Electrodialysis
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Introduction
Electrodialysis (ED) represents a modern progressive electromembrane separation technology gaining recently an increasing attention in various branches of industry. Especially in the field of brackish water desalination representing the largest application of this technology, ED is nowadays competitive to the conventional reverse osmosis process [1-5]. There can be also increasing trend noted in application of ED within the waste water recovery and desalination of process streams in the pharmaceutical and food industry. The reason for that is the electromembrane separation process doesn’t endanger health and nutritious properties of the final product e.g. by adding coagulants or regenerating agents. A demineralization of milk whey or sweetness adjustment of fruit juices can be mentioned as a representative examples.

Description of the electrodialysis process
The ED unit represents a typical plate-and-frame (filter-press, sandwich) type device. The main core of this apparatus represents a membrane stack consisting of planar plate anion (AM) and cation (CM) selective membranes as shown in schematic sketch in Figure 1. The individual membranes are separated by inert (electrically non-conducting) net-like spacers providing mainly a mechanical support of the stack and determining the geometry of the flow channel in the space between the membranes. Two typical geometries of the spacer used in technical practice are depicted in Figure 2. Another function of the spacer net is turbulisation of the solution. Solution flowing through the channel filled by the net follows so called zig-zag flow, see Figure 3(a), leading to an increase of mass transfer coefficients in the direction from the solution bulk towards the membrane surface. Therefore, concentration polarization phenomena occurring in the diffusion layer at the membrane surface are reduced. Typical spacer net is shown in Figure 3(b).

Generally, two independent hydraulic circuitries are considered: (a) diluate stream (D) and concentrate stream (C) supplying diluate and concentrate solutions into the diluate compartment (DC) and concentrate compartments (CC). A part of the membrane stack consisting of one AM and CM with corresponding compartments (DC and CC) then represents a repeating motive of the ED unit often denoted as a membrane pair (MP). The advantage of the plate-and-frame design is flexible increase/reduction of capacity of the ED
unit simply by assembling more/less membrane pairs in the stack. The membrane stack is placed in between two terminal planar-plate electrodes; anode and cathode, see Figure 1. The electrode plates are separated from terminal CMs also by net-like spacer forming anode and cathode compartment. The electrodes are washed by solution of high salinity, which is circulated in closed loop between the storage tank of the electrode solution and electrode compartments. This hydraulic circuit is only auxiliary, different from C and D. Generally identical electrode solution is used for the anode and cathode compartment.

**Figure 1:** Schematic sketch of the ED process; *FD and OD* – feed and outlet of the diluate stream, *FC and OC* – feed and outlet of the concentrate stream, *AF and AE* – feed and effluent of the anode stream, *CF and CE* – feed and effluent of the cathode stream, *am and cm* – anion and cation selective membranes, (+) – cations, (−) – anions; reaction scheme of the electrochemical reaction indicated at the corresponding electrodes.

On imposing direct electric field (*voltage*) on the membrane stack between two terminal electrodes the ED separation process is initiated. That means the electric field represents main driving force of the process. To apply electric field and electric current into the system, an electrochemical reaction must take place at the electrode-solution interface. An oxygen formation takes place at the anode, while reduction of protons to hydrogen runs at the cathode, see Figure 1. The applied electric field induces migration movement of all ions dissolved in the process solutions and contained in the membranes so, that the cations move towards the cathode, while the anions towards the anode. This movement is indicated as an
electric current flow through the ED stack. The ions meet ion-selective membranes on this way. Cations can permeate across the CMs, otherwise are rejected by AMs. On the contrary, anions are allowed to cross AMs, but not through CMs. By a suitable combination of AMs and CMs in the membrane stack in accordance with the orientation of the electric field, see Figure 1, it is possible to induce prevailing transport of dissolved salt from DCs into CCs. The basic principles of this process are thoroughly summarized in the literature [1-5] mostly available online in ICTP’s library. If the salts concentration is to be reduced below certain level, D represents product (e.g. production of drinking water from brackish or sea water) and C waste. Conversely, if solution is about to be concentrated above a certain level, C is a product (e.g. recovery of effluents in metallurgy or salt production) and D effluent.

