Modelling The Electrodialytic Recovery
of Sodium Itaconate

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The mathematical model and experimental procedure, previously developed to describe
the electrodialytic (ED) recovery of the sodium salts of some mono-carboxylic acids
from aqueous solutions, were slightly modified to determine the effective process and
design parameters of ED stacks directed to recover the sodium salt (Na₂Itac) of a bi-
carboxylic acid, i.e. itaconic acid.

1. Introduction

Electrodialysis (ED) is a unit operation for the separation or concentration of ions in
solutions based on their selective electromigration through semi-permeable membranes.
Its largest area of application is in the desalination of brackish water for the production
of potable water and de-ashing of milk whey (Fidaleo and Moresi, 2006a).

Itaconic acid (HOOC-CH=CH-COOH, C₅H₄O₄) is used as monomer or co-monomer for
plastics, resins, synthetic fibres and elastomers (Milson and Meers, 1985) and it is
produced by submerged culture fermentation with Aspergillus terreus in a medium
containing molasses as the sugar source at 32-40°C and pH of 1.8-4.0 under 0.25 to 0.5
volumes of air per volume of medium per minute for 48-72 h (Milson and Meers, 1985).

Use of ED was suggested to enhance the mycelial itaconate productivity in wood waste-
(Kobayashi, 1967, 1978; Nakagawa et al., 1975), pretreated beet juice- or molasses-
(Nakagawa et al., 1991) based media.

The aim of this work was to extend the mathematical model and experimental procedure
previously set up for the recovery of some target sodium salts of mono-carboxylic acids
(Fidaleo and Moresi, 2004, 2005b, 2006b) to the recovery of sodium itaconate to
determine all the engineering parameters needed to design and optimise ED units
dedicated to the downstream processing of itaconic acid fermentation broths.

2. Materials and Methods

A laboratory-scale electrodialyser (Aqualyzer P1, Corning EIVS, Le Vesinet, F),
previously described (Fidaleo and Moresi, 2005a), was used. Several batch recycle runs
were carried out by varying electric current intensity (I=0.75, 1.5 A) under constant feed
solute concentration (cᵢ=55 g Na₂Itac dm⁻³), superficial velocity (vₛ=5.9 cm s⁻¹), and
temperature (T=20°C). The feed solution was prepared by dissolving itaconic acid with

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deionised water and adding the corresponding stoichiometric amount of NaOH, this solution being also used as the electrode rinsing one. The instantaneous Na$_2$Itac concentrations ($c_i$) in the diluting (D) and concentrating (C) streams were indirectly estimated by measuring the electric conductivity ($\chi$) at 20°C with a WTW conductivity meter mod. Inolab Cond Level 1. Limiting current tests at 20 °C were performed to plot voltage (E)-current (I) curves using stacks composed of 19 cation- (CMV) or 19 anion- (AMV) exchange membranes by varying $c_i$, I and $v_S$ in the ranges of 0.7-43.4 g dm$^{-3}$, 0.04-5 A, 5.9-10.9 cm s$^{-1}$ respectively.

3. **Results and discussion**

3.1 **Determination of ion transport numbers in solution**

The primary current-carrying species for the binary electrolyte sodium itaconate (Na$_2$Itac) were supposed to be sodium (Na$^+$) and itaconate (Itac$^-$) ions. The equivalent conductivity ($\lambda$) was expressed as a function of the square root of the salt molar concentration ($\sqrt{C}$) by using the Kohlrausch limiting law:

$$\lambda = \frac{Z}{\nu \sqrt{C}} = \lambda_0 - b \sqrt{C}$$

(1)

with

$$\lambda_0 = \lambda_{o^+} + \lambda_{o^-}$$

(2)

where $\nu$ (=1) and $Z$ (=2) are the stoichiometric and charge number for the Itac$^-$ anion. The least squares method was used to fit $\lambda$ against $\sqrt{C}$ (Fig. 1), thus allowing the equivalent conductance at infinite dilution ($\lambda_0$=9.25±0.07 S m$^{-1}$ kmol$^{-1}$) at 20°C to be estimated. By extracting the Na$^+$ equivalent conductance at infinite dilution at 20°C ($\lambda_{o^+}$=4.495 S m$^{-1}$ kmol$^{-1}$) from Prentice (1991), it was possible to calculate the transport number for the Na$^+$ ion as equal to 0.49 and that for the Itac$^-$ one as 0.51, because the sum of the transport numbers must be equal one.

