

Analysis of the Electrodialytic Recovery of Trisodium Citrate

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By applying sequentially the same experimental procedure formerly developed and based on the Nernst-Planck approach, it was possible to reconstruct the electrodialytic (ED) recovery of trisodium citrate.

The membranes exhibited an almost ideal behaviour and only the citrate anions carried the electric charge passing through the anionic membranes. By performing several voltage-current, electro-osmosis and desalination tests, it was possible to assess in sequence the limiting electric currents and resistances of the anionic and cationic membranes, the transport numbers for anion and cation in the solution and membranes, and for solute and water. Whereas the electric resistance (R_c) of the cationic membranes was found to be approximately constant ($0.15 \pm 0.06 \Omega$) and independent of solute concentration, that for the anionic ones was not only greater than R_c , but also a logarithmic function of the solution electric conductivity in D compartment. Provided that the current applied was less than 2/3 of the limiting current corresponding to the cationic membrane ($i_{lim,c}$), the basic engineering parameters enabled the time course of the voltage applied to the ED stack to be reconstructed with a mean percentage error of 17.5%.

1. Introduction

A potentially interesting sector for the application of electrodialysis (ED) is that of the fermentation industry, especially when the main product of the microbial metabolism is an electrolyte. This may exert an inhibitory effect on cell growth and/or metabolite production in either its free or dissociated form. Alternatively, it may be dissolved in media rich of impurities that are to be removed via numerous and expensive purification steps (Fidaleo and Moresi, 2006a).

Commercial exploitation of electrodialysis to recover lactic acid from microfiltered fermentation broths was reported by Bailly (2002) as an environmentally-friendly process to avoid virtually gypsum waste formation and to yield a polymer-grade monomer to be further converted into biodegradable thermoplastics (i.e., polylactic acid).

Also the environmental impact of citric acid production is burdened by the formation and disposal of enormous amounts of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ (i.e., ~ 2 kg per kg of citric acid monohydrated).

Citric acid recovery by ED was early proposed by Voss in 1986 (Ling et al., 2002). The specific energy consumption depended on the membranes used and was about 1.7-2 kWh or 0.3-0.9 kWh per kg of citrate recovered in the case of bipolar (Novalic et al., 1996) or monopolar (Datta and Bergemann, 1996; Sappino et al., 1996; Ling et al., 2002, Novalic et al., 1995) membranes.

Free citric acid (H_3R) cannot be efficiently recovered by ED owing to its low electric conductivity (Novalic et al., 1995), unless it is converted into the monovalent H_2R^- (at $\text{pH} \cong 3$), divalent HR^{2-} (at $\text{pH} \cong 5$), or trivalent R^{3-} (at $\text{pH} \cong 7$) anion. The recovery of R^{3-} resulted to be by far less expensive than that of the other ionic fractions of sodium citrate (Moresi and Sappino, 1998, 2000).

Aim of this work was to apply the mathematical model and experimental procedure previously set up for the ED recovery of some sodium salts of mono- and di-protic acids of fermentation origin (Fidaleo and Moresi, 2004, 2005ab, 2006b, 2009, 2010) to determine the engineering parameters needed to design and optimise ED stacks directed to recover trisodium citrate.

2. Materials and Methods

A laboratory-scale electrodialyser (Aqualyzer P1, Corning EIVS, Le Vesinet, F), previously described (Fidaleo and Moresi, 2010) was used. It was equipped with 2 graphite electrodes and a sheet-flow stack containing $N_c (=9)$ cation- (CMV) and $N_a (=10)$ anion- (AMV) exchange membranes (Asahi Glass Co. Ltd, Chioda-ku, Tokyo, Japan), separated by spacer gaskets to ensure a flow parallel to the membranes themselves. The top and bottom of the membrane stack were closed by 20.9-mm thick plastic bases with 9 almost rectangular openings. Thus, the overall exposed surface area of the electrodes (a_E) was equal to 44.56 cm², while the geometrical surface area of the membranes (a_{mg}) was 72 cm².