**Figure 2**: Two typical geometries of the spacers used in the electrodialysis unit; (a) tortuous path spacer, (b) sheet flow spacer; figure adopted from [2].

**Operating regimes of the electrodialysis**

**Potentiostatic vs. galvanostatic mode**

The operation of the ED unit at constant voltage (potentiostatic mode) is preferred compared to the operation at constant current (galvanostatic mode) due to safety reasons. During the ED process the concentration, and consequently electric conductivity, of the solution in DC decreases resulting in the increase of electric resistance of the ED unit. In the case of the galvanostatic operating mode it could results in uncontrolled increase of voltage applied on
the ED unit and potential collapse of electric current source or, in extreme cases, membrane stack due to Joule heating.

Figure 3: (A) Zig-zag flow induced while solution flowing through a channel filled with spacer net; (B) photo of real spacer net.

**Process solutions flow regime**

The solutions flow through the ED unit upward to facilitate gas bubbles removal from the active space between the membranes or from the electrode compartments. The presence of the gas phase is undesirable because bubbles (a) increase the electric resistance of the intermembrane space and (b) block (reduce) active membrane surface and thus reduce the performance of the unit. Note, that bubbles can enter into unit with process solutions or gas may desorb from the solutions directly in CC or DC.

**Batch (discontinuous) vs. flow-through (continuous) setup**

Depending on a type of the ED process application and volume of treated solutions, there are two basic operating regimes: (a) batch regime (e.g. in case of milk whey desalination) or (b) flow-through regime (water desalination). In former case, the product stream (D or C) is recycled during the separation until required concentration of salts (high or low concentration) in the corresponding storage tank is attained. In the latter case, the product solution (either D or C) is desalinated or concentrated during single flow-through the ED unit.

The basic difference between these two regimes is apparent from Figure 4 representing arrangements of the batch and flow-through regime used during the laboratory exercise. However, the hydraulic scheme of the process solutions corresponding to those two basic regimes can slightly differ in industrial scale. The main reason is continuous supply of the feed solution in case of the industrial ED process. In Figure 4(A) the diluate and concentrate
solutions circulate in separated circuits resulting in a continuous decrease of salt concentration in D in Tank D and concentration increase in Tank C. Conversely, in the arrangement shown in Figure 4(B) the feed solution for D and C is identical and outlets from DCs and CCs are continuously mixed in the storage tank. Due to this composition of the feed solutions doesn’t change during the experiment.

**Figure 4:** Operational regimes of the ED process: (A) batch (discontinuous) setup, (B) flow-through (continuous) setup; grey arrow indicate direction of electric current, salt and water flux from diluate compartments (DCs) to concentrate compartments (CCs) across membranes; Tank C and Tank D – storage reservoirs for concentrate and diluate solutions (in case A).

**Material balance of ED unit**
Both DC and CC of the ED unit must obey mass balance and material balance of dissolved salt. The balances of flow-through and batch system depicted in Figure 4 are discussed in the following two subchapters. A stationary desalination process is considered. For the purpose of balance of the ED system, a real solution (generally rather complex containing various salt types) is often substituted by model solution of one equivalent compound. This approach was also adopted in the present case and as a model solution a solution of Na₂SO₄ in water is considered.


