Periodica Polytechnica
Chemical Engineering

58(2), pp. 125-130, 2014
DOI:10.3311/PPch.7145

RESEARCH ARTICLE

A Novel Method for Limiting Current Calculation in Electrodialysis Modules

Natália Káňavová [1] * / *Lubomír* Machuča [1]

RECEIVED 31 OCTOBER 2013; ACCEPTED AFTER REVISION 31 JANUARY 2014

Abstract

The purpose of this work was to develop a novel semi-empirical method for calculation of limiting currents in electrodialysis modules. Experiments were carried out at pilot-scale module with five electrolytes. Current-voltage curves were measured and limiting currents were determined. Subsequently, dependence of the mass transfer coefficient on linear flow velocity was evaluated and its parameters a, b were estimated. The main advance of this work is that comparison of electrolytes showed the clear relationship between parameter a, electrolyte diffusion coefficient and the difference of cation transport numbers in membrane and solution. The semi-empirical relationship between the mass transfer coefficient and linear flow velocity was set up, and the limiting current calculation run was proposed. At the same time, dependence of the diffusion layer thickness on linear flow velocity was examined and the way of its calculation was established. The proposed method is unique thanks to its applicability in a broad range of experimental conditions; its use is not limited neither by electrolyte type nor electrodialysis module size.

Keywords

Electrodialysis · desalination · limiting current · current-voltage curve · mass transfer

1 Introduction

1.1 Electrodialysis

Electrodialysis is an electrically-driven membrane separation process using ion exchange membranes to separate ions from the solution. The most frequent and well-known applications of electrodialysis are e.g. desalination of brackish water, production of edible salt from seawater, desalination of cheese whey, potassium tartrate removal from wine [1]. Electrodialysis has been successfully applied also in separation of organic acids, e.g. oxalic acid [2] and formic acid from wastewaters [3], to recover free malic acid from its salt [4] or to recover galacturonic acid from sugar beet pulp's pectin hydrolysate [5], and in food processing, e.g. desalting of soy sauce [6] or fruit juice deacidification [7]. Electrodialysis (ED) module is composed of a membrane stack placed between the cathode and the anode. The membrane stack consists of alternating cation and anion exchange membranes separated by spacers to form individual cells. Spacers separate membranes and provide mixing of the solution in cells.

When the electric potential difference is applied, cations moving towards cathode can pass only through cation exchange membranes (CM) and anions moving towards anode can pass only through anion exchange membranes (AM), assuming absolute selectivity for counter-ions. That means the alternating arrangement of membranes enables the ion accumulation in the space defined by CM on the anode side and AM on the cathode side of the stack (concentrate cell). On the contrary, ions are removing from the space between AM on the anode side and CM on the cathode side of the stack (diluate cell). The electrodialysis performance can be affected by several process variables: membrane type, number of cell pairs, solution path length in the stack, applied voltage, flow rate and concentration of feed solution, temperature etc. [8, 9].

1.2 Limiting current

The ion flux depends on the electric current flowing between electrodes. It is thus desirable to work at high current densities. In a certain range of current, the mass transfer is limited by transport rate of ions through the membrane. At certain current

[1]MemBrain s.r.o., Pod Vinicí 87, 471 27 Stráž pod Ralskem, Czech Republic
*Corresponding author, e-mail: Natalia.Kanavova@membrain.cz

level, the diffusion through laminar boundary layer (diffusion layer) on the membrane surface becomes the mass transfer rate limiting step instead of transport through membrane. This value of electric current is called the limiting current. Reaching limiting current, the concentration of cations on CM surface or the one of anions on AM surface becomes zero; the electric resistance of diluate cells sharply increases as a result of ion depletion and the water splitting takes place on the membrane surface in order to generate ions [10, 11]. Changes in pH appear in cells, and the current efficiency of electrodialysis is decreased as a result of H^+ and OH^- transport. Limiting current is affected by many parameters as membrane properties, type and concentration of electrolyte or hydrodynamic conditions [12].

The limiting current can be determined from experimental current-voltage curve. If the limiting current region is not well-defined, dependence of the electric resistance R on the reciprocal value of current $1/I$ can be used [13]. Rapp and Pfromm [14] modified this method when they used the 4th order polynomial regression of R vs. $1/I$ curve and limiting current was determined by its minimum. Barragán and Ruíz-Bauzá [15] described another method of evaluating experimental current-voltage curves. They derived the equation which permits the adjustment of experimental data where one of the adjustment parameters is i_{lim}, but this method is only applicable when measured current densities are below the limiting current density. Meng et al. [16] used dependence of the desalting efficiency on electric current to determine the limiting current value in their work. Another method for the determination of limiting current density is the evaluation of derivative dI/dU plotted against the electric current I. The limiting current can be found as the value of current when dI/dU equals zero [17].

