



Short communication

Effect of electroconvection during pulsed electric field electro dialysis. Numerical experiments



Aminat M. Uzdenova^a, Anna V. Kovalenko^b, Mahamet K. Urtenov^b, Victor V. Nikonenko^{b,*}

^a Karachaevo-Cherkessky State University named after U.D. Aliev, Karachaevsk, Russia

^b Kuban State University, Stavropolskaya st. 149, 350040 Krasnodar, Russia

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ABSTRACT

One of the ways of improving electro dialysis (ED) and some microfluidic processes is the optimization of current regime. It is recognised now that the use of pulsed electric fields (PEF) in ED allows enhancement of mass transfer and mitigation of fouling. To explain these effects, Mishchuk et al. [1] suggested that due to inertial forces electroosmotic mixing can remain during the pause. By solving fully coupled Nernst–Planck–Poisson–Navier–Stokes equations, we compute the distribution of velocity, concentration and electric fields in an ED channel. We simulate the situation where electroconvective vortices occur or not in the pause, and show that the total vortex attenuation takes tenths of a second. However, inertial forces are effective only first 0.01 s, then the vortices are fed by the chemical energy of non-uniform concentration field, the relaxation time of which is several seconds. The remnant vortices contribute to earlier onset of electroconvection. However, more important is the formation of new vortices after voltage re-application. For the first time, we show that nonuniformity of concentration field produces an effect similar to the action of electrically or geometrically non-uniform surface. It causes formation of spatially non-uniform electric body force, which hastens electroconvection.

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1. Introduction

Electro dialysis is a separation process widely used in water treatment, juices and wine conditioning, recovery of valuable or harmful components from solutions and other [2]. Three main ways to improve this process are considered: improvement of (i) stack design and hydrodynamic conditions; (ii) membranes and ion-conducting fillers; and (iii) current mode. For a long time the use of intensive overlimiting currents has been avoided because of water splitting at membrane/solution interface. The latter leads to a loss in current efficiency and undesirable shift in pH causing in particular precipitation of metal hydroxides. However, recent research has shown that at severe ion concentration polarization where the current density essentially exceeds its so-called limiting value, convective fluid flows occur at ion-selective surface such as membranes [3,4], beads [5], nano-channels [6,7] or electrodes [8]. While gravitational convection may be important at relatively high concentrations (>0.1 M [9]), the main mechanism of the current-induced convection is electroosmosis [9–11]. Electroconvection is a phenomenon intensively studied now in connection with the improvement of not only membrane separation processes [12], but nano- and microfluidic devices as well [13–15]. Note also that water splitting [11], the loss of membrane selectivity and current induced membrane discharge [16] may contribute to overlimiting transfer.

The PEF mode especially applied in overlimiting current range seems a very promising way of developing electromembrane processes. The first application of PEF in ED was apparently made by Karlin and Kropotov [17] who have observed the variation in mass transfer rate when passing from steady state to transient regimes. Mishchuk et al. [1,18] have found that the rate of ED desalination can be higher in PEF mode than in steady state when applying the same average voltage. Similar results were obtained by other authors [19–21], who have found also antifouling and antiscaling effects of PEF. Recently, Malek et al. [22] have shown that the PEF effects are stronger at overlimiting current densities. Moreover, application of PEF helps to minimize water splitting and current efficiency losses. It becomes hence possible to operate at higher voltages while avoiding the problems related to pH changes [21–23].

In pioneer theoretical papers by Mishchuk et al. [1,18], electro-diffusion time scales in PEF mode were examined, and the advantages of the potentiostatic regime compared to the galvanostatic one were established. To explain higher effect of PEF mode in overlimiting current range, the authors [1,18] assumed that due to inertial properties, electroconvective vortices can be conserved in a pause between the pulses thus contributing to a more rapid restoration of concentration at the membrane surface. However, the theory [1,18] was limited by use of electroneutrality assumption and did not take into account electroconvection. In this paper we present the results of mathematical modelling using a recently developed 2D model involving the fully coupled Nernst–Planck–Poisson and Navier–Stokes equations [24].

* Corresponding author. Tel.: +7 8612199 573.

E-mail address: nikon@chem.kubsu.ru (V.V. Nikonenko).