**Flow-through setup**

The material balance of diluate stream and concentrate stream represents Equations (1) and (2), respectively. \( \dot{N}_{D,in} \) and \( \dot{N}_{C,in} \) [mol s\(^{-1}\)] represent inlet molar flux of salt (thought Na\(_2\)SO\(_4\)) into DCs and CCs, respectively, while \( \dot{N}_{D,out} \) and \( \dot{N}_{C,out} \) [mol s\(^{-1}\)] denote outlet molar flux of salt from DCs and CCs, respectively. Term \( \dot{N}_m \) [mol s\(^{-1}\)] describes molar flux of salt across the membranes in the direction from DCs to CCs. Minus/plus sign indicates the inlet and outlet, respectively. An accumulation of the salt in the ED unit is zero (right hand side of these equations) because stationary desalination process is considered.

\[
\dot{N}_{D,in} - \dot{N}_{D,out} - \dot{N}_m = \dot{Q}_{D,in} c_{D,in} - \dot{Q}_{D,out} c_{D,out} - \frac{\eta N_{mp} z F}{z F} = 0 \tag{1}
\]

\[
\dot{N}_{C,in} - \dot{N}_{C,out} + \dot{N}_m = \dot{Q}_{C,in} c_{C,in} - \dot{Q}_{C,out} c_{C,out} + \frac{\eta N_{mp} z F}{z F} = 0 \tag{2}
\]

The fluxes, \( \dot{N}_{D,in}, \dot{N}_{C,in}, \dot{N}_{D,out} \) and \( \dot{N}_{C,out} \), can be described by product of volumetric flow rate, \( \dot{Q} \) [m\(^3\) s\(^{-1}\)], and molar concentration of model salt in the corresponding stream, \( c \) [mol m\(^{-3}\)]. For better understanding to the symbols used in these equations see Figure 4(B). The flux of salt between CCs and DCs is related to the electric current applied to the ED unit, \( I \) [A], according to Faraday’s law, \( \dot{N}_m = \frac{\eta N_{mp} z F}{z F} \), where \( F \) is Faraday’s constant, \( z \) denotes charge number of model salt (number of electrons equivalent to transport of one molecule of model salt from D into C, for Na\(_2\)SO\(_4\) is \( z=2 \)) and \( N_{mp} \) represents number of membrane pairs in the ED stack. \( \eta \) is current (coulombic) efficiency of the ED process (utilization of the applied electric current for transfer of salt from D into C), which is an important process characteristic. It generally ranges in close interval from 0 to 1, where \( \eta = 1 \) corresponds to a theoretical situation of ideally efficient process. Reasons responsible for lower current efficiency are discussed further in chapter Current efficiency losses in ED process. Subscripts \( D \) and \( C \) distinguish diluate and concentrate, respectively, \( in \) and \( out \) inlet and outlet, respectively, and \( m \) denotes flux across the membrane.

The mass balances of D and C are under the assumption of incompressible fluid expressed by Equations (3) and (4), respectively. The inlet volumetric flow rate is equal to the outlet one, unless volumetric flow of solvent (mostly water) from DCs across the membrane to CCs, \( \dot{Q}_m \) [m\(^3\) s\(^{-1}\)], is nonzero. The main causes of the water transport across the membranes and corresponding consequences are discussed in chapter Water flux across the membrane.
\[ \dot{Q}_{D,\text{in}} - \dot{Q}_{D,\text{out}} - \dot{Q}_m = 0 \]  
(3)

\[ \dot{Q}_{C,\text{in}} - \dot{Q}_{C,\text{out}} + \dot{Q}_m = 0 \]  
(4)

For further discussions let’s assume \( \dot{Q}_m = 0 \) and equal inlet and outlet volumetric flow rates as expressed by Equations (5) and (6).

\[ \dot{Q}_{D,\text{in}} = \dot{Q}_{D,\text{out}} = \dot{Q}_D \]  
(5)

\[ \dot{Q}_{C,\text{in}} = \dot{Q}_{C,\text{out}} = \dot{Q}_C \]  
(6)

Combining Equations (1) with (5) and (2) with (6) and rearranging the material balances in the form of Equations (7) and (8) are obtained, where \( \dot{Q}_D \) and \( \dot{Q}_C \) corresponds to volumetric flow rate through DCs and CCs, respectively.

\[ (c_{D,\text{in}} - c_{D,\text{out}}) = -\frac{\eta \text{IN}_{\text{mp}}}{\dot{Q}_D zF} \]  
(7)

\[ (c_{C,\text{in}} - c_{C,\text{out}}) = \frac{\eta \text{IN}_{\text{mp}}}{\dot{Q}_C zF} \]  
(8)

From these equations results that concentration of salt in D decreases during single flow through DCs, while concentration in C increases. The concentration difference between the inlet and outlet is proportional to applied current and inversely proportional to the volumetric flow rate.

