Intensification of electrodialysis by applying a non-stationary electric field

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Abstract

Electrodialysis is an effective method of water desalination. However, the efficiency of the method is limited by the concentration polarization of the ion-exchange membranes. Applying an electric field with special pulse characteristics can diminish the effect of the concentration polarization. A theoretical analysis is carried out for galvanostatic and potentiostatic pulse regimes. The time dependencies of the extent of the concentration polarization near the membrane surface during the pulse are described theoretically for both pulse regimes and a qualitative discussion of the pause duration is presented. The main characteristic of the non-stationary process is the transition time between the state without polarization and the state with stationary polarization. In principle, the electrodialysis process can be intensified significantly when the applied pulse is sufficiently smaller than this transition time. Experimental results are quoted that qualitatively support the model predictions. It is shown that the desalination can be intensified several times, depending on the pulse-pause characteristics. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

Electrodialysis as a method of demineralization of natural and wastewater is ecologically expedient and economically profitable. However, the use of ion-selective membranes is complicated by the phenomenon of concentration polarization, which is caused by a difference between the ion transfer numbers in the solution and in the membranes [1]. The effect is connected with a decrease of the electrolyte concentration in a thin layer near the membrane surface in the desalination cell, and it can be observed in the form of a retardation of the current growth when the applied voltage is increased. In the absence of thermal and hydrodynamic turbulence of the liquid flow, and of the
dissociation of water, the limiting current $i_{\text{lim}}$ can be expressed as follows [1–6]:

$$i_{\text{lim}} = \frac{2FD^+C_0}{L}$$ (1)

where $F$ is Faraday’s constant, $D^+$ is the diffusion coefficient of counterions (for example, cations), $C_0$ is the electrolyte concentration and $L$ is the thickness of the concentration polarization region, that is called the Nernst layer. The limiting value of the current is rather low, especially when electrolytes with millimolar and lower concentrations are used.

Mass transfer through a membrane, and therefore the electrodialyser capacity, are directly proportional to the current density in an electromembrane channel. Consequently the limiting current restricts an electrodialyser capacity. When the voltage drop over the membrane rises above the value providing the limiting current, unproductive expenditure of power takes place. Therefore, an investigation of the possibilities to increase the current density above the limiting value is important.

Traditional methods to prevent current saturation are based on extending the membrane surface and on promotion of turbulence in the electrodialyser channel. The latter can be achieved by means of membrane profiling [7, 8], turbulence promoters [9], conducting spacers [10] and air sparing [11]. However, all these methods are characterized by a common imperfection: due to viscous tension the velocity of liquid motion decreases sharply on approaching a solid surface. Therefore, these methods lead only to moderate increases in current density.

Investigations of polarization processes in stationary and non-stationary regimes [12–16] suggest that a non-stationary regime can lead to a weakening of concentration polarization and to an intensification of electrodialysis. One way to realize a non-stationary regime is to use pulses of current or voltage that alternate with pauses. This type of non-stationarity will be explored in detail in this paper.

For the analysis of the optimal conditions of a pulse regime it is important to consider both the pulse and the pause time. The characteristic time of a pulse has to be smaller than the transition time. This is the time required to build up the concentration polarization layer near a membrane. The pause duration has to be comparable with the duration of pulse in order to enable the concentration profiles to be restored to their initial state (without polarization). However, the pause should not to be too large, otherwise diffusion and osmotic processes through the membrane counteract the desalination.

The theoretical background of both stationary and non-stationary electrodialysis processes will be considered first in order to gain insight into the pulse and pause duration. In the second part of the paper the theoretical predictions will be compared with experimental results, obtained by electro-filtration and electrodialysis.

2. Theory

2.1. General considerations

The concentration polarization of a membrane will be investigated for an ideally selective membrane, for which the flux of coions through a membrane is completely absent. The treatment of the stationary regime of concentration polarization has been analyzed theoretically in Refs. [2–5]. That of the non-stationary concentration regime will be based on the Nernst model [17–20]. In the Nernst model a practically motionless layer of liquid, through which the ions diffuse to the surface, is situated near the electrode or membrane surface.

The concentration will be limited to low electrolyte concentrations ($C_0 < 10^{-2} \text{ mol l}^{-1}$) because at higher electrolyte concentrations, heat processes lead to thermoconvection and modification of the structure of the polarized layer [21].

Water dissociation that usually accompanies the electrodialysis at low electrolyte concentration [16, 21–26] can, however, be neglected because it decreases strongly when a pulse regime is applied.

The processes will be analyzed only at the side of a membrane where in a stationary regime the electrolyte concentration decreases. On this side the main potential drop occurs that limits the
electrodialysis capacity [2–6]. An exact description of the polarization processes is very complicated. It would be necessary to take into account: (1) the non-stationarity of Nernst layer in the desalination channel, (2) the non-stationarity in the concentration channel, (3) the concentration profiles inside the membrane, (4) the interfacial potential drop (Donnan potential) and (5) the polarization of the electrodes. For the moment it will be assumed that an analysis of the non-stationarity of the Nernst layer in the desalination channel is sufficient to obtain the correct order of magnitude of the time scale of the polarization processes.

2.2. Stationary regime

In order to be able to analyze qualitatively and quantitatively the differences between stationary and non-stationary concentration polarization, first the structure of the stationary Nernst layer and its characteristics in weak, moderate and strong electric fields will be discussed.

In Fig. 1, the structure of a stationary Nernst layer with thickness \( L \) is shown schematically for three values of the electric field. Switching on the electric field leads to a decrease of the electrolyte concentration, \( C(x) \), from the value \( C_0 \) in the bulk of the electrolyte solution to some value \( C(0) \) near the membrane surface (more exactly, on the external boundary of electrical double layer). At low values of the electric field, the value \( C(0) \) is essentially greater than zero and the concentration profiles of both ions of the 1-1 electrolyte coincide (Fig. 1, curves 1). Under this condition, the current increases linearly with the potential growth. This regime is usually called ‘sublimiting’.

