

Comparison of different ED stack conceptions when applied for drinking water production from brackish waters

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Abstract

Three types of electro dialysis (ED) and electrodeionization (EDI) stacks are studied when treating NaCl solutions in the range of concentrations from 10^{-5} to 3×10^{-2} M: (1) with a non-conducting network spacer, (2) with a mixed ion-exchange monolayer bed, (3) with profiled membranes. The Sherwood number characterizing the desalination rate is measured in recirculation regime when the concentration of feed solution is slowly decreasing in time. The data obtained are compared with the results calculated and measured for “empty” desalination channels not containing any filling. It was established that the measured Sherwood numbers at overlimiting currents in stacks with filling are higher than that in “empty” channel under the same potential drop, while the latter, in turn, are higher than the Sherwood numbers calculated for limiting current density. The mass transfer rate in several cases (under 2.5 V per cell pair in diluted, $<10^{-4}$ M, solutions and high flow rates, $>7 \text{ dm}^3 \text{ h}^{-1} \text{ dm}^{-2}$, a stack with profiled membranes) may be 4 times higher than that in “empty” channel at limiting current density. The stacks with profiled membranes are shown to be effective in the overall range of concentrations. The stacks with non-conducting spacer can be used if the feed solution concentration is not too low, $>2 \times 10^{-3}$ M in our experiments. The stacks with ion-exchange resins are more preferable in the case of treatment of strongly diluted solutions (e.g. at the second stage following an ED with profiled membranes), as well as in the cases where it is necessary to use a compact unit characterized by a low flow velocity, though the power consumption is slightly higher.

Keywords: Electro dialysis; Electrodeionization; Overlimiting current; Mass transfer

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1. Introduction

Electrodialysis (ED) and electrodeionization (EDI) processes are widely applied in different branches of industry for water treatment, in particular, for producing deionized water of high purity, and drinking water [1,2]. The design of ED and EDI stacks acts an important role by determining the rate of mass transfer and the concentration range of the most effective application.

The conventional ED design implies the use of non-conducting spacer [1], which serves for separation of anion- and cation-exchange membranes and for better mixing of the diluate and concentrate solutions increasing by that the rate of mass transfer.

However, there are several other designs more convenient for treating diluted solutions. EDI stacks contain ion-exchange resins in diluate and sometimes concentrate compartments [1,2] (Fig. 1a). In this case H^+ and OH^- ions resulting from water splitting at ion-exchanger/depleted

solution interface [3] are involved in the separation process. The H^+ ions fill a part of ion-exchange capacity of cation-exchange resins; hence they participate in exchange with salt cations in the solution. Similarly, the OH^- ions are exchanged with salt anions in the solution. The H^+ and OH^- ions being in the solution react giving water molecules, the salt ions are evacuated through the resin beads and membranes into the concentrate compartment.

Another direction of ED stack concept development is the use of membranes with relief (profiled) [4,5] or undulated [6,7] surface. The stacks of this type (Fig. 1b) have a number of advantages in comparison to the stacks formed with flat membranes separated by a conventional network spacer. The main one is the higher rate of mass transfer, which is explained by combination of hydrodynamic and electrochemical effects. The relief on the membrane surface increases the active surface of mass exchange, on the one hand, and