An important characteristic of the electrodialysis process is degree of desalination, \( \varphi \). It represents measure of relative decrease of concentration in diluate product stream, \( c_p \), during the electrodialysis with respect to concentration of salt in the feed solution, \( c_f \). It is traditionally defined by Equation (9).

\[ \varphi = \left(1 - \frac{c_p}{c_f}\right) \cdot 100 \% \]  
(9)

In the case of flow-through regime \( c_p = c_{D,\text{out}} \) and \( c_f = c_{D,\text{in}} \), that is:

\[ \varphi = \left(1 - \frac{c_{D,\text{out}}}{c_{D,\text{in}}}\right) \cdot 100 \% . \]  
(10)

Substituting \( c_{D,\text{out}} \) in Equation (10) using Equation (7) one may express degree of desalination using basic operating parameters \((I, \dot{Q}_D)\), see Equation (11).
\[ \varphi = \frac{\eta I N_{mp}}{c_{D,in} Q_D z F} \cdot 100 \% \] \hspace{1cm} (11)

The maximum theoretical degree of desalination \( \varphi_{max} \) (under assumption of ideal current efficiency \( \eta = 1 \)) for given current load \( I \) and volumetric flow rate \( Q_D \) is then given by Equation (12).

\[ \varphi_{max} = \frac{I N_{mp}}{c_{D,in} Q_D z F} \cdot 100 \% \] \hspace{1cm} (12)

The dependence of current efficiency \( \eta \) on the current load \( I \) can be calculated from Equation (13) resulting from combination of Equations (11) and (12).

\[ \eta = \frac{\varphi}{\varphi_{max}} = \frac{Q_D z F}{I N_{mp}} (c_{D,in} - c_{D,out}) \] \hspace{1cm} (13)

**Batch setup**

According to the material conservation law, the amount of salt (e.g. \( Na_2SO_4 \)) transferred from D into C during the batch electrodialysis \( n \) [mol] is expressed by Equation (14),

\[ n = V_D(0)c_{D,T}(0) - V_D(\tau)c_{D,T}(\tau) = V_C(\tau)c_{C,T}(\tau) - V_C(0)c_{C,T}(0) \] \hspace{1cm} (14)

where \( \tau \) [s] is time of the batch electrodialysis operation, \( V_C \) and \( V_D \) [m\(^3\)] represents volume of the concentrate and diluate circuit (volume of the storage tank, flow channels in the ED unit and volume of corresponding pipeline system), respectively, and \( c_{C,T} \) and \( c_{D,T} \) [mol m\(^3\)] is molar concentration of salt in C and D, respectively, at the beginning (0) and end (\( \tau \)) of the batch electrodialysis, respectively. For the meaning of these symbols see Figure 4(A).

The current efficiency \( \eta \) of the entire batch electrodialysis can be calculated by Equation (15).

\[ \eta = \frac{q}{N_{mp} q_{max}} \cdot 100 \% \] \hspace{1cm} (15)

Here \( q \) [C] is minimum electric charge equivalent to the amount of transferred salt \( n \). It is calculated by means of Faraday’s law as expressed by Equation (16).

\[ q = nzF \] \hspace{1cm} (16)

\( q_{max} \) [C] represents real charge applied to the ED unit from external current source. Its value can be obtained by time integration of the electric current, see Equation (17).
\[ q_{\text{max}} = \int_{0}^{\tau} I(t) dt \] (17)

Realize that charge \( q_{\text{max}} \) is equivalent to maximum amount of salt, which can be transferred from DC to CC in one membrane pair at given current load. Note, that \( q_{\text{max}} \) is in Equation (15) multiplied by number of membrane pairs \( N_{\text{mp}} \) of the ED unit. It is because of the charge \( q_{\text{max}} \) passes through each membrane pair connected in series and, therefore, \( N_{\text{mp}} \) times participates in the desalination in each membrane pair.

