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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 (Na_2Itac) 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, $C_4H_4O_4$) 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 ($c_F \approx 55$ g Na_2Itac dm^{-3}), superficial velocity (v_S=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_2Itac concentrations (c_i) in the diluting (D) and concentrating (C) streams were indirectly estimated by measuring the electric conductivity (χ) 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_F, 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_2Itac) were supposed to be sodium (Na^+) and itaconate ($Itac^=$) ions. The equivalent conductivity (Λ) was expressed as a function of the square root of the salt molar concentration ($\sqrt{C}$) by using the Kohlrausch limiting law:

$$\Lambda = \frac{\chi}{\nu^- |z^-| C} = \Lambda^0 - b\sqrt{C} \quad (1)$$

with

$$\Lambda_o = \lambda_o^+ + \lambda_o^- \quad (2)$$

where ν^- (=1) and z^- (=-2) are the stoichiometric and charge number for the $Itac^=$ anion. The least squares method was used to fit Λ against $\sqrt{C}$ (Fig. 1), thus allowing the equivalent conductance at infinite dilution (Λ_0=9.25±0.07 S m^2 $kmol^{-1}$) at 20°C to be estimated. By extracting the Na^+ equivalent conductance at infinite dilution at 20°C (λ_o^+=4.495 S m^2 $kmol^{-1}$) 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.

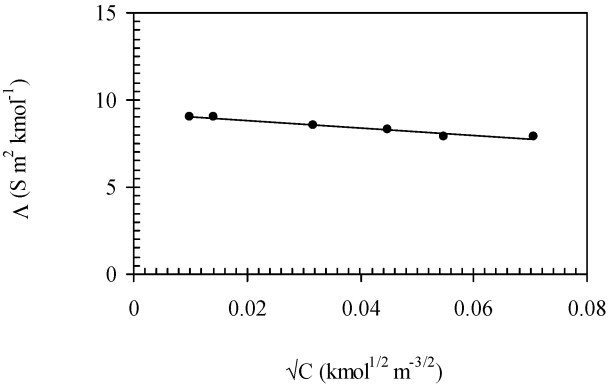

Figure 1 Equivalent conductance of Na_2Itac at 20°C *vs* $\sqrt{C}$.

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:

$$\frac{d(C_C V_C)}{d\tau} = -\frac{d(C_D V_D)}{d\tau} = (t_c^+ - t_a^+)\frac{I}{|z^-|F}N = (t_a^- - t_c^-)\frac{I}{|z^-|F}N = t_s\frac{I}{|z^-|F}N \quad (3)$$

$$\frac{dV_C}{d\tau} = -\frac{dV_D}{d\tau} = t_W V_W \frac{I}{F}N \quad (4)$$

where $t^{\pm}_c$, $t^{\pm}_a$ are the cation or anion transport numbers in cation and anion-exchange membranes; t_s and t_W 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 Na_2Itac in tanks C and D, while V_C and V_D the corresponding volumes; τ, 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 (Δn) or water (Δn_W) masses *vs.* the number of moles of elementary electrical charge transferred (n_F=NI τ/F), as shown in Fig. 2, it was possible to estimate t_s and t_W, these being equal to 0.970±0.004 and 12.9±0.1, respectively.

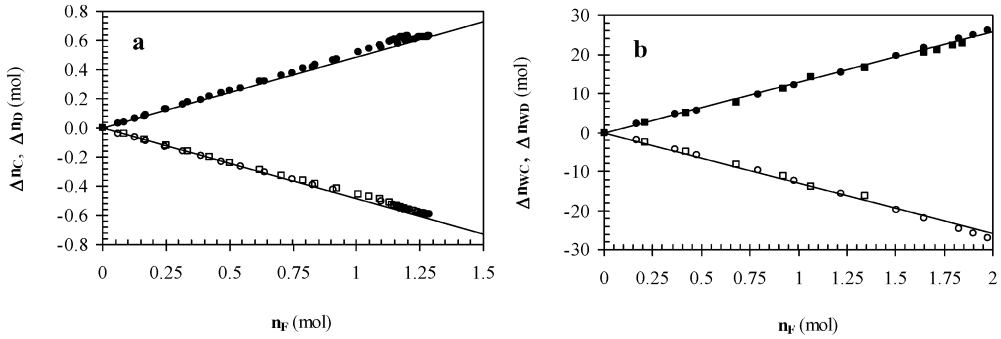

Figure 2 Net increment or decrement in C (closed symbols) or D (open symbols) solute (**a**) and water (**b**) masses *vs.* the moles of elementary electrical charge transferred (n_F) at v_S= 5.9 cm s^{-1}, 20°C and different current intensities (○,●: I=0.75 A; □,■: I=1.5 A).

