membrane area, and thus to decrease the water desalination costs [10]. Now it is proven experimentally and via simulation that the enhancement of mass transfer at overlimiting currents is due to current-induced convection, namely, gravitational convection and electroconvection [11–14].

The understanding of the mechanism of mass transfer increase demands knowledge of concentration distribution near an ion-exchange membrane (IEM). The effect of gravitational convection on the concentration distribution in diffusion layer was studied by Levich [15], Amatore et al. [16–18] and other authors [19–22]. In this study, we will focus on the effect of electroconvection (EC), which is especially important in dilute solutions where the rate of electrodialysis (ED) is low [9] and gravitational convection is negligible [5,23]. This effect is relevant in a great number of applications, such as electromembrane desalination and separation [24–27], analytical chemistry [28–30] micro/nanofluidic [31–37] systems including pores with charged walls [38–40] and electrode [41] devices.

EC generally occurs as current-induced volume transport when an electric field is imposed through the charged solution [20]. At overlimiting currents, an extended space charge region (**SCR**) [42] (up to few microns of thickness [6]) forms at the depleted membrane surface causing electroosmosis (EO) of the second kind [11,43]. This kind of EC effectively enhances mass transport near the depleted interface. At a sufficiently high voltage, unstable vortices mix depleted solutions [44]. When the membrane surface is duly designed, the current density can surpass several times the $i_{\lim}$ value [12,13].

While the effect of forced convection and natural gravitational convection on the diffusion layer structure is studied relatively systematically [15,16,19,22], there are only few papers devoted to the role of EC. EC vortices were visualized using different techniques [7,26, 45–51]; the effective diffusion layer thickness was found as a function

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of current density by treating experimental voltamperograms [6,52], chronopotentiograms [52] and electrochemical impedance spectroscopy [53]. Significant progress in understanding of membrane behaviour in EC conditions was recently achieved due to developing of 2D first principles models based on the coupled Nernst–Planck–Poisson–Navier–Stokes (NPP-NS) equations [7,26,54,55,56,57,58,59,60,61,62,63]. These models allow computation of concentration and electric field in overlimiting current regime, analysis of the EC modes, the role of surface properties and others [7,26,54–56,58,63].

Experimental verification of the results of computations according to the 2D model was carried out in Refs. [7,26,45,55]. Analysis of the mechanism of EC, driven by surface conduction or electroosmotic flow, was recently made by using experimental data by Nam et al. [64].

As for the interpretation of the enhancement of mass transfer by current-induced convection, many researchers agree that the diffusion layer can be partially destroyed by the EC vortices occurring at the depleted membrane surface [7,44,45,61,65,66]. It was found experimentally [7] and via simulation [9,26,55,58,61] that EC mixing near the surface results in formation of a depletion zone where the concentration profile is unstable: the time-average profile becomes more and more flat with increasing voltage [7,58], while the concentration gradient oscillates with time and periodically changes its sign [45,49,55]. The effective diffusion layer outside of the depletion zone shrinks [7] allowing the increase of counterion flux at higher voltage [12]. Urtenov et al. [6] have evaluated the thickness of this layer as a function of voltage when considering it as fitting parameter in the Peers equation [67]. Rotating vortices perturb the concentration field at a distance essentially higher than their diameter. This leads to increasing the overall diffusion layer near the membrane [45,49]. EC vortices produce oscillations of concentration experimentally detected by laser interferometry [50] and other methods [7]. The concentration oscillations result in the oscillations of potential difference, when the current density is fixed. These potential oscillations are detected in voltamperograms [12,14,68,69] and chronopotentiograms [12,70,71].

The handling of overlimiting transfer needs better understanding of interfacial phenomena. In this paper, we focus on the structure of diffusion layer, which is examined experimentally and via mathematical modelling. We give accurate definitions of different zones of the diffusion layer and discuss transport mechanisms in these zones and their thickness as functions of the increasing current density.

2. Visualization of concentration profiles

The electrochemical response of electrode/membrane systems (chronopotentiometry, voltammetry, impedance) allows determination of interfacial concentration [72], the thickness of diffusion boundary layer [21,52] and even reconstruction of concentration profile, when a movable measuring electrode [73–75] or an appropriate mathematical model [21] is applied. However, these methods do not give a visual image of the concentration profile near an interface.

The use of fluorescence dyes (such as anionic Alexa Fluor 488 or cationic Rhodamine 6G) allows visualization of fluid flow and variation of salt concentration near ion-selective surfaces in different systems: beds of ion-permselective particles [76], micro-nanochannel structures [48,77], membrane systems [8] and capacitive deionization [78]. This technique is based on the fact that the electrophoretic mobility and concentration of fluorescent dyes are functions of (local) pH and ionic strength [8,79,80].