The degree of desalination can be also calculated by means of Equation (9) using values of salt concentration in D at actual time or at the end of the batch electrodialysis.

**Current efficiency losses in ED process**

Current efficiency is the measure of utility of electrical supply for salt transfer between DC and CC (proportion of current used on its own desalination). There are three main effects responsible for loss of current efficiency of the ED process, as discussed below.

**Ion selectivity of the membranes**

A membrane used in technical practice is not ideally selective for counter-ions, *i.e.* ions, which can preferentially cross the membrane (*cations in case of CM and anions in case of AM*). But also the co-ions (*anions in case of CM and cations in case of AM*) can partially migrate through the membrane, which decreases the membrane selectivity. To quantify the selectivity of the membrane, transport numbers corresponding to cations \( t_+ \) and anions \( t_- \) are introduced. The transport numbers \( t_+ \) and \( t_- \) represent relative portion of electric charge transported by cations and anions, respectively, as defined by Equation (18).

\[
1 = \frac{j_+ + j_-}{j} = t_+ + t_- \quad (18)
\]

Here \( j_+ \) and \( j_- \) [A m\(^{-2}\)] represents current density transported by cations and anions respectively, which can be calculated from molar flux of cations and anions, respectively. For the case of water solution of \( \text{Na}_2\text{SO}_4 \) total current density and \( j_+ \) and \( j_- \) can be calculated from Equation (19).

\[
j = j_+ + j_- = \dot{N}_{\text{Na}^+}z_{\text{Na}^+}F + Fz_{\text{SO}_4^{2-}}\dot{N}_{\text{SO}_4^{2-}} \quad (19)
\]

For ideally selective AM the \( t_+ = 1 \) and \( t_- = 0 \), while for ideally selective CM \( t_- = 0 \) and \( t_+ = 1 \). Transport numbers of counter-ions for real membrane is of around 0.95 and for co-ions of
0.05. This might finally lead to approx. 5 % loss of current efficiency of the electrodialysis. If membrane exhibits transport numbers for counter-ions below 0.9, its applications for given process becomes uneconomic because of unacceptable current efficiency loss.

The selectivity of ion selective membrane strongly depends on concentration of salt in the external solution. With increasing concentration the intensity of diffusion flux from external solution into the membrane phase increases. It results in increase of relative concentration of co-ions in the membrane and finally to reduction of current efficiency.

**Backward salt diffusion**

Another phenomena leading to current efficiency loss is backward diffusion. It is related to the diffusion transport of ions across the membrane back from C to D. The backward diffusion flux ($\dot{N}_{m,\text{back}}$) is frequently quantified by Equation (20). According to this equation $\dot{N}_{m,\text{back}}$ is proportional to a difference between mean concentrations of salt in C and D and to a transport coefficient $D_m$. The flux is further inversely proportional to the membrane thickness $w_m$.

$$\dot{N}_{m,\text{back}} = \frac{D_m}{w_m} (c_C - c_D)$$  \hspace{1cm} (20)

Note that local concentration directly at the membrane is lower or higher than the bulk value on DC and CC side, respectively. It is due to the formation of thin diffusion (boundary) layer at the membrane surface during the electrodialysis. This phenomena is known as “concentration polarization” [1-3,5]. Therefore, the current efficiency loss due to backward diffusion is not only dependent on the difference between the mean concentrations in D and C, but also on the extension of the concentration polarization.