1.3 Theoretical background

The limiting current I_{lim} can be calculated using modified equation for limiting current density i_{lim} [18]. The relationship between mass transfer coefficient k, salt diffusion coefficient D and diffusion layer thickness δ is taken into account and for conditions of real electrodialysis module, the current efficiency η is employed. Then, the equation can be expressed as follows:

$$I_{\lim} = \frac{c_l^D \left| z_C \nu_C \right| F k A_{mem}}{\eta \left(t_C^M - t_C^S \right)} \tag{1}$$

where c_l^D is the mean logarithmic electrolyte concentration in diluate, z_C the valence of cations, ν_C the stoichiometric coefficient of cations, F Faraday constant, k the mass transfer coefficient, A_{mem} the effective membrane area, η the electric current efficiency and t_C^M and t_C^S the transport numbers of cations in membrane and solution at infinite dilution, respectively.

The mass transfer coefficient is usually unknown, but it can be calculated from experimentally determined limiting current using reordered Equation (1). Assuming the mass transfer coefficient is independent on inlet electrolyte concentration (results described by Nikonenko et al. [19] show that this is reasonable in the used concentration range), the following equation could be written:

$$k = au^b \tag{2}$$

where u is the diluate linear flow velocity and a, b are empirical parameters.

After the integration of electrolyte mass balance equation from zero (inlet) to the membrane length l (outlet), Equation (3) for the calculation of outlet electrolyte concentration in diluate $c_{D,out}$ can be derived:

$$c_{D,out} = c_{D,in} \exp\left(-\frac{k.N.w.l.\eta}{\dot{V}_D \left(t_C^M - t_C^S \right)} \right) \tag{3}$$

where $c_{D,in}$ is the inlet electrolyte concentration in diluate, k the mass transfer coefficient, N the number of cell pairs, w the effective width of the membrane, l the effective length of the membrane, η the electric current efficiency, V_D the diluate flow rate and t_C^M and t_C^S the transport numbers of cations in membrane and solution at infinite dilution, respectively.

When the sufficient amount of experimental results is available, the mass transfer coefficient dependence on linear flow velocity can be determined and parameters a, b in Equation (2) can be estimated. Equations (1-3) then enable to calculate the limiting current at any inlet electrolyte concentration, diluate linear flow velocity and module geometry (keeping the same type of membrane and spacer).

When the mass transfer coefficient is known, the diffusion layer thickness δ could be calculated:

$$\delta = \frac{D}{k} \tag{4}$$

where D is the electrolyte diffusion coefficient and k the mass transfer coefficient.

2 Experiments

Ammonium nitrate (ion valence ratio 1:1), sodium chloride (1:1), sodium sulfate (1:2), calcium nitrate (2:1) and magnesium sulfate (2:2) (Lach-Ner, Neratovice, the Czech Republic) and RO water were used to prepare test solutions for experiments. Cation and anion exchange membranes RALEX (MEGA, Stráž pod Ralskem, Czech Republic) were used in the pilot-scale ED module (MEGA, Stráž pod Ralskem, Czech Republic) for the determination of limiting currents. The scheme of the electrodialysis unit is drawn in Figure 1. The module consisted of 15 cell pairs with the whole effective membrane area 0.6 m^2. The spacer thickness was 0.8 mm.

Feed solution from the tank with temperature 25°C was passing through the ED module in three circuits for diluate, concentrate and electrode solution and then was carried back to the same tank. Inlet electrolyte concentration was in the range of 0.5 – 3.0 g l^{-1} and linear flow velocity of diluate in the range of 4.05 – 15.05 cm s^{-1}. Samples for the measurement