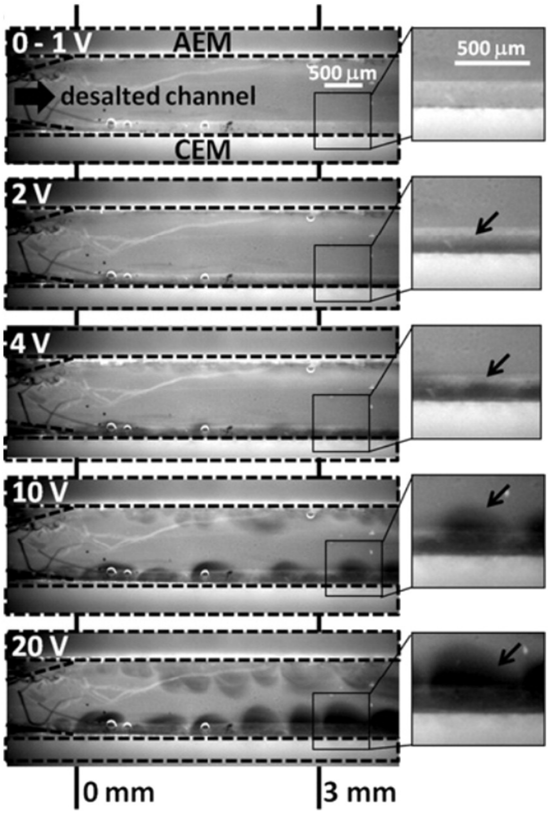

Fig. 1. Visualization of salt concentration distribution using Rhodamine 6G in the initial part of the desalination compartment of a microscale ED cell at 0, 2, 4, 10 and 20 V. Two lines indicate 0 and 3 mm from the inlet, respectively. Darker zones relate to depleted solution. Arrows in the magnified images show the diffusion boundary layer at the CEM. The monotone concentration distribution at 2 V is disturbed at higher voltages: circular depletion zones are well seen. The circular depletion zones near the AEM are visualized as well. A 10 mM NaCl solution flows from left to right with the flow rate of 10 µL/min. The figure is taken with permission from [8].

Fig. 1 shows patterns produced by Rhodamine 6G in an ED desalination channel obtained by Kwak et al. [8]. It can be seen that at low voltages (≤2 V), there is a net diffusion layer (DL) of the thickness about 200 µm near a cation-exchange membrane (CEM), where the salt concentration is lower (the shade of grey is darker). With increasing voltage, EC vortices appear within the DL near the CEM. They capture desalted solution from the interface and drag it towards the bulk. As a result, circular depletion zones occur and the DL thickness increases. At about 6 V, the size of vortices attains the same value as the DL thickness, and at higher voltages, vortices go beyond the DL [8]. The patterns produced by vortices at the anion-exchange membrane (AEM) are similar to those at the CEM, but the course of EC development is shifted by about 1 V. It is due to the fact that the mobility of the Cl^- ion, which is the counterion for the AEM, is 1.5 times higher than that of the Na^+ ion. As a result, the limiting current density at the AEM is also 1.5 times higher. Hence, when a current density equal to $i_{\lim Na+}$ flows across the ED cell, the limiting state occurs at the CEM, but not yet at the AEM.

Another technique of concentration visualization is the laser holographic interferometry, which is successively used for visualization of concentration profiles in ED [46,49,81,82] and pressure-driven processes [83,84]. Concentration profile is visualized as interference fringe patterns [45,85].

The cell used for visualization of concentration profiles by laser interferometry contains a central compartment with transparent walls allowing laser beam passage and fringe patterns video registration [45,49,50]. Fig. 2 shows schematically a cell in the case of ED with IEMs. In order to exclude gravitational convection, the membranes forming the central compartment are taken the same (two CEMs in the considered case, Fig. 2), and they are put in a horizontal position. Then the depleted (lighter) diffusion layer is below the upper membrane in the compartment under study, hence, on the top of the central compartment. The enriched (heavier) layer is at the bottom of the compartment. In these conditions, the buoyancy force does not occur. The number of compartments in the cell may be different, e.g. five ones as shown in Fig. 2. It is important that a CEM faces the cathode, and an AEM faces the anode in order to avoid the passage of the OH^- and H^+ ions, produced at the cathode and the anode, respectively, into the

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