**Parasitic (by-pass) current**

The process solutions are distributed or collected along the membrane stack into the individual DCs and CCs via feed and outlet channels, as schematically depicted in Figure 1. These channels thus form additional electrically conductive paths between the electrodes outside the membrane stack. The electric current (or electric charge) passing through this external hydraulic circuits doesn’t participate in the desalination process (salt transfer from D to C). Therefore, this portion of the total current supplied from the external current source is without any desalination effect; thus causing current efficiency loss. In most of the existing
industrial applications of the ED process, the value of parasitic current is acceptably low. However, this current efficiency loss mechanism should not be underestimated in case of design of new ED process applications. For example, in case of sea water desalination the parasitic current might be high because of high electric conductivity of the feed solutions.

**Water flux across the membrane**

Water (in general solvent) can also penetrate through the membranes mainly in the direction from D to C. It is mainly due to two effects: (a) osmosis and (b) electroosmosis. In the former case the water molecules diffuses from the solution of lower salinity towards solution with higher concentration of salts leading to the so called ‘osmotic pressure’. Logically, this water transport mechanism is dependent on the salt concentration difference between D and C. The latter mechanism is mainly associated with transport of water molecules in a solvation shell surrounding each ion dissolved in water. The solvation shell consists of water molecules, which dipole is oriented with respect to the charge of the central ion. Due to the attractive electric forces the water molecules in the 1st solvation shell are bonded to the central ion and move across the membrane along with it. From this results that the amount of transported water due to electroosmosis is proportional to the amount of salt transported from D to C, i.e. it is directly proportional to the electric current (charge) passing through the membranes.

In the case of the batch electrodialysis shown in Figure 4A, the transport of water from D into C results in decrease of the volume of solution contained in D ($V_{T,D}$), while the volume of solution in C ($V_{T,C}$) increases during the electrodialysis. The effect of the water flux is clear from Equation (21). It is derived from Equation (14), where $c_{D,T}(\tau)$ was expressed to the left-hand side and $V_{T,D}(\tau)$ is substituted by $V_{T,D}(\tau) = V_{T,D}(0) - \Delta V$. $\Delta V$ represents the total volume of solution transported from D to C during the batch ED.

$$c_{D,T}(\tau) = \frac{V_{T,D}(0)c_{D,T}(0) - n}{V_{T,D}(0) - \Delta V} \quad (21)$$

The water transport ($\Delta V \times 0 \text{ m}^3$) leads to a higher concentration of salt in D at the end of the batch electrodialysis compared to the case without water transfer, when equal amount of $n$ is transferred from the D to C. In conclusion, the water transfer reduces the desalination effect and therefore the utilization of the electric current (electric energy) imposed to the system. Similar qualitative effect of water transfer can be observed also in the case of flow-through regime.
Membrane scaling and fouling

Another major problem affecting performance of the ED process is membrane fouling and scaling due e.g. to precipitation of scales (like CaCO$_3$, Mg(OH)$_2$, etc.) on the membrane surface. This problem is solved effectively by reversing polarity of the electrodes (switching anode to cathode and cathode to anode) in regular intervals. By switching the electrode polarity and reversing current and salt flux direction, freshly precipitated scale is flushed from the membrane before it can solidify.

Faraday’s law

The electric current is applied in to the system via electrochemical reactions taking place at the electrode surface in cathode and anode compartment. In the case of the water treatment application of the ED process, which is the main application of the ED, the overall electrochemical process represents water electrolysis. The amount of gas evolved during the electrodialysis process can be calculated by means of Faraday’s law representing a fundamental relationship of electrochemistry. The Faraday’s law in the form applicable for this purpose represents Equation (22),

$$V_i = \frac{v_i q_{max} R T}{n_e F \frac{p}{p}}$$  \hspace{1cm} (22)

where $V_i$ represents volume of the developed $i$-th gas ($H_2$ or $O_2$), $q_{max}$ is electric charge applied to the ED unit calculated according to Equation (17), $n_e$ and $v_i$ corresponds to number of electrons exchanged during the electrochemical reaction and stoichiometric coefficient of $i$-th gas, $R$ [J K$^{-1}$ mol$^{-1}$] is universal gas constant, $T$ [K] is thermodynamic temperature and $p$ [Pa] is gas storage pressure.