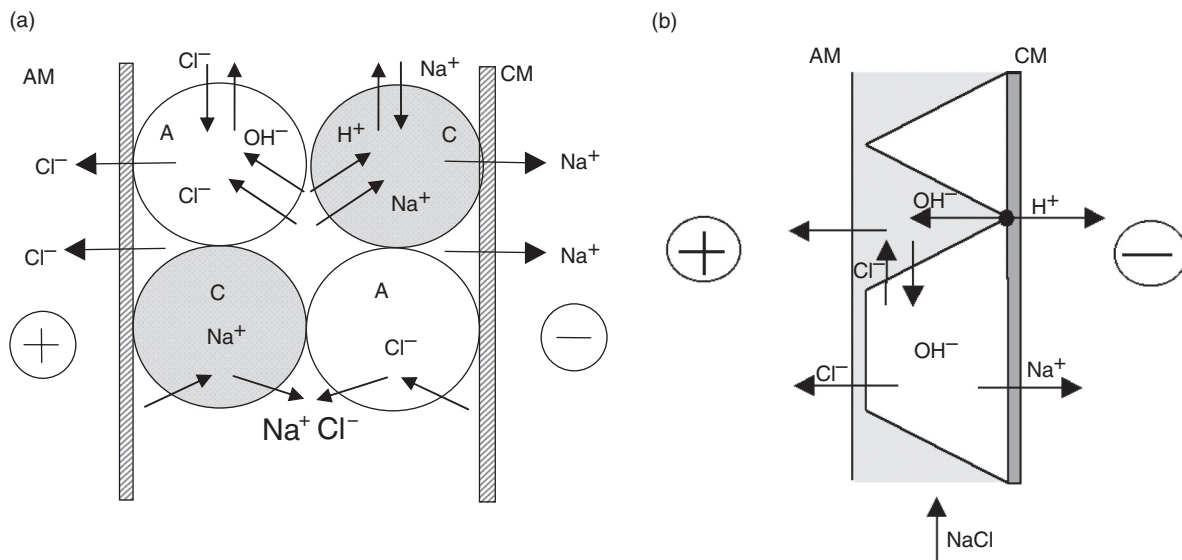


Fig. 1. Scheme of ion fluxes in an ED diluate compartment with an ion-exchange bed (a) and with profiled membranes (b). AM: anion-exchange membrane; CM: cation-exchange membrane; A: anion-exchange bead; C: cation-exchange bead.

acts like flow turbulence promoters reducing the diffusion layer thickness, on the other. The hydraulic and electric resistance of the space between profiled membranes is lower than that in the case of non-conducting spacer. The screening effect and the stagnant zones are considerably reduced in the stacks with profiled membranes that results in reducing water splitting and increasing current efficiency.

In the cases of stacks with ion-exchange resins and profiled membranes, the mass exchange surface is not flat and homogeneous. This peculiarity is important in initiating electroconvection, which is the phenomenon of electroosmotic mixing of depleted solution near an ion-exchange surface [8–12]. Dukhin and Mishchuk [8], Rubinstein and Zaltzman [9] as well as other authors [10] have shown that the electroconvection is more intensive near a curved or electrically non-homogeneous surface.

There are other effects coupled with current transfer through an ion-exchange membrane [11], which influence the rate of mass transfer. The role of H^+ and OH^- ions generation resulting from the water splitting reaction at ion-exchanger/solution interface is not single-valued. When this reaction takes place at a contact A/C (the arrow shows the current direction), as shown in Fig. 1a, this leads to the ion-exchange improving the desalination process. However, when the water splitting occurs at a membrane/solution interface, this results not only in decreasing current efficiency (because the H^+ and OH^- ions participate in the current transfer through the membrane), but in reducing electroconvection. The explanation of the latter phenomenon is in the mechanism of water entrainment in the course of electroconvection. The water molecules are entrained by the current of ions forming a space charge in the depleted solution near an ion-exchange membrane. Higher the Stokesian radius of ions, higher the electroconvection [12]. The Stokesian radius of H^+ and OH^- ions tends to zero: these ions carry the charge by “tunnelling” from one water molecule

to another without bringing liquid volume into motion. Water splitting results in invasion of the space charge region by H^+ (OH^-) ions that suppress the electroconvection [13].

One more effect resulting from the water splitting is the exaltation of counterion transfer by the electric field varying due to the emergence of water dissociation products in the depleted solution near the membrane [11,14]. However, this increase in the counterion transfer is not significant [14].

In this paper, several conceptions of ED and EDI stacks are studied, in order to make a justified choice when resolving a water treatment problem and to improve stack design. The range of solution concentrations is related to rather diluted ones, hence overlimiting current modes are considered as more effective.