2. Mathematical model

The model used here differs from the “basic” model described in [24] only by the boundary conditions at the inlet ($y = 0$):

$$\frac{\partial \varphi(x, 0, t)}{\partial y} = -\frac{RT}{F(z_1^2 D_1 + z_2^2 D_2)c_0} \left(z_1 D_1 \frac{\partial c_1(x, 0, t)}{\partial y} + z_2 D_2 \frac{\partial c_2(x, 0, t)}{\partial y} \right) \quad (1)$$

and at the outlet ($y = L$) of the desalination channel:

$$\left(\frac{\partial c_i}{\partial y} + z_i c_i \frac{\partial \varphi}{\partial y} \right) (x, L, t) = 0, \quad i = 1, 2 \quad (2)$$

Eq. (1) follows from the condition that the tangential current is set zero at $y = 0$. Eq. (2) shows that the sum of diffusion and migration tangential components of fluxes is zero at $y = L$ for cation ($i = 1$) and anion ($i = 2$). All the notations are the same as used in [24].

3. Results and discussion

The calculations are made for a desalination channel of length $L = 4$ mm, intermembrane space $H = 1$ mm, formed by an anion-exchange membrane (AEM) and a cation-exchange membrane (CEM) both assumed ideally permselective. A 0.01 mol m^{-3} NaCl solution enters the channel and flows between the membranes with an average velocity of $V_0 = 0.8 \text{ mm s}^{-1}$. The diffusion coefficients are taken as $D_1 = 1.33 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$, $D_2 = 2.05 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$. A potential difference $\Delta\varphi$ across the channel (involving both membranes, the space between them and two half-cells of the concentration compartment) is set as a known function of time. Then the distribution of cation and anion concentrations, potential, velocity and current density is calculated as functions of time. Note that only a diffusion layer (including the electrical double layer (EDL) on the membrane surface) was the subject of study in Refs [4,25].

The concentration used in computations is rather small compared to the concentrations used in ED practice. The first reason for this choice is that the electrokinetic effects are more pronounced in dilute solutions; the second one, the computational difficulties arise essentially with increasing concentration as EDL becomes thinner and a denser grid is needed. An analysis of the concentration effect on electroconvection is the subject of further work.

Fig. 1b shows the response of current density on variation of $\Delta\varphi$ (Fig. 1a) in our numerical experiments. Before $t_1 = 201$ s and after $t_2 = 201.5$ s, $\Delta\varphi$ is equal to -2 V; between t_1 and t_2 , $\Delta\varphi = 0$ V, hence, the pause duration is 0.5 s as in the experimental study [23]. In the pause, the current density changes its sign: the cell works as a source of electric current similarly as in reverse electro dialysis [26]. Just after setting $\Delta\varphi = 0$, there is a jump of the current (with negative sign), which is due to partial discharge of the space charge region (SCR). Then the current is stabilized; generally it tends to zero as the concentration gradients are vanishing. However, since this process is rather long (several minutes), it cannot be seen in Fig. 1b. After restarting $\Delta\varphi = -2$ V, there is a current surge, which is favoured by the decrease in resistance caused by concentration restoration. Then concentration polarization increases, and the current density declines. It is remarkable that the fast current decline lasts for a very short time, about 0.05 s. Then a little jump in current occurs, and the decline slows. 0.5 s after restarting voltage, the current density slightly grows and becomes higher than its steady-state value, i_{st} , before the pause. It attains i_{st} only 7 s after restarting voltage (not shown in Fig. 1b). Note that there is no real steady state: when $\Delta\varphi$ is maintained constant, the current density oscillates [24] due to electroconvection occurring in the Rubinstein–Zaltzman unstable mode [27]. The slow return to the state before the pulse is a type of hysteresis similar to that described by Pham et al. [25].