Experimental part

Pilot-plant ED unit

The photography and schematic sketch of the ED unit, the surrounding pipeline system and supporting equipment can be seen in Figure 6 and Figure 5, respectively. The heart of the device represents membrane stack consisting of 200 membrane pairs. Active area of one membrane is of 0.32 x 0.64 m$^2$. Both sides, left and right, are bordered by electrode compartments equipped with platinized titanium terminal electrodes washed by Na$_2$SO$_4$ solution. Volumetric flow rate of the electrode solutions is controlled by rotameters $V1$ and
V6. There are two transparent plastic columns, where H\textsubscript{2} and O\textsubscript{2} in the electrode compartments are accumulated. There are additional four rotameters V2 through V5 controlling volumetric flow rate of concentrate and diluate solutions. Na\textsubscript{2}SO\textsubscript{4} water solution is used for both the D and C. The set of four conductometers are used for measuring an electric conductivity of solution in the D and C at the feed and outlet side. The conductometry is used to continual measurements of the Na\textsubscript{2}SO\textsubscript{4} concentration. About the detail function of this ED pilot-plant unit you will be instructed during the laboratory exercise.

**Figure 5:** Scheme of the overall pilot plant electrodialysis unit installed in ICT Prague; V# – valves, D# - diaphragm valves, R# - rotameters, F# - filters, T# – reservoirs, P# - pumps, C1 and C2 – storage columns for H\textsubscript{2} and O\textsubscript{2} evolved in the electrode compartments
Figure 6: Photography of the pilot-plant electrodialysis unit installed in ICT Prague, *ED* - membrane stack, *R2 through R5 and D2 through D5* - rotameters and valves for controlling volumetric flow-rate of solution in D and C, *R1 and R6 and D1 and D6* - rotameters and valves for controlling volumetric flow-rate of electrode solutions, *V13, V14* – valves on the output of D and C, *C1 and C2* – storage cylinders for gasses produced at the electrodes, *P1, P2, P3* – pumps of C,E,D, *DCV* – power supply, *SW* – control switchboard (pumps, direct current power source) plus voltmeter and ammeter
The conductivity of water solution of Na$_2$SO$_4$, $\kappa(T_{\text{ref}})$ [mS cm$^{-1}$], at reference temperature, $T_{\text{ref}}$ [°C], can be recalculated to mass concentration, $x$ [g dm$^{-3}$], by means of calibration curve represented by Equation (23).

$$x = a \kappa(T_{\text{ref}})^3 + b \kappa(T_{\text{ref}})^2 + c \kappa(T_{\text{ref}})$$

(23)

The values of coefficients $a$, $b$, and $c$ at two different reference temperatures in case of water solution of Na$_2$SO$_4$ are summarized in the following table.

<table>
<thead>
<tr>
<th>$T_{\text{ref}}$ [°C]</th>
<th>$a$/ g dm$^{-3}$ cm$^3$ mS$^{-3}$</th>
<th>$b$/ g dm$^{-3}$ cm$^2$ mS$^{-2}$</th>
<th>$c$/ g dm$^{-3}$ cm mS$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>$-6.99 \times 10^{-4}$</td>
<td>$2.66 \times 10^{-2}$</td>
<td>$7.01 \times 10^{-4}$</td>
</tr>
<tr>
<td>25</td>
<td>$-3.08 \times 10^{-4}$</td>
<td>$1.84 \times 10^{-2}$</td>
<td>$6.34 \times 10^{-4}$</td>
</tr>
</tbody>
</table>

To convert conductivity, $\kappa(T)$ [mS cm$^{-1}$], measured at experimental temperature, $T$, different from $T_{\text{ref}}$, to the conductivity corresponding to $T_{\text{ref}}$, one may use linear relationship of conductivity on temperature expressed by Equation (24). Here $k$ [% mS cm$^{-1}$°C$^{-1}$] is coefficient of proportionality.

$$\kappa(T) = \kappa(T_{\text{ref}}) \cdot \left[1 + \frac{k}{100 \%} (T - T_{\text{ref}})\right]$$

(24)

Values of $k$ are summarized in the following table.