2. Experimental

2.1. ED and EDI stacks

The main characteristics and test conditions of ED and EDI stacks are gathered in Table 1. The length of desalination channels for all stacks is 20 cm. The inter-membrane distance (h) and the porosity (g) of the space between the membranes are given in Table 1, as well as the pressure drop across the stack (ΔP) and the flow rate through one desalination channel (w) normalized to the width equal to 1 dm. The average velocity of solution flow (V) in desalination channel is found with taken into account the porosity: $V = w/(hg)$; the Reynolds number $Re = \frac{2hV}{\nu}$, where ν is the solution kinematic viscosity. All experiments are made with NaCl solutions under the potential drop per cell pair $\Delta\varphi = 2.5$ V. The membranes used were sulfonic heterogeneous MK-40 and anion-exchange heterogeneous MA-40 with secondary and tertiary ionogenic amino groups, produced by SchekinoAzot, Russia. The profiled membranes (MA-40P) were made from commercial MA-40 ones by hot pressing.

Table 1

Main characteristics of desalination channels in ED and EDI stacks studied

No	Desalination channel filling	h , mm	g	ΔP , bar	w , dm ³ h ⁻¹ dm ⁻¹	V , dm s ⁻¹	Re
1	Non-conducting spacer	0.5	0.85	0.6	3.6	0.26	27
2	Mixed ion-exchange monolayer bed [15]	0.8	0.4	0.6	2.5	0.22	40
3	Profiled membrane [4]	0.8	0.88	0.6	7.4	0.29	55
3'		0.8	0.88	0.3	2.5	0.10	18

Concentration channels of stacks studied (Table 1) are identical. They contain a non-conducting network spacer. NaCl solution circulates through these channels with normalized flow rate $w = 0.5 \text{ dm}^3 \text{ h}^{-1} \text{ dm}^{-1}$.

2.2. Testing ED and EDI stacks

The method of testing ED and EDI stacks is described in [16]. The main feature is in the use of quasi-steady state conditions when the feed solution is recirculated through the ED desalination compartments and its concentration is slowly decreasing. The potential drop over the stack, the feed solution pH and flow rate are maintained constant during the measurements. The inlet and outlet NaCl concentrations in desalinating stream for an ED stack were estimated from the conductivity and pH measurements.

When studying the “empty” channel, the method [17] allowing the feed concentration to be maintained constant was applied. The desalted outlet solution is titrated to restore the electric conductivity and pH of the inlet solution. The rate of desalination is determined through the rate of titration by material balance equations.

3. Results and discussion

When determining the inlet (C^{in}) and outlet (C^{out}) concentrations, the degree of desalination (γ) is calculated:

$$\gamma = (C^{\text{in}} - C^{\text{out}}) / C^{\text{in}} \quad (1)$$

The balance equation for a channel of length L is written as

$$(C^{\text{in}} - C^{\text{out}})w = \frac{i_1}{F}L \quad (2)$$

where i_1 is the partial current density of the salt counterion, which controls the ED desalination process, and F the Faraday constant. In our cases, we have generally obtained slightly acidified outlet NaCl solutions, hence, a NaCl and HCl mixture. Thus, the rate of Na^+ transfer controls the ED desalination.

If the mass transfer coefficient (k) is defined as:

$$k = \frac{i_1}{C^{\text{in}}F}, \quad (3)$$

a combination of Eqs. (1–3) gives

$$k = \frac{\gamma w}{L} \quad (4)$$

When k is found, it is easy to calculate the Sherwood number:

$$\text{Sh} = \frac{kh}{D_1} = \frac{i_1 h}{D_1 C^{\text{in}} F} \quad (5)$$

where D_1 is the diffusion coefficient of the counterion in solution, which controls the ED desalination process. Fig. 2a shows the Sherwood number calculated as described above for ED and EDI stacks presented in Table 1.