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,), that is:

$$E = E_{el} + R_{ers}I + N\{E_j + E_D + [R_{bs} + R_{fs} + R_a + R_c]\, I\} \quad (5)$$

where E_{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_{ers}, R_{bs}, and R_{fs} are the electric resistances of the electrode rinsing solution, C and D bulk solutions and boundary layers, respectively; R_a and R_c are the AMV and CMV membrane resistances. Any of the ohmic resistances (R_k) can be estimated by applying the 2nd Ohm's law:

$$R_k = \int_0^s \frac{ds'}{\chi a} \quad (6)$$

where a is the effective surface area involved in the ion flow pattern while χ 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 $I_{lim,a}/I_{lim,c}=(t^+_c-t^+)/(t^-_a-t^-)$ 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: $t_c^+= 1.02$ and $t_a^-=0.95$. 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.* $E_{el}\approx 2.6$ V) and slopes for $I<0.75\ I_{lim}$, this being an indirect confirmation of negligible contribution of solute polarisation.

By neglecting the contribution of E_j, E_D and R_{fs}, 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:

$$E=E_{el}+[R_kN_k+R_b(N_k-1)+2R_{ERS}]I \qquad (7)$$

where R_k 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

$$R_{MP}=\frac{E-E_{el}}{I}-\frac{2\ h_{ERS}}{a_E\ \chi_{ERS}}=R_k\ N_k+\frac{h\ (N_k-1)}{a_{me}}\frac{1}{\chi} \qquad (8)$$

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

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

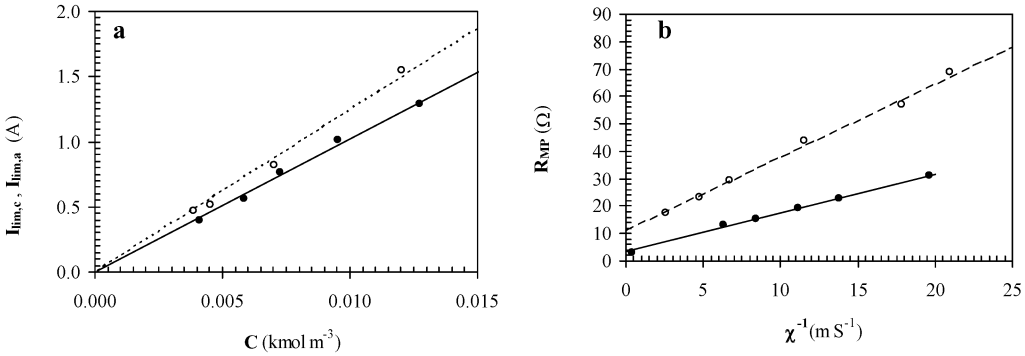

Figure 3: Main results of limiting current tests referred to CMV (•) or AMV (○) membranes: (**a**) limiting current intensity (I_{lim}) *vs*. solute molar concentration (C) and (**b**) electrical resistance of membrane pack (R_{MP}) *vs.* the reciprocal of conductivity (χ).

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_E=44.6 cm^2) and significantly different from the geometrical membrane surface area (a_{mg}=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 (h/a_{me}) had been assessed, it was possible to calculate the anionic membrane resistance (R_a) as a function of χ and observe that R_a hyperbolically decreased from 2.1 to 0.5 Ω as χ 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:

$$R_a = R_{a,\infty} + k/\chi \qquad (9)$$

allowed the couple of unknown parameters $R_{a,\infty}$ and k to be estimated as 0.57 Ω and 0.07 Ω 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_s, R_a, R_c, a_{me}) were used to predict the instantaneous voltage applied to the membrane pack ($E_{MP}=E-E_{el}-R_{ers}I$) for a batch desalination under I=0.75 A, v_s=5.9 cm s^{-1} and T=20°C. Fig. 4 shows quite a satisfactory agreement between the experimental and calculated E_{MP} values against the diluting compartment conductivity (χ_D).

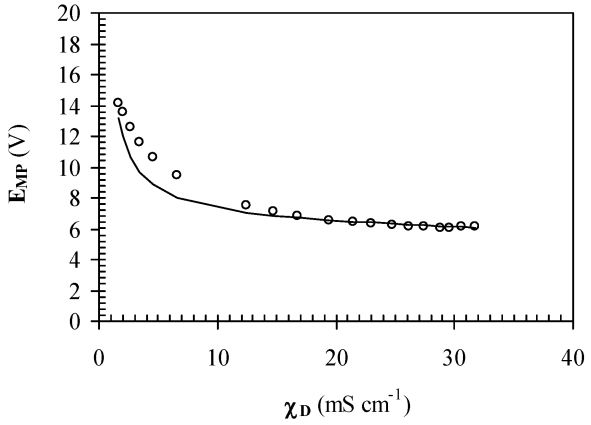

Figure 4 Comparison between the experimental (○) and calculated (-) voltage applied to the ED membrane pack (E_{MP}) as a function of the experimental conductivity in the

diluting compartment (χ_D) throughout a desalination run performed at I=0.75 A, v_s=5.9 cm s^{-1} and T=20°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

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