When the value of \( C(0) \) is close to zero, both ion concentrations in the Nernst layer decrease linearly to zero (Fig. 1, curves 2) and the current density approximates its limiting value \( i_{\text{lim}} \). The electric field range corresponding with this situation is called the ‘limiting’ regime. For both the sublimiting and the limiting regime the electroneutrality behind the electrical double layer of the membrane is conserved.

Further growth of the electric field leads to the appearance of an extended region of low ion concentrations and to a deviation from the electroneutrality, because the concentration of counterions, \( C_+ \), is substantially higher than that of the coions, which is negligibly small (Fig. 1, curves 3). This range of the electric field is called ‘overlimiting’. The polarization processes in these strong electric fields have been analyzed for flat [2–6] and for curved [27,28] surfaces. It has been shown that the charge density or the counterion concentration \( C_+ \) and the thickness \( S_0 \) of the induced charge layer depend on the bulk electrolyte concentration, the current or the voltage and the thickness of the Nernst layer. The conductivity in this region is \( C_+/C_0 \) times lower than in the bulk solution (or inside this layer without concentration polarization). The thickness of the diffusion part of the Nernst layer \( \delta = L - S_0 \) decreases with the expansion of the induced space charge.

The term ‘overlimiting’ for this regime points towards to two different aspects. On the one hand it takes into account that the electrodialyser works in the regime where the limiting current is reached. So, a voltage is applied above a value that can lead to an increase of the current. This causes an excessive expenditure of power. On the
Fig. 2. The current in the stationary regime as a function of the potential drop across the Nernst layer for different magnitudes of the concentration polarization as expressed by the parameter \( \gamma = \kappa^{-1} / L \). Without concentration polarization (1); limiting current for \( \gamma \to 0 \) (2); overlimiting regime at \( \gamma = 10^{-4} \) (3); \( 10^{-3} \) (4); \( 10^{-2} \) (5).

The current value in the overlimiting regime is connected to the structure of the polarization region. When the diffusion layer is formed in weak or moderate electric fields (Fig. 1, curves 1 and 2), the current through the Nernst layer is given by diffusion flow and the nature of current leads to Eq. (1) for the limiting current. When the induced space charge appears, the nature of the current is more complicated. In the region of the induced space charge the counterion concentration is approximately constant and the current is provided by electromigration (almost without diffusion).

In the diffusion part of the Nernst layer, the current maintains its diffusion nature. Owing to the continuity of the ion flux, the current should have the same value in all sections of the channel and can be described as [27,28]

\[
i_{\text{st}} = \frac{2FD^+C_0}{\delta} = \frac{2FD^+C_0}{L - S_0} = \lim_{L - S_0} L
\]

or

\[
\tilde{i}_{\text{st}} = \lim_{\tilde{i}_{\text{lim}}} \frac{1}{\delta} = \frac{1}{1 - S_0}
\]

where \( \delta = \delta / L \), and \( \tilde{S}_0 = S_0 / L \). According to Eqs. (2a) and (2b) the current density is \( L / (L - S_0) \) times higher than the limiting one. For example, the concentration profiles shown by curves 3 in Fig. 1 correspond to the situation that \( \tilde{i}_{\text{st}} = \lim_{\tilde{i}_{\text{lim}}} = 2 \).

However, the current density cannot be much larger than \( \lim_{\tilde{i}_{\text{lim}}} \) because the decrease of the diffusion layer thickness is accompanied by a very strong growth of the potential drop over the region of the low electrolyte concentration. For example, the limiting current \( \tilde{i}_{\text{st}} = 1 \) can be reached by the voltage \( \phi \approx 0.25 \) V or \( \tilde{\phi} \approx 10 \), whereas the overlimiting value \( \tilde{i}_{\text{st}} = 2 \) for \( \gamma = 10^{-3} \) is realized at \( \phi \approx 10.5 \) V or \( \tilde{\phi} \approx 420 \).

In the hypothetical absence of the concentration polarization the current growth is proportional to the voltage and \( \tilde{i}_{\text{st}} = 2 \) can be reached by a voltage of only \( \phi \approx 0.5 \) V or \( \tilde{\phi} \approx 10 \). So, for \( \tilde{i}_{\text{st}} = 2 \) only 0.5 V (4.7% of 10.5 V) is used effectively. The situation changes for the worse with an increase of \( \tilde{i}_{\text{st}} \) and a decrease of \( \gamma \).
2.3. Non-stationary processes

The analytical expressions describing the situation in the stationary regime have been obtained after various simplifications [5]. For the analysis of a non-stationary regime, further simplifying assumptions have to be made.

After switching on an electric field, the electrolyte concentration near the membrane surface gradually decreases. In the sublimiting and limiting cases where the electroneutrality is conserved, the non-stationary process reduces to a solution of the diffusion problem in the Nernst layer, as will be shown below.

In the overlimiting case, directly after switching on an electric field, the electrolyte concentration near the membrane is accompanied by a violation of the electroneutrality and an induced space charge appears. In this case it is impossible to reduce the problem to a solution of the diffusion equation. To avoid this problem we restrict the present investigation to the very short time interval in which the region of induced space charge has not yet been formed. In this limiting case the problem reduces to solving the diffusion problem.

Although this seems a rather strong simplification, the present treatment will show that it is still a valuable theoretical exercise. Moreover, when the region of induced space charge is not formed, the potential drop within the polarization region is not very large and the unproductive expenditure of electric power is small. Therefore this regime is also interesting from a practical point of view.