It is also of interest to know how much times the mass transfer rate in an ED channel is higher

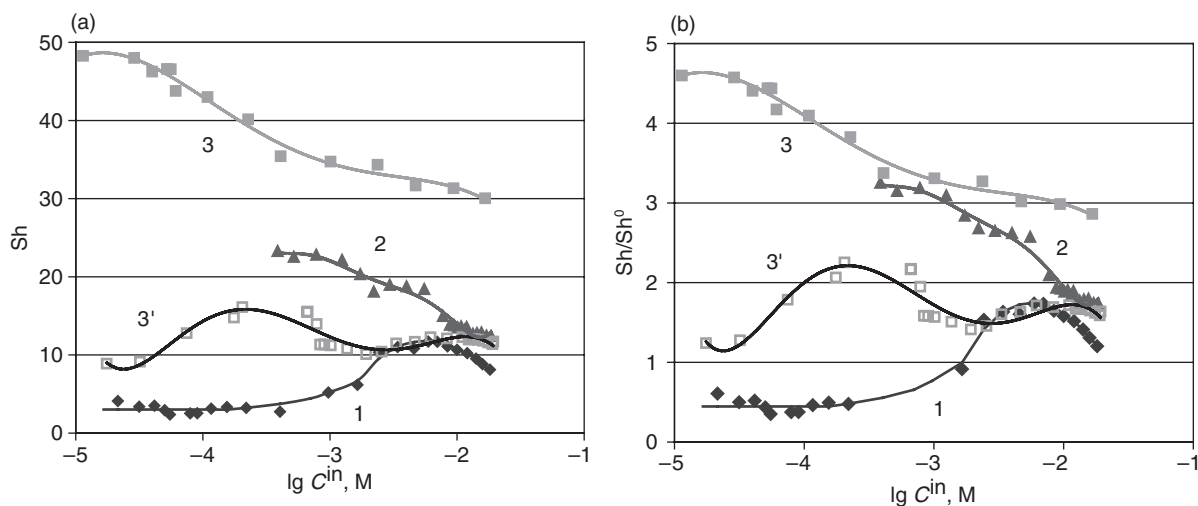


Fig. 2. The Sherwood number, Sh (a) and the ratio Sh/Sh^0 and (b) as functions of the inlet feed NaCl solution concentration for different ED and EDI stacks of length $L = 20$ cm. The numbers near the curves correspond to those in Table 1 presenting the main characteristics of the stacks as well as the pressure drops and flow rates of the feed solution. The potential drop per cell pair in all cases was 2.5 V.

than that in an “ideal” channel with smooth membranes and no filling where no coupled effects improving ED process occur. The Sherwood number for such a channel (Sh^0) may be calculated using the convective-diffusion model [18–20] by applying the following equation approximately verified if the length $L \leq 0.04V^0h^2/D$ [19,20]:

$$Sh^0 = 1.85 \left(Re^0 Sc \frac{2h}{L} \right)^{1/3} - 0.4 \quad (6)$$

where $V^0 = w/h$, $Re^0 = \frac{2hV^0}{\nu}$, $Sc = \frac{\nu}{D}$ is the Schmidt number, D is electrolyte diffusion coefficient. Eq. (6) is similar to the asymptotic L ev eque equation [19], however the range of L values where Eq. (6) may be applied is larger. Fig. 2b presents the ratio of the Sh experimental value to Sh^0 , the latter being calculated at the same normalized flow rate w that was applied for a studied channel.

The comparison of mass transfer rate for different stacks are made under the same pressure drop or under the same flow rate. When a constant

pressure drop ($\Delta P = 0.6$ bar) is applied, w decreases with decreasing porosity (g) (Table 1). The highest flow rate is for the stack with profiled membranes, which has the smallest hydraulic resistance. (Note that the solution input/output device was different for different stacks, hence, the pressure drop within the diluate channel was not the same for different stacks; only qualitative comparison can be made point) When the flow rate is the same, the linear velocity and pressure drop are higher for the stack with monolayer ion-exchange bed in comparison to the profiled membrane stack because of higher g for the latter.