<table>
<thead>
<tr>
<th>$T_{\text{ref}}$ / °C</th>
<th>$k$/ % mS cm$^{-1}$°C$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>2.37</td>
</tr>
<tr>
<td>25</td>
<td>2.12</td>
</tr>
</tbody>
</table>

**Goals of the laboratory work**

Perform electrodialysis tests in the batch and flow-through setup using the ED pilot-plant. In the latter case, perform experimental parametrical studies of the effect of applied voltage and volumetric flow rate on the performance (degree of desalination, current efficiency, minimum electric energy input) of the ED process. The experimental procedure and conditions will be specified during the introductory part of the laboratory exercise. During the measurements record the values of the applied voltage, electric current, specific conductivity of D and C solutions in feed and outlet solution. Make following plots:
Flow-through continuous setup

- dependence of current load, I, on total voltage, U, for two different volumetric flow rates of process solutions;
- dependence of measured and maximum (theoretical) degree of desalination, φ, on current load, I, total voltage, U, and on the minimum electric power input defined by $P = UI \,[\text{W}]$ for two different volumetric flow rates of process solutions and discuss observed results;
- and dependence of current efficiency of electrodialysis process, η, on applied voltage, U, for two different volumetric flow rates of process solutions.

Batch setup

- dependence of current load, I, over time of the batch electrodialysis, t,
- dependence of electrical resistance of ED unit, R, over time of batch electrodialysis, t;
- dependence of concentration of model salt in D and C, $c_{\text{D,in}}$, $c_{\text{D,out}}$, $c_{\text{C,in}}$, and $c_{\text{C,out}}$, at the feed and outlet side over time of batch electrodialysis, t,
- and dependence of instantaneous and total degree of desalination, φ and φt, respectively, over time of batch electrodialysis, t.

For the case of batch electrodialysis calculate the total current efficiency and the total degree of desalination of the entire processes, see chapter Material balance of ED unit.

Safety instructions

Keep in mind that here is worked with electrically conductive solutions under high direct voltage and current respectively. According to regulation of European Union the safety direct current is $I_{\text{sf}} < 10 \, \text{mA}$ and safety voltage is $U_{\text{DC,sf}} < 60 \, \text{V} \,(\text{in dangerous areas})$ and $U_{\text{DC,sf}} < 25 \, \text{V} \,(\text{in especially dangerous areas – wet environment})$. Manipulate only with valves ($V1$ – $V6$, $D1$ – $D6$, $V13$ and $V14$) and controls ($SW$, $DCV$) mentioned within this instruction or discussed by instructor on the place.

**TOUCHING THE DEVICE WHILE OPERATING CAN CAUSE DEATH!**

**INSERTING A VOLTAGE TO THE DEVICE WITH TOO LOW FLOWRATE OF OPERATIONAL SOLUTIONS CAUSES ITS DESTRUCTION!**

A short speech about safety will take place right before the work starts. Please listen carefully and ask immediately if you need.
Questions
- What was the main aim of this laboratory work?
- Which quantities represent input parameters and which were measured?
- What are the main reasons of different current efficiency of electrodialysis when operated in batch or flow-through setup?
- What are the main reasons of current efficiency losses during electrodialysis?
- How the current supplied to the electrodes relates to the achieved degree of desalination?
- What parameters directly affect the performance of electrodialysis (degree of desalination, current efficiency, minimum input power) and how?

References
6. MEGA corp., www.mega.cz