The direct current (D.C.) generator could supply voltage (E) and current (I) in the ranges of 0-60 V and 0-5 A, respectively. The dilute (D), concentrated (C) and electrode rinsing solution (ERS) were stocked into three 1.6-dm³ PVC tanks and re-circulated through the ED stack by means of 3 polypropylene centrifugal pumps. Each tank was equipped with a 2-m high Plexiglas tube provided with a millimetre scale to assess precisely volume variation in C and D tanks. As reported previously (Fidaleo and Moresi, 2010), the membranes were routinely cleaned-in-place, the solution conductivity in C and D compartments was on-line measured, and the process temperature monitored and automatically controlled.

The feed solutions were prepared by dissolving analytical grade trisodium citrate (Na_3R) in de-ionised water to vary the salt concentration (c_B) from 0.5 to 128 kg m⁻³. The ERS was an aqueous solution of the same salt at 33-50 kg m⁻³. The electric conductivity (χ) at 20 °C of the aqueous solutions containing 1-373 kg Na_3R m⁻³ was determined by using a conductivity meter model Inolab Cond Level 1 (WTW, Germany) and empirically correlated to c_B using a polynomial function. All the experiments were carried out at $T = 20$ °C in the batch mode by recycling continuously not only the dilute (D) and concentrate (C) under constant flow rate (~ 60 dm³ h⁻¹, equivalent to a superficial velocity (v_s) of 5.9 cm s⁻¹), but also the ERS. Samples of 10-20 cm³ were withdrawn from C and D streams at regular time intervals during any trial to measure pH and then re-introduced into the respective reservoirs. Before the start of each experiment the ED membrane pack was equilibrated with the feed solution for at least 12 h. This solution was then discarded and the apparatus rinsed with deionised water. Hold-up volume for C and D compartments was estimated as equal to $\sim 0.31 \pm 0.03$ dm³.

A first series of runs (electro-osmosis tests) was carried out to measure water permeation flux. Both C and D tanks were initially charged with the same feed solution to fill partially the aforementioned Plexiglas tubes, this being re-circulated through the ED stack and corresponding reservoir till monitoring a constant electric conductivity in both tanks. The DC generator was next switched on and regulated to set the current to 0.75 A. Each trial was prolonged as long as the voltage applied increased up to 60 V. A desalination test was then performed to assess citrate permeation flux in C and D compartments. To assure perfect mixing, C and D tanks were initially fed with 1.8-1.9 dm³, these volumes being quite smaller than those used in the electro-osmosis tests. A final series of runs (current-voltage tests) was carried out to investigate the effect of c_B in the range 0.4-40 kg m⁻³ on voltage-current (E-I) curves by using an ED stack composed of 19 AMV or CMV membranes, accordingly to Fidaleo and Moresi (2010).

3. Results and discussion

3.1 Determination of ion transport numbers in solution

Citric acid is a weak acid showing three successive dissociations and three degrees of dissociation α_1 , α_2 , and α_3 , the equilibrium constants at 20 °C being (Weast and Astle, 1982): $K_1 = 7.1 \times 10^{-4}$, $K_2 = 1.68 \times 10^{-5}$, $K_3 = 4.07 \times 10^{-7}$. Thus, the electric conductivity of the solution undergoing ED might be estimated by accounting for all ionic contributions as:

$$\chi = \sum_i |z_i| C_i \lambda_i = (\alpha_1 \lambda_{H_2R^-} + 2 \alpha_2 \lambda_{HR^{2-}} + 3 \alpha_3 \lambda_{R^{3-}}) C_B + C_{H^+} \lambda_{H^+} + C_{Na^+} \lambda_{Na^+} \cong 3 (\lambda_{R^{3-}} + \lambda_{Na^+}) C_B \quad (1)$$

where λ_i is the equivalent conductance for the i -th ionic species.

When dissolving Na_3R in water, the concentrations of the ionic species and the pH of the solution depend on the salt molar concentration (C_B). By accounting for water dissociation and the 3 dissociation equilibrium reactions together with the electroneutrality and mass balance equations, the trivalent anion R^{3-} was estimated as the prevailing ionic fraction of citric acid under the conditions tested. Thus, Na_3R behaved as a strong electrolyte with $C_{Na^+} = 3 C_B$ and $C_{R^{3-}} = C_B$. Once the equivalent conductance at infinite dilution for R^{3-} ($\lambda_o^- = 6.51$ S m² kmol⁻¹) and Na^+ ($\lambda_o^+ = 4.72$ S m² kmol⁻¹) at 20 °C had been extracted from Weast and Astle (1982), it was possible to estimate the equivalent conductance at infinite dilution ($\Lambda_o = 33.69$ S m² kmol⁻¹) for Na_3R , thus determining the transport number for Na^+ ($t^+ = 0.42$) and R^{3-} ($t^- = 0.58$).