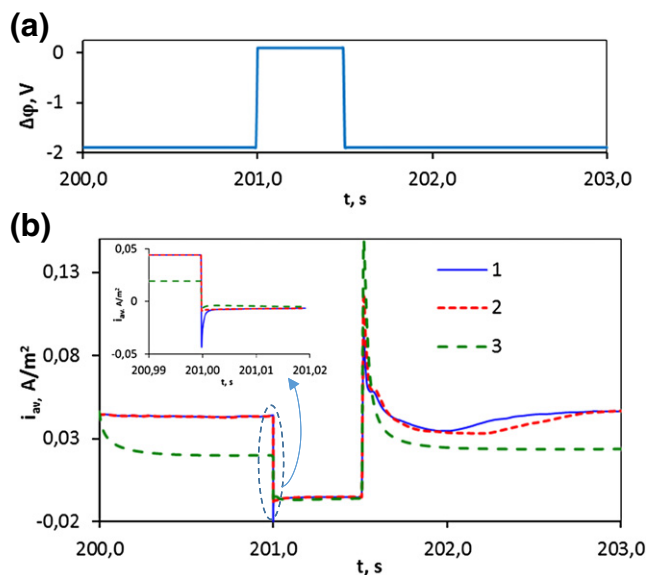


Fig. 1. (a) Pulse mode of electric potential; (b) response of the current density: 1—viscosity $\nu = 0.01 \text{ cm}^2 \text{ s}^{-1}$ for the entire time; 2— $\nu = 0.01 \text{ cm}^2 \text{ s}^{-1}$ for $t < t_1 = 201$ s and $t > t_2 = 201.5$ s, $\nu = 1.0 \text{ cm}^2 \text{ s}^{-1}$ for $t_1 \leq t \leq t_2$; and 3— $\nu = 1.0 \text{ cm}^2 \text{ s}^{-1}$ for the entire time. The insertion shows the response just after voltage cutoff.

Fluid flow and electric current streamlines as well as the concentration distribution are shown in Fig. 2. In the conditions used, the calculated limiting current density $i_{lim} = 0.0185 \text{ A m}^{-2}$. This value is in a good agreement with that calculated by the L ev eque equation [9].

At $\Delta\varphi = -2$ V, electroconvective vortices are developed at both membranes (Fig. 2a). They are stronger near the CEM, as in the case of NaCl i_{lim} at this membrane (0.0185 A m^{-2}) is about 1.5 times lower than that at the AEM (0.028 A m^{-2}). It can be seen that after setting $\Delta\varphi = 0$, the vortices do not decay immediately: after 0.01 s they are clearly seen near both membranes (Figs. 2b and 3a). Even after 0.5 s a small vortex of about $1 \mu\text{m}$ remains near the CEM (Fig. 3b).

In order to study the effect of remnant vortices on further development of electroconvection, we examine the case where within the pause the viscosity is set $1.0 \text{ cm}^2 \text{ s}^{-1}$, hence 100 times higher than its normal value, $0.01 \text{ cm}^2 \text{ s}^{-1}$. After re-applying voltage, the viscosity takes its normal value. Fig. 2c shows that really the increase in viscosity suppresses the vortices. However, it gives only a small effect on the concentration field: the remnant vortices are too small (Fig. 3) to enhance considerably mass transfer. The relaxation of concentration field (which is weak during 0.5 s of the pause, Fig. 2d and e) is mainly due to diffusion. The diffusion relaxation time, $t_{rel} = \delta^2/D$, for characteristic length $\delta = 100 \mu\text{m}$ of the concentration field heterogeneity is about 10 s.

After restarting voltage, the vortices reappear in 0.01 s near the CEM and in 0.4 s near the AEM. After 0.6 s they are well developed near the AEM in the case of normal viscosity (Fig. 2f) and not yet seen near this membrane if $\nu = 1.0 \text{ cm}^2 \text{ s}^{-1}$ within the pause (Fig. 2g). Namely the appearance of vortices near the AEM gives rise to the current density at $t = 202$ s (Fig. 1b).

The third calculation is made for an elevated viscosity ($\nu = 1.0 \text{ cm}^2 \text{ s}^{-1}$) during the entire time (line 3, Fig. 1). In this case no vortices are formed. In steady state $i = 0.020 \text{ A m}^{-2}$ that is slightly higher than $i_{lim} = 0.0185 \text{ A m}^{-2}$ given by the L ev eque equation. The deviation is due to reduction in the diffusion layer thickness produced by the extended SCR [28].

As Fig. 3c shows, the decay of the vortex after setting $\Delta\varphi = 0$ occurs initially rather fast. However, 0.02 s after the voltage cutoff, the vortex decay slows.

The relaxation time of vortex decay may be evaluated from the Navier–Stokes equation [29]: $t = \frac{\delta^2}{12\nu} \ln\left(1 - \frac{\nu}{\bar{V}}\right)$, where \bar{V} is the steady-

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