In general, the ion fluxes \( j^\pm \) of either the cation (+) or the anion (-) in the non-stationary regime are connected with the changes of the cation and anion concentrations \( C^\pm \) by the continuity equations

\[
\text{div} \, j^\pm (x,t) = - \frac{\partial C^\pm (x,t)}{\partial t}
\]

with

\[
j^\pm (x,t) = - D^\pm \frac{\partial C^\pm (x,t)}{\partial x} \pm D^\pm C^\pm (x,t) \frac{F}{RT} \frac{\partial \phi(x,t)}{\partial x}
\]

where \( x \) is a distance from the membrane surface and \( t \) is the time. Eqs. (3) and (4) lead to the following expressions for the rate of change of the cation and anion concentration

\[
\frac{\partial C^+ (x,t)}{\partial t} = D^+ \frac{\partial^2 C^+ (x,t)}{\partial x^2} + D + \frac{\partial}{\partial x} \left( C^+ (x,t) \frac{F}{RT} \frac{\partial \phi(x,t)}{\partial x} \right)
\]

(5a)

\[
\frac{\partial C^- (x,t)}{\partial t} = D^- \frac{\partial^2 C^- (x,t)}{\partial x^2} + D - \frac{\partial}{\partial x} \left( C^- (x,t) \frac{F}{RT} \frac{\partial \phi(x,t)}{\partial x} \right)
\]

(5b)

The solution of Eqs. (5a) and (5b) can be noticeably simplified by assuming that the diffusion coefficients for cations \( D^+ \) and anions \( D^- \) are equal:

\[
D^+ = D^- = D
\]

Furthermore, the electroneutrality condition \( C^+ (x,t) = C^- (x,t) = C(x,t) \) applies for any time in the sublimiting and limiting regime and for the initial stage of the process at the overlimiting regime. Under these conditions and using reduced variables, Eqs. (5a) and (5b) may be written as:

\[
\frac{\partial \tilde{C} (\tilde{x}, \tilde{t})}{\partial \tilde{t}} = \frac{\partial^2 \tilde{C} (\tilde{x}, \tilde{t})}{\partial \tilde{x}^2}
\]

(7)

and the differential equation for potential distribution becomes

\[
\frac{\partial}{\partial \tilde{x}} \left( \tilde{C} (\tilde{x}, \tilde{t}) \frac{\partial \phi(\tilde{x}, \tilde{t})}{\partial \tilde{x}} \right) = 0
\]

or

\[
\tilde{C} (\tilde{x}, \tilde{t}) \frac{\partial \phi(\tilde{x}, \tilde{t})}{\partial \tilde{x}} = \text{const}
\]

(8)

where \( \tilde{x} = x/L, \tilde{t} = t/2t_d \) and \( \tilde{C} = C/C_0 \). The time \( \tilde{t} \) is normalized with respect to the characteristic time of diffusion, \( t_d \), through the Nernst layer

\[
t_d = \frac{L^2}{2D}
\]

(9)

In Eq. (9), \( L \) appears rather than \( \delta \) because, for the present approximation, the thickness of the
The diffusion layer $\delta$ is equal to the thickness of the Nernst layer $L$.

The constant in Eq. (8) is independent of the time and can be obtained from the transition to the stationary regime. According to Eq. (4), one finds for $t \to \infty$

$$2\alpha C(x) \frac{F}{RT} \frac{\partial \phi(x)}{\partial x} = j(x,t)|_{t \to \infty} = \tilde{i}_{\text{st}}$$

or

$$\tilde{C}(\tilde{x}) \frac{\partial \phi(\tilde{x})}{\partial \tilde{x}} = \tilde{i}_{\text{st}}$$

(11)

Thus, by using the simplifications described above, one can analyze the peculiarities of non-stationary polarization near a membrane surface by solving the diffusion Eq. (7) using Eq. (11) for the potential distribution.

The boundary and initial conditions for Eq. (7), and correspondingly, the peculiarities of the transition processes that occur, essentially depend on the electrodialysis regime. Two regimes can be distinguished: (1) using a fixed current through the membrane (galvanostatic regime) and (2) using a fixed voltage (potentiostatic regime). Below these two regimes will be analyzed.

2.4. Concentration polarization and pulse time at the galvanostatic regime

To solve Eq. (7) at the galvanostatic regime ($i = \tilde{i}_{\text{st}} = \text{const}$), use can be made of (1) the boundary and initial condition for the electrolyte concentration

$$\tilde{C}(1,\tilde{t}) = 1 \quad \text{and} \quad \tilde{C}(\tilde{x},0) = 1$$

(12)

and (2) the boundary condition for the gradient of electrolyte concentration

$$\left. \frac{\partial \tilde{C}(\tilde{x},\tilde{t})}{\partial \tilde{x}} \right|_{\tilde{x} = 0} = \tilde{i}_{\text{st}}$$

(13)

In the stationary regime, Eq. (12) is fulfilled for all values of $\tilde{x}$, and it leads to a linear change of the concentration in the diffusion layer. In the non-stationary regime the gradient of electrolyte concentration is not constant in the entire diffusion layer. Switching on an electric field leads to a decrease of the electrolyte concentration first of all near the membrane surface. At slightly larger distances the electrolyte concentration during some time is still equal to the bulk concentration $C_0$. Thus, the diffusion layer appears near the surface and gradually moves to the external boundary of the Nernst layer. So, Eq. (13) is written for $\tilde{x} = 0$.

The solution of Eq. (7) with the conditions (Eqs. (12) and (13)) may be presented in the following form

$$\tilde{C}(\tilde{x},\tilde{t}) = 1 - \tilde{i}_{\text{st}} \left\{ 1 - \tilde{x} \right\} - 2 \sum_{n=1}^{\infty} \frac{1}{Q_n^2} \exp(-Q_n^2 \tilde{t}) \cos(Q_n \tilde{x})$$

(14)

with

$$Q_n = \frac{2n - 1}{2} \pi.$$ 

In spite of the restriction of the time interval to very short times, this expression leads for the limiting case, $t \to \infty$, to the stationary distribution of the electrolyte concentration in the diffusion layer for all possible regimes: sublimiting, limiting and overlimiting.