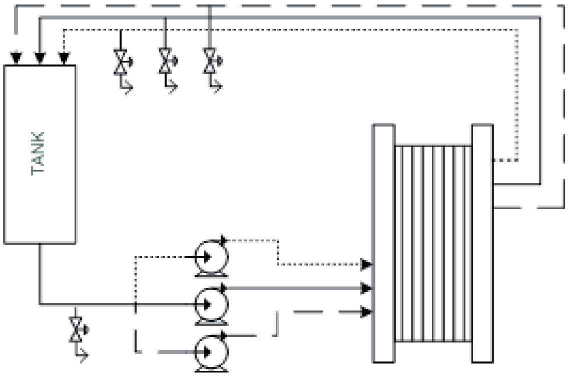


Fig. 1. Scheme of ED unit for the determination of limiting current with three circuits for diluate (dotted line), concentrate (dashed line) and electrode solution (full line)

of conductivity, pH and temperature were collected before and after the passage through the stack. Applied voltage was increasing in the range of 0.5 – 5 V/cell pair and the corresponding current values were recorded.

3 Results and discussion

Determination of limiting current from the electric resistance *R* vs. reciprocal current *1/I* plot is widely used, but some authors consider it not so exact and underestimating the limiting current values [20]. For this reason, the derivative method [17] was used in this work. Up to now, it has been applied mainly in electrolysis field, but authors' recent work [21] proved that it was appropriate and accurate also for electrodialysis.

Dependence of the mass transfer coefficient *k* [cm s^{-1}] on linear flow velocity *u* [cm s^{-1}] was evaluated for each electrolyte and parameters of Equation (2) were estimated; this is demonstrated in Figure 2 and parameters estimated from experimental data are listed in Table 1. Parameter *a* is different for each electrolyte. As parameter *b* remains the same, it obviously presents the effect of hydrodynamic conditions in the stack. The relationship between parameter *a*, the electrolyte diffusion coefficient and the difference of cation transport numbers in membrane and in solution was observed. The semi-empirical equation was proposed as follows:

$$a = p.D[cm^2.s^{-1}].\left(t_C^M - t_C^S\right) \tag{5}$$

where *p* is empirical parameter unique for the combination of used membrane and spacer type. The summary of electrolyte diffusion coefficients and differences of cation transport numbers in membrane and solution at infinite dilution for each electrolyte is shown in Table 2 together with parameters *p* calculated from parameters *a* of single electrolytes according to Equation (5). It is supposed that cation transport number in membrane is equal to 1 in all cases. Final *p* value was calculated as an average of them. As various types of electrolytes (1:1, 1:2, 2:1, 2:2) were tested, it can be supposed that Equation (5) with parameter *p* (*p* = 138) could be applied in case of any electrolyte.

Tab. 1. Estimated parameters *a, b* of mass transfer coefficient dependence on linear flow velocity.

	a [cm^{1-b} s^{b-1}]	b [-]
Ammonium nitrate	0.001232	0.6667
Sodium chloride	0.001337	
Sodium sulfate	0.001163	
Calcium nitrate	0.000882	
Magnesium sulfate	0.000713	

Tab. 2. Summary of electrolyte diffusion coefficients, differences of cation transport numbers in membrane and in solution and calculated parameters *p* for each electrolyte

	D.10^5 [cm^2 s^{-1}]*	$\left(t_C^S - t_C^M\right)$ [-]*	p [cm^{-1-b} s^b]
Ammonium nitrate	1.90	0.5	129.68
Sodium chloride	1.60	0.6	139.27
Sodium sulfate	1.23	0.6	157.59
Calcium nitrate	1.30	0.55	123.36
Magnesium sulfate	0.85	0.6	139.80
Average			138

* Lide, D.R., CRC Handbook of Chemistry and Physics, 88th Edition, CRC Press, 2008.

Dependence of the diffusion layer thickness δ [cm] on linear flow velocity *u* [cm s^{-1}] could be derived from Equations (2), (4) and (5):

$$\delta = \frac{1}{p\left(t_C^M - t_C^S\right)} u^{-b} \tag{6}$$

It is clear that in given experimental system (membrane and spacer type, hydrodynamic conditions), the diffusion layer thickness is dependent only on the difference of cation transport number in membrane and solution at infinite dilution. The diffusion layer thickness in the range of linear flow velocity is depicted in Figure 3. Dependence of the diffusion layer thickness on linear flow velocity of sodium chloride, sodium sulfate and magnesium sulfate is expected to be the same as the difference of cation transport number in membrane and solution at infinite dilution has the same value for these three electrolytes; this is confirmed by experimental data. In general, the good agreement is observed between diffusion layer thickness values calculated from experimentally determined limiting currents (using Equations (1) and (4)) and the ones calculated according to Equation (6).