![Figure 1](image.png)

**Figure 1** Equivalent conductance of Na$_2$Itac at 20°C vs $\sqrt{C}$.

3.2 **Mass and volume balances in an ED system**

The differential mass and volume balances in the dilute (D) and concentrated (C) tanks of the electrodialyzer unit can be written as follows:
\[ \frac{d(C_j V_j)}{dt} = \frac{d(C_k V_k)}{dt} - (t_e^+ - t_a^-) \frac{1}{F} N = (t_e^+ - t_a^-) \frac{1}{F} N = \frac{1}{F} N \]  

\[ \frac{dV_c}{dt} = - \frac{dV_d}{dt} = - \frac{\tau}{F} N \]  

where \( t_e^+ \) and \( t_a^- \) are the cation and anion transport numbers in cation and anion-exchange membranes; \( t_e \) and \( t_a \) the effective solute and water transport numbers; \( V_w \) is the water molar volume; \( C_c \) and \( C_d \) are the instantaneous molar concentrations of NaCl in tanks C and D, while \( V_c \) and \( V_d \) the corresponding volumes; \( \tau \), I, N and F are the process time, current intensity, number of cells (each one being composed of a couple of compartments), and Faraday constant (~96,500 C mol\(^{-1}\)), respectively. By plotting the net increment (or decrement) in C or D solute (\( \Delta n \)) or water (\( \Delta n_w \)) masses vs. the number of moles of elementary electrical charge transferred (\( n_i \)), as shown in Fig. 2, it was possible to estimate \( t_e \) and \( t_a \), these being equal to 0.970±0.004 and 12.9±0.1, respectively.

![Figure 2](image_url)  

**Figure 2** Net increment or decrement in C (closed symbols) or D (open symbols) solute (a) and water (b) masses vs. the moles of elementary electrical charge transferred (\( n_i \)) at \( v_s = 5.9 \text{ cm s}^{-1}, 20^\circ \text{C} \) and different current intensities (○: I=0.75 A; □, ■: I=1.5 A).

### 3.3 Overall potential drop across an ED stack

The overall stack voltage (E) may be written as a sum of several terms (Fidaleo and Moresi, 2005a, b), that is:

\[ E = E_{\text{el}} + R_{\text{er}} \Delta I + \{ E_j + E_D + [R_{\text{bs}} + R_{\text{ls}} + R_{\text{c}} + R_{\text{s}}] I \} \]  

where \( E_{\text{el}} \) is the thermodynamic potential and overpotential of electrodes; \( E_j \) the junction potential difference across boundary layers, \( E_D \) the Donnan potential difference; \( R_{\text{er}} \), \( R_{\text{bs}} \), and \( R_{\text{s}} \) are the electric resistances of the electrode rinsing solution, C and D bulk solutions and boundary layers, respectively; \( R_{\text{c}} \) and \( R_{\text{ls}} \) are the AMV and CMV membrane resistances. Any of the ohmic resistances (\( R_{\text{s}} \)) can be estimated by applying the 2\(^{nd}\) Ohm’s law:

\[ R_{\text{s}} = \int_{x}^{x'} \frac{ds'}{a} \]
where a is the effective surface area involved in the ion flow pattern while \( \chi \) and s are the electric conductivity and thickness of the electrolyte solution involved.

### 3.4 Limiting current tests

A series of E-I experiments using CMV or AMV membranes allowed the limiting current intensity (I_{lim,c} or I_{lim,a}) and overall stack resistance to be determined (Cowan and Brown, 1959). By plotting \( I_{lim,c} \) or \( I_{lim,a} \) vs. the solute concentration (C), two linear graphs were obtained (Fig. 3a), the ratio between their corresponding slopes \( I_{lim,c}/I_{lim,a} = (t_c^{-1} - t^{-1})/((t_a^{-1} - t^{-1}) \) being equal to 1.22. This allowed the ion transport numbers in AMV and CMV membranes to be evaluated (Krol et al., 1999) as follows: \( t_c^{-1} = 1.02 \) and \( t_a^{-1} = 0.95 \). Therefore, the current within the electro-membranes is almost exclusively carried by the counter ions, even if the anion-exchange membranes appear to be less selective than the cation-ones. For \( v_s \) ranging from 5.9 to 10.9 cm s\(^{-1}\), E-I curves were coincident and linear with constant intercepts (i.e. \( E_{eq} = 2.6 \) V) and slopes for 1<0.75 \( I_{lim} \), this being an indirect confirmation of negligible contribution of solute polarisation.