Results of the numerical calculation of the concentration profiles in the Nernst layer as function of time are presented in Fig. 3a,b. Fig. 3a shows the concentration as a function of the distance for five values of the time and $\tilde{i}_{\text{st}} = 1$. Owing to the galvanostatic regime the decrease of the electrolyte concentration is uniform with time. Fig. 3b shows the concentration profiles in the Nernst layer for five different values of the current density at a fixed time $\tilde{t} = 0.1$. One can see that the non-stationary concentration distribution essentially depends on the value of current. For example, in the sublimiting ($\tilde{i}_{\text{st}} = 0.5$, curve 1) or limiting ($\tilde{i}_{\text{st}} = 1$, curve 2) regimes, the decrease of the concentration near the membrane is very small. However, in the overlimiting regime ($\tilde{i}_{\text{st}} = 4$, curve 5), the electrolyte concentration near the membrane reaches zero. Starting with Eqs. (8) and (14), an expression can be found for the potential drop within the region of the concentration polarisation:
The electrolyte concentration at $\tilde{x} = 0$ decreases in time, so the potential drop increases. The deterioration of the electrodialysis characteristics with the development of the concentration polarization can be demonstrated by the calculation of the potential growth (the potential difference between the non-polarized state at $t = 0$ and the potential at time $t$) for different values of the current density

$$
\Delta \phi = \tilde{i}_a \int_0^1 \frac{d\tilde{x}}{C(\tilde{x}, t)} - \tilde{i}_a \int_0^1 \frac{d\tilde{x}}{1} = \tilde{i}_a \left( \int_0^1 \frac{d\tilde{x}}{C(\tilde{x}, t)} - 1 \right)
$$

(16)

Fig. 4a,b shows some results. In the sublimiting regime (Fig. 4a, curves 1 and 2) the potential growth $\Delta \phi$ over the Nernst layer is increasing slowly with time, but in the limiting (curve 3) and overlimiting (curves 4–6) regimes, $\Delta \phi$ increases...
strongly. For example, for $\bar{t} = 0.25$ at the sublimiting regime ($\bar{t}_{st} = 0.5$) $\Delta \bar{\phi} \approx 0.068$, at the limiting regime ($\bar{t}_{st} = 1$) $\Delta \bar{\phi} \approx 0.34$ and at the overlimiting regime ($\bar{t}_{st} = 1.5$) $\Delta \bar{\phi} \approx 1.27$. So, at $\bar{t}_{st} = 1.5$, $\Delta \bar{\phi}$ is 3.7 times larger than at $\bar{t}_{st} = 1$ and almost 20 times larger than at $\bar{t}_{st} = 0.5$. Hence, at the appearance of a substantial region of induced space charge the potential drop is expected be 10–100 times higher than that at the sublimiting regime and the unproductive power consumption is large. The pulse of current has to end before this situation occurs.

To estimate the pulse duration of the non-stationary process Eq. (14) can be used. On the basis of this equation one can obtain the maximum time, $\bar{t}^*$, up to which the region of induced space charge is not yet formed. In the time interval $0 < \bar{t} < \bar{t}^*$, the concentration polarization is weak, but in the time interval $\bar{t} > \bar{t}^*$ it strongly increases. The pulse duration should therefore be smaller than $\bar{t}^*$.

The time $\bar{t}^*$ is connected with the period to decrease the initial electrolyte concentration at $x = 0$ to the value of $C_{st}$ at the beginning of the appearance of region of induced space charge. The charge density $C_{io}$ depends on the electrolyte concentration $C_{io}$, the current density and the thickness of the Nernst layer [3–5]. Thus, $\bar{t}^*$ has to be a function of these parameters too. However, for practical purposes it is enough to evaluate $\bar{t}^*$ for a concentration decrease at $\bar{x} = 0$ to some value $C^*$, which is connected only with the bulk concentration of electrolyte $C_{io}$. Let us suppose that $C^* = C_{io}/10$ or $C^* = 0.1$ for the overlimiting regime and $C^* = 1.1 C_{st}$ for sublimiting regime.

For the calculation of $\bar{t}^*$, we have to take into account that the time dependence of the concentration decrease is provided by the exponential series in Eq. (14). The main contribution to the series is its first term ($n = 1$). By neglecting the next terms one finds for the relation between $\bar{C}^*$ and $\bar{t}^*$

$$\bar{C}^* = 1 - \bar{t}_{st} + \frac{8}{\pi^2} \bar{t}_{st} \exp\left(-\frac{\pi^2}{4} \bar{t}^*\right)$$  \hspace{1cm} (17)

So that the characteristic time or the maximum pulse time is found as

$$\bar{t}^* = \frac{4}{\pi^2} \ln\left(\frac{8 \bar{t}_{st}}{\pi^2 (i_{st} - 1 + C^*)}\right)$$ \hspace{1cm} (18a)

or

$$t^* = \frac{8 t_{st}}{\pi^2} \ln\left(\frac{8 t_{st}}{\pi^2 (i_{st} - 1 + C^*)}\right)$$ \hspace{1cm} (18b)

where the subscript $i$ indicates the galvanostatic regime. Note that these expression are only adequate to provide a rough evaluation of the characteristic time, for more exact values, it is necessary to use the full Eq. (14).

For a comparison of the concentration decrease and the potential growth in overlimiting regime the concentration $\bar{C}(\bar{x} = 0, \bar{t})$ and the potential growth $\Delta \bar{\phi}$ are shown in the same picture (Fig. 4b). The value of potential growth $\Delta \bar{\phi}$ is normalized on the stationary potential growth $\Delta \bar{\phi}_{st}^* = \Delta \bar{\phi}_{st}$ ($\bar{t}_{st} = 0.9$), because the value of current $i_{st} = 0.9$ corresponds to the stationary value of the concentration $\bar{C}(0, t \rightarrow \infty) = \bar{C}^* = 0.1$. One can see (Fig. 4b) that the reduced electrolyte concentration $\bar{C}(0, \bar{t})$ (curves 1–5) reaches the value $\bar{C}^* = 0.1$ (curve 6) at approximately the same time as the ratio $\Delta \bar{\phi}/\Delta \bar{\phi}_{st}^*$ (curves 1–5) reaches the value 0.9.

Some values of the characteristic times as a function of $\bar{t}_{st}$, calculated with Eqs. (18a) and (18b), are shown in Fig. 5 for $\bar{C}^* = 0.1$ and the thickness of the Nernst layer ranging from 0.025 (curve 4) to 0.1 (curve 1). The traditional electrodialysis regimes are represented by curve 4.

