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# Mathematical sigmoid-model approach for the determination of limiting and over-limiting current density values

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## ABSTRACT

The effect of successive limiting current density (LCD) determination procedures on electro dialysis with ultrafiltration membrane (EDUF) system was studied in order to evaluate their impact on ion-exchange (IEM) and ultrafiltration membranes (UFM) integrity by measuring *in situ* the membrane potential difference. In the first protocol, two successive LCD determination procedures were carried-out by increasing the voltage by 2 V from 0 to 40 V, spaced by a rest period of 60 min. In the second protocol, the LCD determination procedures were performed every 20 min during 60 min. For both protocols, voltage-current curves were plotted for IEM and UFM and  $I_{lim}$  values were determined. Results showed that only anion-exchange membrane (AEM) showed a typical sigmoidal curve for both protocols. Moreover, it was demonstrated that a rest time period of 60 min between two successive LCD determination procedures had no impact on system current density and membrane potential difference while four successive LCD determinations spaced by a constant rest period of 20 min allowed delaying the appearance of  $I_{lim}$  and over-limiting current region. A mathematical sigmoid-model approach was also proposed allowing for the first time the calculation of the different parameters typical of water splitting phenomenon from a voltage-current curve.

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## 1. Introduction

Electrodialysis (ED) is defined as an electrochemical separation process used to separate ionic species from an aqueous solution and other uncharged components [1]. Several design parameters such as feed flow velocities, ion concentrations and stack design affect the performance of ED system and contribute to the appearance of concentration polarization phenomenon at the surface of ion-exchange membranes (IEM) resulting in the appearance of limiting current density (LCD) [2]. During conventional electro dialysis experiment, LCD appears since the concentration of ion species at the surface of the cation-exchange membrane (CEM) and/or anion exchange membranes (AEM) in the depleted solution (diluate) compartment reached zero [3]. Consequences of LCD

phenomenon are water molecule dissociation, salt precipitation and drastic changes of ED system performances [4]. Consequently, LCD represents a key parameter to control and, its determination before ED experiments is primordial.

In this context, practical and mathematical methods were developed and used to determine or estimate the limiting current density value ( $I_{lim}$ ). Hence, Cowan and Brown [5] proposed a graphical method to determine the LCD value by quickly increasing the voltage applied to the electrodes of the electro dialysis system and recording the corresponding current density. The global system resistance was then plotted *versus* the reciprocal of the current intensity ( $1/I$ ). At the inflection point on this graph, the current intensity divided by the membrane area is considered as the  $I_{lim}$  value of the system. Another method, reported in the literature [6–10] consists in plotting typical current-voltage data to determine graphically the  $I_{lim}$  value. The curve could be separated into three specific regions. Region I represents a linear relationship between current and voltage and referred to the ohmic region. Region II, named limiting current region, is characterized by a plateau caused by ion-depletion in the hydrodynamic boundary layer. Finally, region III is followed by the electro-convection or over-limiting current region (OLCR) (region III) in which the slope of the current-potential curve increases again [6–10]. For this type of curve,  $I_{lim}$  value is the inflection point

**Abbreviations:** AEM, anion-exchange membrane; CEM, cation-exchange membrane; ED, electro dialysis; EDUF, electro dialysis with ultrafiltration membranes; IEM, ion-exchange membrane; LCD, limiting current density; LCR, limiting current region; MWCO, molecular weight cut-off; OLCR, over-limiting current region; UFM, ultrafiltration membrane

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of the two slopes belonging to the ohmic and the plateau region [8,11–14]. The mathematical approach used for the determination of  $I_{lim}$  of an ion-exchange membrane (AEM or CEM) is based on the Nernst-diffusion model and is represented as

$$I_{lim} = \frac{FDC}{\delta(\bar{t}_i - t_i)} \quad (1)$$

where  $F$  represents the Faraday constant ( $A \text{ s eq}^{-1}$ ),  $D$  the salt diffusion coefficient,  $C$  the bulk solution concentration,  $\delta$  the diffusion boundary layer thickness,  $\bar{t}_i$  the electromigration number of counter ion in the membrane and  $t_i$  the transport number in the solution [12,15]. However, in practice, it is very difficult to determine the thickness of the diffusion boundary layer ( $\delta$ ) but some methods, such as chronopotentiometry [16], laser interferometry [17] or optical systems [18], were successfully used to observe and characterize it.

Although observed for conventional ED, LCD impact on electro-dialysis with ultrafiltration membranes (EDUF) system is still unknown. Indeed, typically before EDUF experiments, a constant voltage difference was determined according to the Cowan and Brown method [5] to limit water splitting and pH fluctuations. In addition, the impact of successive LCD determination procedures on IEM and UFM stacked in an ED or EDUF system has never been studied. Consequently, the objectives of the present work were (1) to apply successive LCD determination procedures on EDUF system with constant rest times, (2) to evaluate the impact of these successive LCD determination procedures on IEM and UFM integrity and (3) to propose a mathematical model allowing the calculation of  $I_{lim}$  value and other parameters.