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 electro dialyzer unit can be written as follows:

$$\frac{d(C_C V_C)}{d\tau} = -\frac{d(C_D V_D)}{d\tau} = (t_c^+ - t_a^+) \frac{I}{|z^-| F} N = (t_a^- - t_c^-) \frac{I}{|z^-| F} N = t_s \frac{I}{|z^-| F} N \quad (2)$$

$$\frac{dV_C}{d\tau} = -\frac{dV_D}{d\tau} = t_w V_w \frac{I}{F} N \quad (3)$$

where t_c^+ , t_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_3R in tanks C and D, while V_C and V_D the corresponding volumes; τ , I , N and F are the process time, current, number of cell pairs, and Faraday constant ($=96,500 \text{ C mol}^{-1}$), 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 ($n_F = N I \tau / F$), as shown in Fig. 1, it was possible to estimate t_s and t_w , these being equal to 0.990 ± 0.004 ($r^2=0.9991$) and 10.88 ± 0.07 ($r^2=0.9995$), respectively.

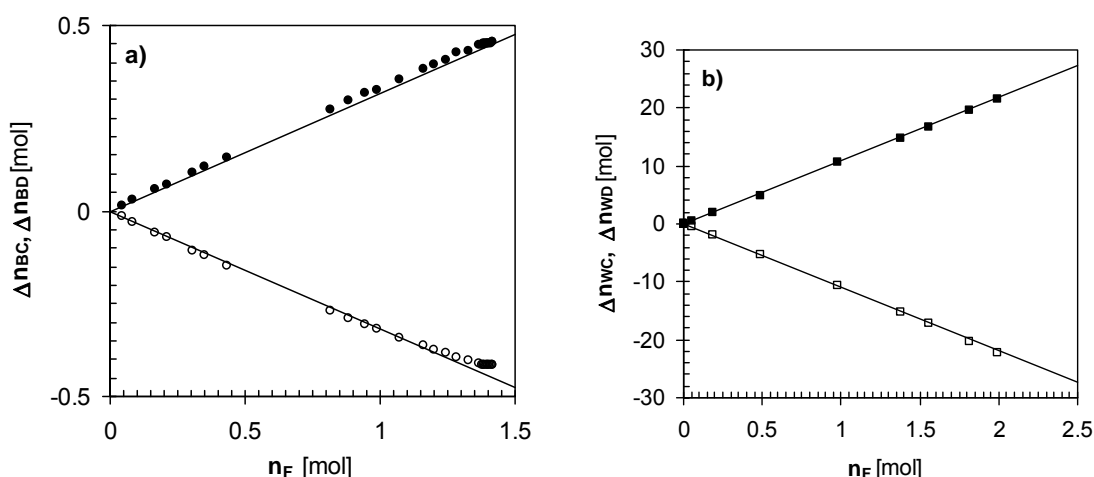


Figure 1: Net increment or decrement of citrate (a) and water (b) masses in C (closed symbols) or D (open symbols) compartments against the moles of elementary electrical charge transferred (n_F) under constant values of superficial velocity (5.9 cm s^{-1}), electric current (0.75 A) and temperature ($20 \text{ }^\circ\text{C}$).

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):

$$E = E_{el} + R_{ERS} I + N [E_j + E_D + I (R_{bs} + R_{fs} + R_a + R_c)] \quad (4)$$

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 well known 2nd Ohm's law, by accounting for the effective surface area (a_E or a_{me}) involved in the ion flow pattern.