It follows that the characteristic time can be equal to several minutes in the case of a large Nernst layer. However, $t^*$ sharply decreases to less than 1 min with a growth of current density and a decrease of the Nernst layer thickness.

2.5. Concentration polarization and pulse time at the potentiostatic regime

The description of the transition processes at the potentiostatic regime ($\bar{\phi}(t) = \text{const}$) is more complicated than that at galvanostatic conditions, even in the case of the idealized model of a fixed potential drop over only one Nernst layer. Although it is impossible to realize this situation in practice, the simple model can still be used to obtain a reasonable estimate of the transition time.
In the potentiostatic regime a growth of the concentration polarization with time leads to a decrease of the number of current carriers (ions) in the polarization layer and to an increase of the resistance. Consequently, the current through the membrane decreases with time. But right after switching on the power the current is very large, especially in the case of the overlimiting regime, when the concentration of electrolyte near the membrane reaches zero almost instantaneously.

Taking into account the similarity of the transition processes for a membrane and an electrode, the following conditions [20,29] can be used for the solution of Eq. (7):

\[ \tilde{C}(1, \tilde{t}) = 1, \quad \tilde{C}(\tilde{x} > 0, 0) = 1 \]  

(19)

The first condition is the same as for the galvanostatic regime, the second one indicates that at \( \tilde{t} = 0 \), the electrolyte concentration on an infinitely small distance \( \tilde{x} > 0 \) is still equal to the initial value \( C_0 \).

Furthermore, instead of Eq. (13), we now have to use the condition that the potential drop is constant. On the basis of Eqs. (8), (11) and (15), this condition can be expressed as

\[ \tilde{\phi} = i_{\text{st}} \int_0^{\tilde{t}} \frac{d\tilde{x}}{\tilde{C}(\tilde{x}, \tilde{t})} = \tilde{\phi}_{\text{st}} \]  

(20)

where \( \tilde{C}(\tilde{x}, \tilde{t}) \) is an unknown function. However, at all times the potential drop \( \tilde{\phi} \) is equal to the potential drop in the stationary regime \( \tilde{\phi}_{\text{st}} \). The value of \( \tilde{\phi}_{\text{st}} \) in the sublimiting regime is related to the stationary current \( i_{\text{st}} \) by the following expression [20,29]

\[ \tilde{\phi}_{\text{st}} = \ln(1 - i_{\text{st}}) \]  

(21)

Although the potentiostatic regime is analyzed, the parameter \( i_{\text{st}} \) indicates, as before, the dimensionless stationary current density. For both the galvanostatic and potentiostatic regime this choice allows a convenient comparison of the time dependencies of the electrolyte concentration in the Nernst layer.

Unfortunately, the quick decrease of the electrolyte concentration at \( \tilde{x} = 0 \) makes it impossible to use the diffusion Eq. (7) for the overlimiting regime. Even at very short times after switching on the power, the electrolyte concentration near the membrane decreases so sharply that first of all the region of the induced space charge forms and only thereafter the concentration of electrolyte decreases at larger distance from the membrane surface. So, in order to simplify the situation we are forced to limit the investigation to currents \( i_{\text{st}} \leq 1 \).

The solution of Eq. (7) using the complicated conditions expressed by Eqs. (19)–(21) can be obtained only in a numerical way. The calculated concentration profiles in the Nernst layer at the potentiostatic regime as a function of time are presented in Fig. 6 for \( 0.005 < \tilde{t} < \infty \) and two values of \( \tilde{i}_{\text{st}} \). The parameter \( \tilde{i}_{\text{st}} \) accounts for the fact that the potential drop over the Nernst layer corresponds to the one in the stationary regime at the indicated value of the current. This allows us to compare the two non-stationary regimes on an equal basis. In Fig. 6, a gradual increase in concentration polarization with time is observed. For an impression of the effect of the current density \( \tilde{i}_{\text{st}} \) on the concentration profiles in the Nernst layer the results of Fig. 6a,b can be compared.

One can see, first of all, a steep decrease of the electrolyte concentration in a narrow region near the surface (curve 1). The value of \( C_s \) becomes
Fig. 6. The electrolyte concentration in the Nernst layer as a function of the distance from the membrane at potentiostatic regime. Panels (a) and (b) show the behavior at \( i^0 \) = 0.4 and 0.8, respectively and different values of the pulse time \( t \): \( t = 0.0025 \) (1); 0.025 (2); 0.1 (3); 0.25 (4); \( \infty \) (5). Curve 4 can be compared with curve 4' obtained for the galvanostatic regime at \( t^0 = 0.25 \) (note the y-scale difference in panel (a) and (b)).

The change of the concentration profile leads to the change of the current. At the beginning of the pulse, when the steep change of concentration occurs in a narrow region, the diffusion flux to the membrane is essentially higher than for longer pulse times, when the concentration decrease occurs over the entire Nernst layer and its local value near the surface, \( C_s \), increases.

The time dependence of the real current through the membrane in the potentiostatic case can be obtained with an equation similar to Eq. (10). Similarly as at the galvanostatic regime, the diffusion layer is engendered near the membrane surface and the current density at time \( t \) can be obtained from the electrolyte concentration gradient at \( \tilde{x} = 0 \):

\[
\tilde{i}(t) = \frac{\partial \tilde{C}(\tilde{x}, t)}{\partial \tilde{x}} \bigg|_{\tilde{x} = 0}
\]

(22)

In general, the current density decreases with time and at \( t \to \infty \) it reaches the stationary value \( \tilde{i}_m^s \).

To arrive at the pulse time range for an effective electrodialysis in the potentiostatic regime it is necessary to analyze the mass transfer (integral transport of ions) through the membrane as a function of time \( \tilde{t} \). The mass transfer can be obtained by the integration of the current over the time as expressed by Eq. (23)

\[
\tilde{M}(\tilde{t}) = \frac{1}{\tilde{t}} \int_0^{\tilde{t}} \tilde{i}(\tilde{t}) \, d\tilde{t}
\]

(23)

where \( \tilde{M}(\tilde{t}) \) is normalized on the limiting value of mass transfer \( \tilde{M}_{\text{lim}} = \tilde{h}_{\text{lim}} \).