As it can be seen from Fig. 2, the relative mass transfer rate expressed by Sh increases with decreasing inlet concentration, and, for several stacks, passes through a maximum and then decreases. The increase in Sh with decreasing concentration is explained by the action of coupled effects, mainly by the electroconvection, which is more intensive in diluted solutions [8–11,17]. The value of concentration (C_{max}) at which Sh reaches its maximum is not the same for different

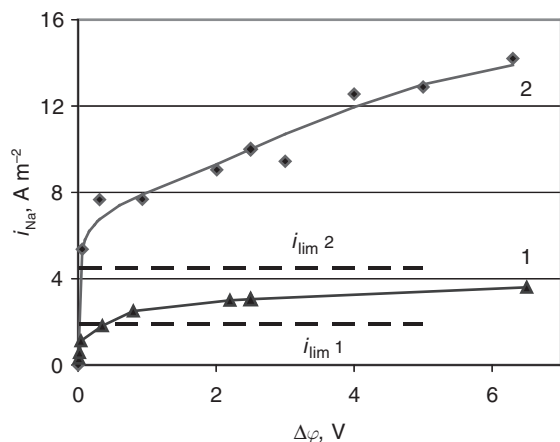


Fig. 3. Current density of Na^+ ions through a MK-40 cation-exchange membrane limiting (together with an MA-40 anion-exchange membrane) a desalination “empty” channel without filling vs. potential drop per cell pair; $L = 10$ cm, $h = 0.8$ mm. The values related to $\Delta\varphi = 2.5$ V are shown by dark points. The limiting current densities calculated with Eqs. (5) and (6) are presented by dash lines. The numbers near the curve correspond to those in Table 2. A 0.002 M NaCl solution is used as the feed solution.

ED designs; it is highest for ED with inert spacer, in this case $C_{\max} \approx 5$ mM NaCl. The smallest C_{\max} , for ED and EDI studied in this paper, is in the case of ED3 with mixed monolayer ion-exchange bed. The decrease in Sh with decreasing C^n is due to two effects resulting from the water splitting: the first one is the deviation from the neutral pH value in the diluate (concentrate) chambers; and the second one is

the reduction of electroconvection caused by the emersion of H^+ (OH^-) ions within the space charge region (see Introduction).

In order to better understand the effect of ED design on the mass transfer rate, we have studied an “empty” desalination channel formed by MK-40 and MA-40 membranes. The current density of Na^+ ions as a function of the potential drop per cell pair for such a channel is shown in Fig. 3. The length of the channel is $L = 10$ cm, the space between the membranes is $h = 0.8$ mm. The flow rates and velocities used in experiments are presented in Table 2, which shows also the limiting current density ($i_{\text{lim Na}}^0$) calculated with Eqs. (5) and (6), the Na^+ partial current density (i_{Na}) measured through the MK-40 at $\Delta\varphi = 2.5$ V per cell pair, the Sherwood number found with Eq. (5) for $L = 10$ cm (Sh_{10}). The subscript “0” in notations $i_{\text{lim Na}}^0$, Sh_{10}^0 and Sh_{20}^0 shows that the value is found for an ideal channel where there are no coupled effects influencing the boundary diffusion layer thickness and the limiting current density.

The Sherwood numbers Sh_{20} are extrapolated to $L = 20$ cm under the assumption that the local flux density of salt counterion at a distance z from the entrance is proportional to the average salt concentration in the section z of the channel. In this case a differential balance equation similar to Eq. (2) is obtained:

$$wdC = -\frac{i_1(z)}{F} dz \quad (7)$$

Table 2

Normalized flow rate (w), velocity (V), limiting current density ($i_{\text{lim Na}}^0$, Eqs. (5) and (6)), current density at $\Delta\varphi = 2.5$ V (i_{Na}), Sherwood numbers measured for $L = 10$ cm (Sh_{10}) and extrapolated for $L = 20$ cm (Sh_{20}), for an “empty” channel formed by a MK-40 and a MA-40 membranes, $h = 0.8$ mm