The proposed method for limiting current calculation consists of three steps:

1. Mass transfer coefficient calculation:
   $k = p.D.\left(t_C^M - t_C^S\right)u^{2/3}$
2. Calculation of diluate outlet concentration according to Equation (3)
3. Limiting current calculation according to Equation (1)

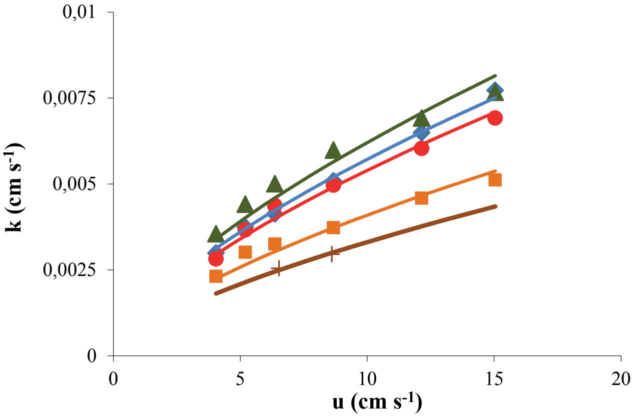


Fig. 2. Experimentally determined mass transfer coefficients k at various linear flow velocities *u* for ▲ sodium chloride, ♦ ammonium nitrate, ● sodium sulfate, ■ calcium nitrate and + magnesium sulfate and fitted dependences $k = au^b$ (full lines) for each electrolyte

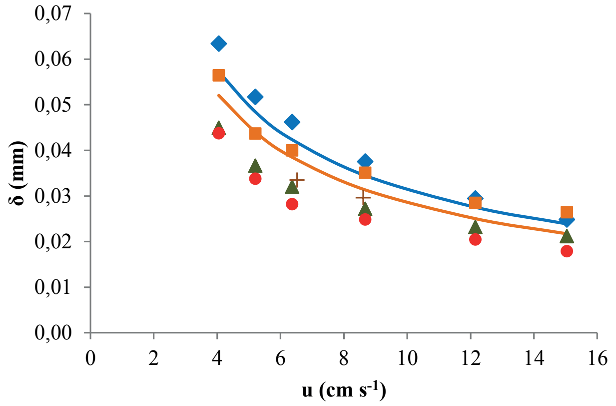
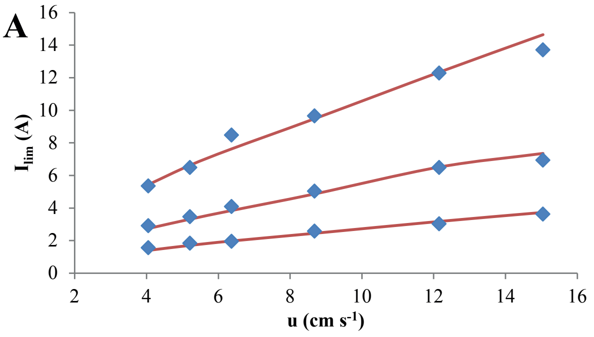


Fig. 3. Diffusion layer thickness δ in the range of linear flow velocities u for ▲ sodium chloride, ♦ ammonium nitrate, ● sodium sulfate, ■ calcium nitrate and + magnesium sulfate and fitted dependence $\delta = f(u)$ according to Equation (6) for sodium chloride, sodium sulfate and magnesium sulfate (dashed line), calcium nitrate (dotted line) and ammonium nitrate (full line)

The described method enables the calculation of limiting current of any electrolyte solution in a broad range of linear flow velocity and electrolyte concentration. Moreover, another authors' results show this method could be applied not only in case of pilot-scale ED module, but it is applicable in the whole range from the laboratory to the industrial-scale electrodialysis module [21] if the membrane and spacer type are kept. In Figure 4, the agreement between experimentally determined limiting currents and the ones calculated by the proposed method is depicted. The average deviation of calculated limiting currents was 7%.