Some results of numerical calculations of both \( \tilde{h}(\tilde{t}) \) (curves 1 and 1') and \( \tilde{M}(\tilde{t}) \) (curves 2 and 2') are shown in Fig. 7. The normalized value of the mass transfer at \( \tilde{t} \to 0 \) coincides with the value of
the current. Later, at a fixed time \( t_1 \), the mass transfer is always higher than the current because it is calculated as the integral of the current over the time till \( t_1 \) is realized (\( 0 < t < t_1 \)) and for \( t < t_1 \), the current is higher than its value at time \( t_1 \).

On the basis of the results presented in Fig. 7, one can see that the current and the mass transfer through a membrane (or the electrodialyser productivity) both quickly decrease with time. For example, at \( \bar{t} = 0.005 \) the current (curves 1 and 1') is 10 times stronger than at the stationary regime (curves 3 and 3'), whereas at \( \bar{t} = 0.05 \) and 0.075, the current is, respectively three and two times stronger.

Because the electrolyte concentration \( \tilde{C}(\tilde{x}) = 0 \) in the non-stationary regime is lower than in the stationary one, the characteristic time for the pulse duration, \( \tilde{t}^* \), cannot be calculated for the potentiostatic regime in the same way as for the galvanostatic regime. Instead, it is convenient to use for this purpose the current density. Two expressions can be used for the characteristic time \( \tilde{t}^*_\phi \) (subscript \( \phi \) indicates the potentiostatic regime). In the first place this time can be regarded as the time to increase the current from its stationary value by 10%:

\[
\tilde{t}^*_\phi = 1.1 \tilde{t}_{\text{st}}
\]  

Some values of the characteristic time \( \tilde{t}^*_\phi \) based on Eq. (24) are presented in Fig. 8 (curve 1) as function of parameter \( \tilde{t}_{\text{st}} \).

Alternatively, one can consider \( \tilde{t}^*_{\phi} \) as the time required for a 10-fold decrease of the initial current:

\[
\tilde{t}(\tilde{t} = \tilde{t}^*_{\phi})/\tilde{t}(\tilde{t} = 0) = 0.1
\]  

Fig. 8, curve 1' shows that \( \tilde{t}^*_{\phi} \) based on Eq. (25) is essentially lower than the time based on Eq. (24) (curve 1). As we want to increase the mass transfer, we have to terminate the pulse at a value of the current that is sufficiently large. For practical purposes the time based on Eq. (25) is therefore more relevant than \( \tilde{t}^*_\phi \) based on Eq. (24).

For the sake of comparison, the time \( \tilde{t}^*_\tilde{t} \) at the galvanostatic regime is shown in Fig. 8 too. Curves 2 and 2' are calculated on the basis of the condition

\[
\tilde{t}(\tilde{t} = \tilde{t}^*_{\tilde{t}}) = 0.9 \tilde{t}_{\text{st}}
\]  

Alternatively, curve 2' describes the characteristic time \( \tilde{t}^*_{\tilde{t}} \), when

\[
\tilde{C}(0, \tilde{t}^*_{\tilde{t}}) = 1.1 \tilde{C}_{\text{st}}(0)
\]

These two times are comparable and much larger than those for the potentiostatic regime. The transition process at the potentiostatic regime is quicker than that at the galvanostatic one. The difference may be compared with the difference in the time dependence of the electrolyte concentration for both conditions, see Fig. 3 (galvanostatic) and Fig. 6 (potentiostatic).

2.6. Comparison of the potentiostatic and the galvanostatic regimes

The desalination of water or mass transfer through the membrane is caused by the current density. A higher current density means a higher ion flux through the membrane and a higher degree of desalination. In the stationary case the peculiarities of the structure of the Nernst layer and the power expenditure are the same in the galvanostatic and potentiostatic cases: at a fixed current density \( \tilde{t} \) a certain potential drop \( \tilde{\phi} \) occurs and at a fixed potential drop \( \tilde{\phi} \) the certain current density \( \tilde{t} \) occurs. Consequently, for \( \tilde{t} = \text{const}, \tilde{\phi}_{\text{st}} = \text{const} \) and the power consumption of electrodialyser, \( \tilde{t}_{\phi}\tilde{\phi}_{\text{st}} \), is constant too.
The two processes lose their identity in non-stationary conditions. At the galvanostatic regime, where \( \tilde{i}(\tilde{t}) = \tilde{i}_a = \text{const} \), the removal of ions away from the membrane surface is independent of the time. Therefore, the non-stationarity is related to the growth of the potential. With the growth of the potential the power expenditure increases \( (\tilde{i}(\tilde{t}) \approx \tilde{i}_a \tilde{\phi}_a) \), but the desalination remains the same.

At the potentiostatic regime the potential \( \tilde{\phi} \) is constant and the non-stationarity is related to the change of the current density \( \tilde{i}(\tilde{t}) \). The current is maximal when the power is switched on and decreases with time. It reaches its minimum value at the stationary regime where \( \tilde{i}(\tilde{t}) \approx \tilde{i}_a (= \text{const}) \). Hence, the desalination in the initial stage of the potentiostatic regime corresponds to a high value of the current. This means that for a given value of the stationary current \( \tilde{i}_s = \text{const} \) the desalination in the potentiostatic regime is quicker than in the galvanostatic regime. Consequently, the concentration decrease in the Nernst layer is stronger and the transition time to the stationary regime or characteristic time \( \tilde{t}_s^* \) is shorter than \( \tilde{t}_s \). The power expenditure at the potentiostatic regime decreases with time \( \tilde{i}(\tilde{t}) \tilde{\phi} \approx \tilde{i}_a \tilde{\phi}_a \), but this decrease is not useful as it is caused by a decrease of the current and this decrease leads to a decrease of the desalination.