By neglecting the contribution of \( E_f, E_p \) and \( R_b \), the overall potential drop across an ED stack consisting of only anion- or cation-exchange membranes can be derived from Eq. (5) and (6) as:

\[
E = E_{eq} + \left[ R_b N_b + R_a (N_k - 1) + 2 R_{ERS} \right] \frac{I_a}{I_c}
\]  

(7)

where \( R_b \) and \( N_k \) are the resistance and overall number of the generic k-th electro-membrane used. Eq. (7) was used to evaluate the apparent membrane pack resistance (\( R_{MP} \)) as

\[
R_{MP} = \frac{E - E_{eq}}{I_c} \frac{2 R_{ERS}}{a_c} = R_b + \frac{h (N_k - 1)}{a_m c} \frac{1}{\chi}
\]  

(8)

In the circumstances, \( R_{MP} \) should be a linear function of the inverse of the bulk-solution electrical conductivity (\( \chi \)), its intercept and slope being proportional to the electro-membrane resistance (\( R_b \)) and membrane gap per unit effective membrane surface area (\( h/a_m \)), respectively.

As shown in Fig. 3b, such a linear pattern held for both the anion- and cation-exchange membrane packs.

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**Figure captions:**

**Figure 3a:** Plots of \( I_{lim,c} \) vs. \( C \) for CMV and AMV membranes.

**Figure 3b:** Plot of \( R_{MP} \) vs. \( \chi^{-1} \) for both anion- and cation-exchange membranes.
Figure 3: Main results of limiting current tests referred to CMV (●) or AMV (○) membranes: (a) limiting current intensity ($i_{lim}$) vs. solute molar concentration (C) and (b) electrical resistance of membrane pack ($R_{MP}$) vs. the reciprocal of conductivity ($\chi$).

Thus, use of the least squares method to fit the cationic membrane set of data yielded the following couple of unknown parameters:

$$R_c = 0.19 \pm 0.02 \ \Omega; \ a_{me} = 51.7 \ cm^2.$$

It can be noted that the effective membrane surface area ($a_{me}$) was 16% greater than the exposed surface area of electrodes ($a_i=44.6 \ cm^2$) and significantly different from the geometrical membrane surface area ($a_{me}=72 \ cm^2$), but in line with the values recently reported for the same electrodialyzer by Fidaleo and Moresi (2004, 2005a, 2005b, 2006b). Once the membrane gap per unit effective membrane surface area ($b/a_{me}$) had been assessed, it was possible to calculate the anionic membrane resistance ($R_a$) as a function of $\chi$ and observe that $R_a$ hyperbolically decreased from 2.1 to 0.5 $\Omega$ as $\chi$ was increased from 0.5 to 12 S m$^{-1}$ (this corresponding to a solute concentration ranging from 0.0038 to 0.1 kmol m$^{-3}$). The least squares fitting of $R_a$ vs. ($1/\chi$) data via the following equation:

$$R_a = R_{k,c} \times k/\chi \quad (9)$$

allowed the couple of unknown parameters $R_{k,c}$ and $k$ to be estimated as 0.57 $\Omega$ and 0.07 $\Omega$ S m$^{-1}$, respectively.

3.5 Prediction of the voltage applied to the membrane pack

As an example, the above model and design parameters ($t_i$, $R_c$, $R_a$, $a_{me}$) were used to predict the instantaneous voltage applied to the membrane pack ($E_{MP}=E_{ct}-R_{ct}I$) for a batch desalination under $I=0.75 \ A$, $C_i=5.9 \ cm \ s^{-1}$ and $T=20^\circ C$. Fig. 4 shows quite a satisfactory agreement between the experimental and calculated $E_{MP}$ values against the diluting compartment conductivity ($\chi_D$).

![Figure 4](image)

**Figure 4** Comparison between the experimental (○) and calculated (-) voltage applied to the ED membrane pack ($E_{MP}$) as a function of the experimental conductivity in the
diluting compartment (\(\chi_0\)) throughout a desalination run performed at \(I=0.75\ \text{A}, \ \nu_e=5.9\ \text{cm s}^{-1}\) and \(T=20^\circ\text{C}\).

4. Conclusions

The sequence of independent experimental trials (such as solute- and water-transfer, and limiting-current tests) and the mathematical modelling, previously set up to assess the main process and design parameters of ED stacks dedicated to the recovery of the sodium salts of some mono-carboxylic acids (Fidaleo and Moresi, 2006a), was slightly modified to estimate the itaconate anion transport number and anionic membrane resistance and yielded quite a satisfactory prediction of the ED recovery of sodium itaconate.

5. References