Conditions	w , $\text{dm}^3 \text{h}^{-1} \text{dm}^{-1}$	V , cm s^{-1}	$i_{\text{lim Na}}^0$, A m^{-2}	i_{Na} at $\Delta\varphi = 2.5$ V, A m^{-2}	Sh_{10}	$\frac{\text{Sh}_{10}}{\text{Sh}_{10}^0}$	$\frac{\text{Sh}_{20}}{\text{Sh}_{20}^0}$
1	0.70	0.24	1.88	3.05	9.51	1.62	1.24
2	8.4	2.92	4.48	9.4	29.3	2.11	2.39

When substituting $i_1(z) = \tilde{k}FC(z)$ in Eq. (7) with local mass transfer coefficient \tilde{k} , we find

$$\frac{dC}{C} = -Adz \quad (8)$$

where $A = \tilde{k}/w$. The integration of Eq. (8) gives

$$\frac{C(z)}{C^{\text{in}}} = e^{-Az} \quad (9)$$

In particular, it follows from Eq. (9) that

$$\frac{C_{20}}{C^{\text{in}}} = \left(\frac{C_{10}}{C^{\text{in}}} \right)^2 \quad (10)$$

After calculating the outlet concentration for $L = 20$ cm, the i_{20} and Sh_{20} values can be found with Eqs. (2) and (5), respectively.

Table 2 shows that the desalination rate in overlimiting current regimes, namely, at 2.5 V, is higher than that at the limiting current density. There is the same tendency as is shown in Fig. 2b: the ratio Sh/Sh^0 increases with increasing flow rate in the channel. The explanation involves three reasons. First, the decrease in the diffusion layer thickness (δ) caused by increasing flow rate results in a redistribution of the potential drop. The overall potential drop remains constant; however as the region where there is no concentration variation increases, the electric field intensity within the diffusion layer grows. Second, the lower δ , the higher part of the diffusion layer is occupied by the space charge region, hence, the role of electroconvection is more important. Third, there is a real saturation of the counterion current corresponding to full desalting of the feed solution, i.e. when $C^{\text{out}} = 0$. In case 2 (Table 2) of low flow rate, we are close to this situation. Hence, the possibilities to increase i_1 and Sh are more limited in this case; and these possibilities decrease with increasing L .

4. Conclusion

The use of overlimiting current regimes in ED and EDI apparatuses allows more intensive

mass transfer to be attained when treating diluted solutions. The enhancement of mass transfer is mainly due to the electroconvection effect which increases when the ion-exchange surface is curved or electrically non-homogeneous. This fact opens possibilities to improve ED process by perfecting the design of stacks. The role of water splitting in desalination channels is ambiguous. On the one hand, in several designs (EDI stacks), the exchange of H^+ and OH^- ions, being in ion-exchange filling, with salt ions in solution results in higher degree of desalination. On the other, water ions emerging within the space charge region in depleted solution reduce the electroconvection. Besides, the water splitting can change solution pH and decrease the current efficiency. As a result, the rate of desalination (expressed for instance by Sherwood number) firstly increases with diluting feed solution that is due to the intensification of electroconvection. Then, after passing a maximum at a certain concentration, C_{max} , Sh decreases owing to increasing negative effects of water splitting, which become more intensive with diluting solution. It is of interest that the value of C_{max} depends highly on the ED (EDI) stack design determining by that the range of application. Thus, the stacks with non-conducting spacer can be applied for desalting brackish waters (with TDS in the range 500–3000 mg/L). For producing water of high purity, EDI stacks with ion-exchange resin bed can be used, in particular, stacks with monolayer bed are effective up to 1 MOhm cm of resistance. The stacks with profiled membranes have a number of advantages showing high desalination rate in a very large concentration range, from 10^{-5} to 3×10^{-2} M (or from 1 to 2000 mg/L of TDS). An important condition for effective employment of this type of stacks is the use of high flow rates when turbulized flow regime takes place.

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