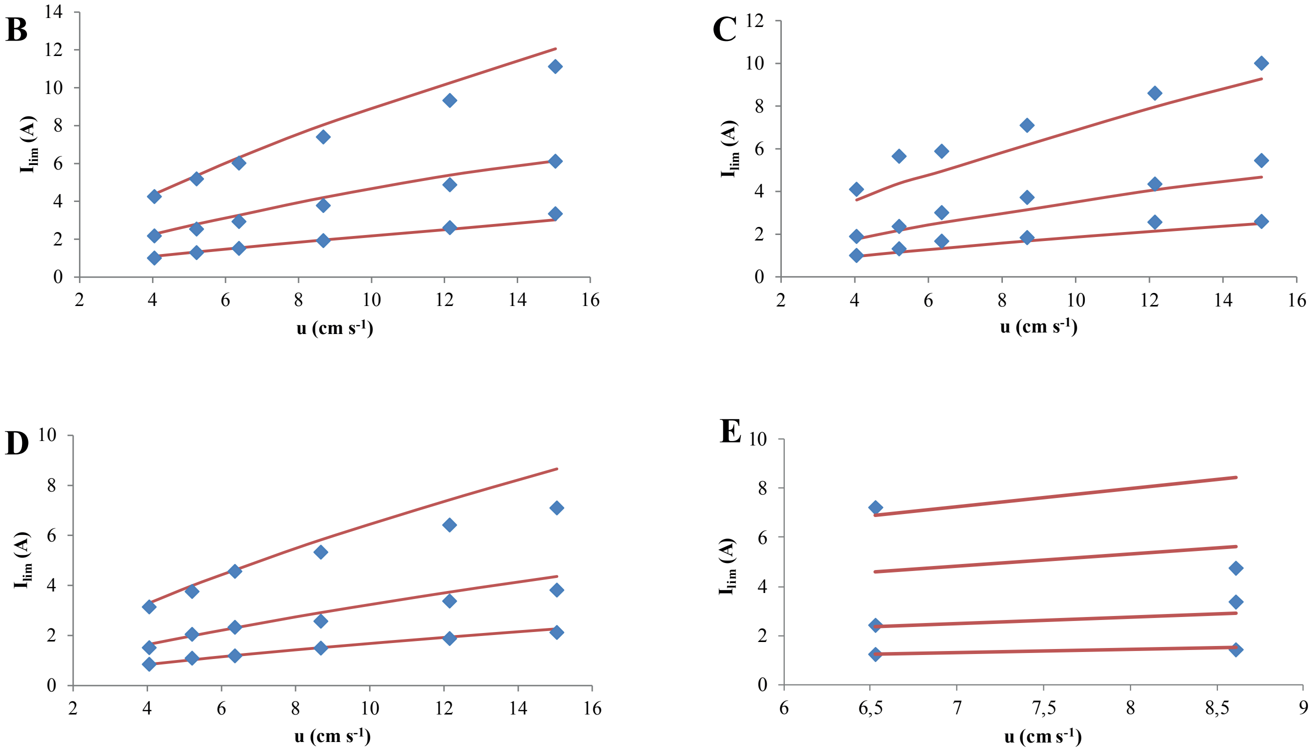


Fig. 4. Agreement between experimentally determined limiting currents (♦) and limiting currents calculated by proposed method (full line; single lines are for different electrolyte concentrations) for A sodium chloride, B ammonium nitrate, C sodium sulfate, D calcium nitrate and E magnesium sulfate

4 Conclusions

The current-voltage curves were measured in a broad range of experimental electrodialysis conditions in order to determine the limiting currents using pilot-scale ED module. Limiting current is an important process parameter because working in overlimiting regions could cause undesirable pH changes and current efficiency decrease. Five electrolytes of different types (1:1, 1:2, 2:1, 2:2) were tested, and diluate linear flow velocity and inlet concentration were changing through the experiments. In each case, the limiting current was determined using derivative method and then mass transfer coefficient and diffusion layer thickness were calculated. By this manner, dependences of the mass transfer coefficient k and diffusion layer thickness δ on linear flow velocity u were obtained for all five electrolytes. Parameters of dependence $k=au^b$ were estimated and their relationship with electrolyte properties evaluated. The clear connection of parameter a with electrolyte diffusion coefficient and the difference of cation transport numbers in membrane and solution was observed, which is the main benefit of this work. Based on these results the method for limiting current calculation was proposed, and its agreement with experimental data was recognized as satisfying. The proposed method could be used for any electrolyte and in a broad range of process variables.

Acknowledgement

The work was supported by the Ministry of Industry and Trade of the Czech Republic within the framework of the project “Research, development and application of new generation electromembrane modules” program TIP No. FR-TI4/398, using the infrastructure of the Membrane Innovation Centre (No.CZ 1.05/2.1.00/03.0084).

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