It should be noted that forced water dissociation is unimportant in the pulse regime. This water dissociation is due to the fact that the polarization processes lead to local electrolyte concentrations below \( 10^{-7} \text{ eq. l}^{-1} \) [23]. Thus, the concentration of electrolyte in the region of the induced space charge reaches a value corresponding to the local equilibrium of the water dissociation reaction \( (C_{\text{H}2\text{O}} \approx 10^{-14} \text{ eq. l}^{-1}) \). If the process of the concentration decrease is limited to times \( \tilde{t} < \tilde{t}_s \), the electrolyte concentration is higher than \( 10^{-7} \text{ eq. l}^{-1} \) in every point of the Nernst layer and forced water dissociation does not occur.

It is necessary to stress that the theory developed is based on the notion of electroneutrality. Due to non-stationarity the induced space charge can appear in the sublimiting regime and can increase in the overlimiting regime.

### 2.7. Pause duration

The choice of a characteristic time of the pause is also important. The optimal time for the intensification of the electrodialysis is the time required to restore the initial state of the electrolyte concentration near the membrane surface (without any concentration polarization). At present it is not possible to analyze the restoration time quantitatively, but a qualitative analysis will already give an indication of the length of the restoration time compared to that of the pulse duration time.

The transition time to the initial state depends strongly on the degree of the concentration polarization, so, on the duration of the pulse and on the value of the current or the voltage. By taking into account only the diffusion process through the Nernst layer, one can show [14,15] that the transition time is of the same order of magnitude as the pulse time for the sublimiting regime. However, the transition time quickly increases above this value with current growth in the limiting and overlimiting regimes.

Several other processes also influence the restoration time. First of all, the return to the initial state is connected with diffusion and osmotic ion transport through the membrane. Both are caused by the different electrolyte concentrations at the two sides of the membrane.

Secondly, the restoration is connected with liquid movement near the membrane, as it is well known that in the stationary regime a slight electro-osmotic flow occurs through the membrane [30]. After switching off the power, the local electric field does not disappear absolutely. The existence of a diffusion layer in the absence of the external electric field means that a potential difference is preserved. Therefore, a slight movement of liquid directed to the membrane surface still continues.

Thirdly, because in the non-stationary regime the electro-osmotic flows inside and outside the
membrane cannot be compensated, a microturbulence of liquid near the membrane results, that speeds up the restoration process.

In the fourth place, partial restoration of the initial state of the electrolyte concentration during the pause is possible through hydrodynamic transport of salt along the membrane surface. The effect of hydrodynamic transport on the concentration polarization is not important when the external electric field is applied, but it is important in the absence of the field.

Finally, the pulse regime can stimulate the instability of the induced space charge at the over-limiting regime, as has been predicted by Rubinstein [1–4] for the stationary regime. This instability also speeds up the restoration.

Based on these arguments one may expect that the return to the state without concentration polarization is significantly quicker than a common diffusion process. Therefore, it may be concluded that the pause duration has to be about 10–50% of the pulse duration.

The argumentation presented above is related only to the restoration of the initial state of the electrolyte near the membrane surface. However, on the basis of a general notion about electroosmosis of the second kind, we can predict a new form of this process related to the deviation from electroneutrality in the non-stationary regime. Similarly to electroosmosis of the second kind near a flat heterogeneous membrane [1,12] this phenomenon can be responsible for the intensification of electrodialysis. Moreover, due to inertial properties this electroosmotical mixing of liquid can exist not only in the period of the pulse, but also in the period of pause. This complicated problem will be analyzed in a future paper.

3. Comparison with experimental results

In the present section experimental results will be compared with theoretical predictions based on the equations derived above. All results are obtained with a traditional electrodialyser cell equipped with an anion-exchange membrane MA-40 and a cation-exchange membrane MK-40 produced in Russia.

3.1. Investigation of the transition processes by transport of macroions in electrofiltration

The processes of electrofiltration and electrodialysis are similar. The difference between the two is that the liquid in the electrofilter contains not only the salt ions, but, for instance, also macroions. If the concentration of macroions is not very large they will not change the membrane polarization and this is especially true in the beginning of process. As we can analyze the concentration of macroions in the membrane channel independently of the salt concentration, additional information can be obtained about the distribution of the electric field in the channel. Electrofiltration is therefore a suitable method to illustrate the transition processes near the membrane surface.

For the present analysis use can be made of the results presented in Ref. [16], on the electrofiltration of a polyelectrolyte solution (1.6 mg l\(^{-1}\)) in distilled water. The electrofiltration was carried out at constant pH in a channel with a length \(l = 4\) cm and a thickness \(h = 1\) cm. The current density during filtration was 1.5 mA cm\(^{-2}\). The potential drop \(\phi\) over the channel in the stationary regime was 180 V. The polyelectrolyte concentration at the exit of the channel was determined spectrophotometrically. The resulting polyelectrolyte concentration as a function of time is presented in Fig. 9 (curve 1).

For the analysis of the results it should be realized that in the beginning of the electrofiltration all macroions sediment on the membrane surface and form an immobile layer. Under these conditions, the decrease of the concentration of macroions in the liquid flow with time can be expressed by the following equation [16,30]

\[
\frac{C(t)}{C_0} = 3\left(\frac{h - \Delta h(t)}{h}\right)^2 - 2\left(\frac{h - \Delta h(t)}{h}\right)^3
\]

(28)

where \(C(t)\) is the measured polyelectrolyte concentration at the exit of the channel at time \(t\); \(C_0\) its initial concentration; \(h\) the thickness of the channel and

\[
\Delta h = U_{eq} Et
\]

(29)
is the distance passed by the polyelectrolyte in the direction normal to the membrane surface in the time \( t \). In Eq. (29), \( U_{ef} \) is the electrophoretic mobility of the impurity and \( E \) is the electric field strength in the channel.