## 2. Materials and methods

### 2.1. Chemicals

HCl and NaOH 1.0 M solutions were obtained from Fisher Scientific (Montreal, QC, Canada). NaCl and  $\text{Na}_2\text{SO}_4$  were purchased from Laboratoire MAT (Québec, QC, Canada). KCl was purchased from ACP Inc (Montreal, QC, Canada).

### 2.2. Raw material

The snow crab by-products hydrolysate was obtained from Merinov (MAPAQ, Gaspé, QC, Canada). The hydrolysate was elaborated according to a procedure described previously [19]. The initial concentration of peptides in the snow crab hydrolysate was 100 g/L (10% w/w). The water content was 87%, ash was 2.12% and lipids were below detection level.

### 2.3. Electrodialysis cells and configuration

The electrodialysis (ED) cell used was a EUR-2C cell (200  $\text{cm}^2$  of effective surface area) manufactured by Eurodia Company (Wis-sous, France). The EDUF cell configuration was the same as the one described by Doyen et al. [20]. Briefly, the cell configuration consisted of three Neosepta CMX-SB cationic membrane (Tokuyama Soda Ltd, Tokyo, Japan), one Neosepta AMX-SB anionic membrane (Tokuyama Soda Ltd, Tokyo, Japan) and six polyether-sulfone ultrafiltration membranes (UFMs) with molecular weight cut-off (MWCO) of 20 kDa (GE, France) (Fig. 1). The compartments defined four closed loops containing the feed solution (snow crab hydrolysate), a potassium chloride solution (2 g/L KCl) for the recovery of anionic (compartment named KCl1) or cationic peptides (compartment named KCl2) and an electrolyte solution (20 g/L  $\text{Na}_2\text{SO}_4$ ) for rinsing both electrode compartments. Each closed loop was connected to a separate external reservoir to allow

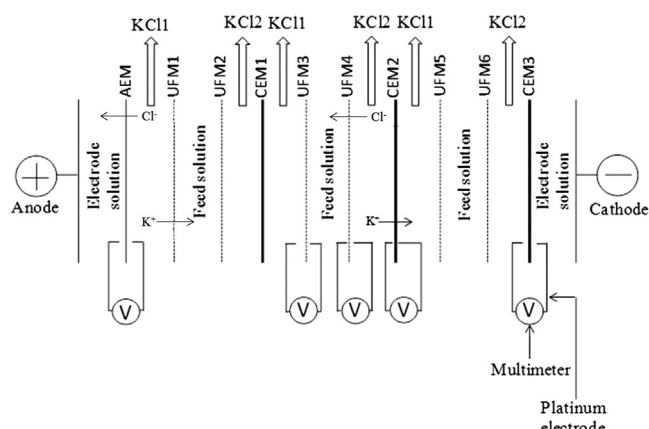


Fig. 1. Configuration of the electro-dialysis with ultrafiltration membranes cell. UFM: ultrafiltration membrane. AEM: anion-exchange membrane. CEM: cation-exchange membrane.

continuous recirculation of the solutions. The KCl and feed solution flow rates were 1 L/min while the flow rate of the electrode solution was 3 L/min.

### 2.4. Potential difference measurements

Electrical potential difference measurements during EDUF experiments were performed according to Doyen et al. [20] and Ling Teng Shee et al. [21]. Briefly, five platinum (Pt) electrodes pairs (GoodFellow, Huntingdon, UK), covered with silver at their ends, were disposed at membrane interfaces (Fig. 1). The ends of electrodes were in contact with the different membranes. Each Pt electrode pair was connected to a digital multimeter.

### 2.5. Limiting current density measurements

Two protocols were used to determine the effect of successive LCD determination procedures on IEMs and UFMs integrity. The first protocol, repeated three times, was achieved by increasing the voltage by 2 V from 0 to 40 V. At every voltage increment, the electrical potential differences of IEM and UFM and the corresponding intensity values were recorded. Afterwards, the EDUF system was left to rest during 60 min and another LCD determination procedure was performed as previously. The second protocol, also repeated three times, was the same as the previously described except for LCD determination procedure which was performed every 20 min during 60 min. For both protocols, electro-separations were performed at pH 9 since this value allowed the highest peptide recovery [20]. The pH of hydrolysate and permeate solutions (KCl1 and KCl2) was adjusted at pH 9 before each run with 1.0 M NaOH and maintained during EDUF process to avoid retromigration phenomenon. Finally, new snow crab by-products hydrolysate and KCl solutions were used after each repetition for both protocols.

### 2.6. Statistical analyses

The current densities and membrane potential differences obtained at 0 and 60 min during the first experiment were subjected to a nonparametric comparisons  $t$ -test ( $P < 0.05$  as probability level for acceptance) while these parameters obtained at 0, 20, 40 and 60 min for the second experiment were subjected to a repeated measure analysis of variance (ANOVA, LSD (Least Significant Difference)  $P < 0.05$  as probability level for acceptance) using SAS software version 9.1 (SAS Institute Inc, Cary, North Carolina, USA). Finally,  $I_{lim}$  and  $I_{olc}$  values determined by the

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