If we suppose that the concentration polarization is absent, the electric field strength can be calculated as \( E = \rho_0/h = 180 \text{ V cm}^{-1} \). On the other hand, an electric field strength in the core of the channel of about \( E = 2 \text{ V cm}^{-1} \) has been calculated in the presence of concentration polarization [24]. For these two extreme values of the field strength the decrease of the polyelectrolyte concentration can be calculated with Eqs. (28) and (29) using the experimental value of the polyelectrolyte mobility \( U_{ef} = 5 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1} \). The results are presented in Fig. 9 as curves 2 (180 V cm\(^{-1}\)) and 3 (2 V cm\(^{-1}\)). One can see that the experimental curve (1) is located between the two theoretical curves. This shows that the process of building up the concentration polarization and its influence on the transport properties inside the membrane channel governs the actual electrofiltration.

3.2. Transition time at the galvanostatic regime

Further proof of the correctness of the galvanostatic model can be obtained by a comparison of the experimental transition times and the calculated characteristic times for the process of water desalination. Experimental results reported by Karlin and Kropotov [31] can be used for this purpose.

The experiment has been carried out with an electrodialyser channel with a length \( l = 10 \text{ cm} \) and a thickness \( h = 1 \text{ cm} \). The liquid velocity was 18 cm s\(^{-1}\). The measured transition times to the standard state are plotted in Fig. 10 (symbols and curve 1) together with the calculated characteristic times \( \tau_{sl}^* \) (Eq. (18b)) for the same conditions (curve 2).

One can see that at \( \tilde{I}_a = 1 \), the theoretical \( (\tilde{I}_a) \) and the experimental \( (\tilde{I}_{st}) \) results coincide. This is evident, because a 10 times decrease of the electrolyte concentration \( \tilde{C}(0) \) at \( \tilde{I}_a = 1 \) is almost equivalent to reaching the stationary state. At larger values of \( \tilde{I}_a \), the difference between the stationary and the intermediate states increases.
So, the difference between the theoretical ($\bar{t}_{0}^*$) and the experimental ($\bar{t}_{0}$) times increases too. For example, for $i_{0} = 3$ the values of $\bar{t}_{0}^*$ and $\bar{t}_{0}$ differ by a factor of two, for $i_{0} = 4$ this difference increases by another factor of two and so on. In general, Fig. 10 shows that the rate of the transition processes is rather fast and that the characteristic time of the concentration polarization depends strongly on the current.

According to Eqs. (18a) and (18b), $\bar{t}_{0}^*$ is approximately proportional to $1/i_{0}^2$ for $i_{0} > 1$. The results of Karlin and Kropotov [31] show a similar dependency for the experimentally observed transition times $\bar{t}_{0}$. Both this and the results of Fig. 10 confirm that the derived model is qualitatively correct.

3.3. Transition process at the potentiostatic regime and water desalination at a pulse regime with a fixed potential drop

Finally the transition process and the desalination are investigated at potentiostatic conditions in a specifically designed experiment. An electrodialyser channel with a thickness $h = 0.15$ cm, a length $l = 4$ cm and a flow regime with a small liquid velocity of $V = 0.1$ cm s$^{-1}$ with a recirculation scheme (liquid is returned in the channel in a closed circle) has been used. The electrolyte concentration as a function of time has been calculated on the basis of the measured electrolyte conductivity. The investigations were carried out at a starting electrolyte concentration $C_{0} = 10^{-3}$ mol l$^{-1}$ (NaCl) and voltages ranging from 5 to 55 V. Numerical calculations of the structure of the Nernst layer and the potential drop over this layer (using the calculation scheme presented in Ref. [16]) show that the dimensionless current $\bar{i}_{0}$ under the conditions of the present experiment changes from 0.2 to 1.4.

The investigation of transition process was carried out for 10 pulses. The frequency of the pulse regime, $\omega$, was 1 Hz (duration of the pulses $t_{1} = 0.8$ s and the duration of the pauses $t_{2} = 0.2$ s). The transition time to the stationary regime is measured with the condition that the deviation of the measured current $i(t)$ from the stationary value $i_{0}^*$ equals 10%: $i(t) = i_{0}^* = 1.1$.

The measured transition time as a function of the applied voltage for the first, the second and tenth voltage pulse are shown in Fig. 11. The decay of the current density as a function of time is shown in Fig. 12 for an applied potential of 30

4. Conclusions

Theoretical and experimental investigations have shown that the non-stationary concentration polarization of membranes increases with time. Applying a non-stationary regime with short current or voltage pulses can intensify the process of electrodialysis.

The intensification of the electrodialysis will be most noticeable if the duration of the current or the voltage pulses is considerably shorter than the calculated characteristic time to build up the polarization layer.

The experimental investigation of the desalination process in the pulse regime shows that the pulse–pause duration ratio and the pulse frequency are important parameters for the optimization of the desalination. Under optimal conditions an increase of the desalination of about three times could be achieved.

5. Nomenclature

$C_0$ initial electrolyte concentration
The concentration distribution in the Nernst layer is given by $C(x,t)$, the concentration of impurity is $C_i(t)$, the initial concentration of impurity is $C_{i0}$, the density of induced space charge is $C_s$, and the ion distribution in the Nernst layer is $C^\pm(x,t)$. The critical value of the electrolyte concentration is $C^*$. The diffusion coefficients of the ions are $D^\pm$, the electric field strength is $E$, the Faraday constant is $F$, the limiting current is $i_{lim}$, the stationary current density is $i_0$, the thickness of the channel is $h$, the length of the channel is $l$, the thickness of the Nernst layer is $L$, the gas constant is $R$, the thickness of the induced space charge layer is $S_0$, the absolute temperature is $T$, the time is $t$, the characteristic time for galvanostatic regime is $t^*_g$, the characteristic time for potentiostatic regime is $t^*_p$, the diffusion (transition) time is $t_d$, the pulse duration is $t_1$, the pause duration is $t_2$, the electrophoretic mobility of the macroion is $U_{ef}$, the distance from the surface of the membrane is $x$, the thickness of the diffusion layer is $\delta$, the thickness of the electrical double layer (Debye layer) is $\kappa^{-1}$, the potential distribution is $\varphi(x,t)$, the potential drop over the Nernst layer is $\varphi$, the potential drop within the electrodi-alyser channel is $\varphi_o$, and the frequency of pulses is $\omega$.

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