3.4 Voltage-current tests

When the ED stack was composed of cationic membranes only, the E -vs- I curves shown in Fig. 2a displayed two different regions. In the first one (i.e., the so called ohmic region), E and I are linearly correlated. At higher currents than the limiting one ($I_{lim,c}$), the increase in E is no more linear owing to the concentration polarisation effect (Krol et al., 1999). The curves corresponding to the ED stack composed of anionic membranes (Fig. 2 b) exhibited a different behaviour: a very small linear region at $I \leq 0.2 \text{ A}$ followed by another one exhibiting a downward concavity instead of an upward one. For such solutions it

was impossible to assess the limiting current ($I_{lim,a}$), as also observed by Novalic et al. (1995). For the only curves exhibiting the upward concavity, the methods by Cowan and Brown (1959) and Rapp and Pfromm (1998) were applied to assess $I_{lim,c}$ or $I_{lim,a}$ values as a function of C_B . From Fig. 3a two linear relationships between $I_{lim,c}$ or $I_{lim,a}$ and C_B were obtained, the ratio between their corresponding slopes $I_{lim,a}/I_{lim,c} = (t_c^+ - t^+)/(t_a^- - t^-)$ being equal to 1.73. This allowed the ion transport numbers in AMV and CMV membranes to be evaluated as follows (Krol et al., 1999): $t_c^+ = 1.054$ and $t_a^- = 0.945$. Therefore, the current within the electro-membranes is almost exclusively carried by the counter ions, even if the anionic membranes appear to be less selective than the cationic ones.

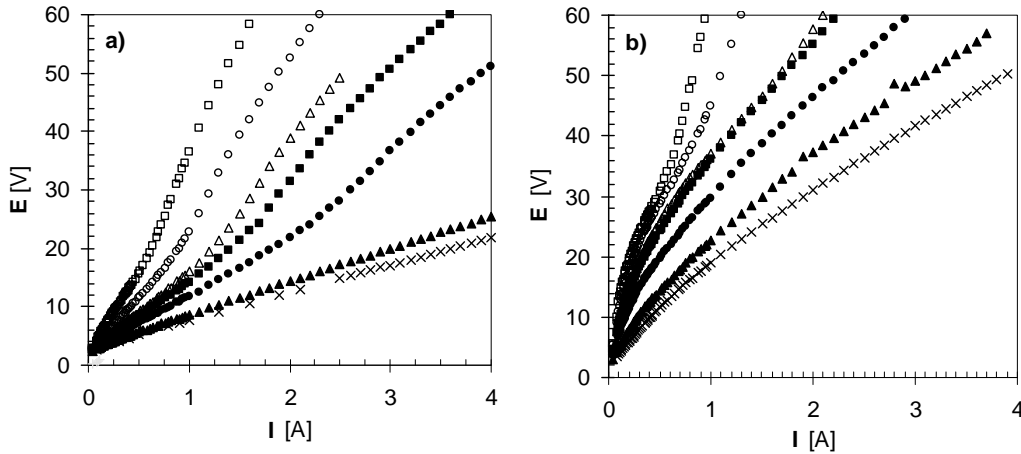


Figure 2: Voltage (E) versus current (I) when recirculating aqueous solutions of Na_3R having different electric conductivity (χ) at a superficial velocity of 5.9 cm s^{-1} and $20 \text{ }^\circ\text{C}$ through an ED stack composed of CMV (a: \square , $\chi = 0.074 \text{ S m}^{-1}$; \circ , $\chi = 0.108 \text{ S m}^{-1}$; \triangle , $\chi = 0.149 \text{ S m}^{-1}$; \blacksquare , $\chi = 0.186 \text{ S m}^{-1}$; \bullet , $\chi = 0.27 \text{ S m}^{-1}$; \blacktriangle , $\chi = 0.933 \text{ S m}^{-1}$; \times , $\chi = 2.09 \text{ S m}^{-1}$) or AMV (b: \square , $\chi = 0.061 \text{ S m}^{-1}$; \circ , $\chi = 0.09 \text{ S m}^{-1}$; \triangle , $\chi = 0.177 \text{ S m}^{-1}$; \blacksquare , $\chi = 0.21 \text{ S m}^{-1}$; \bullet , $\chi = 0.43 \text{ S m}^{-1}$; \blacktriangle , $\chi = 1.22 \text{ S m}^{-1}$; \times , $\chi = 2.22 \text{ S m}^{-1}$) membranes.

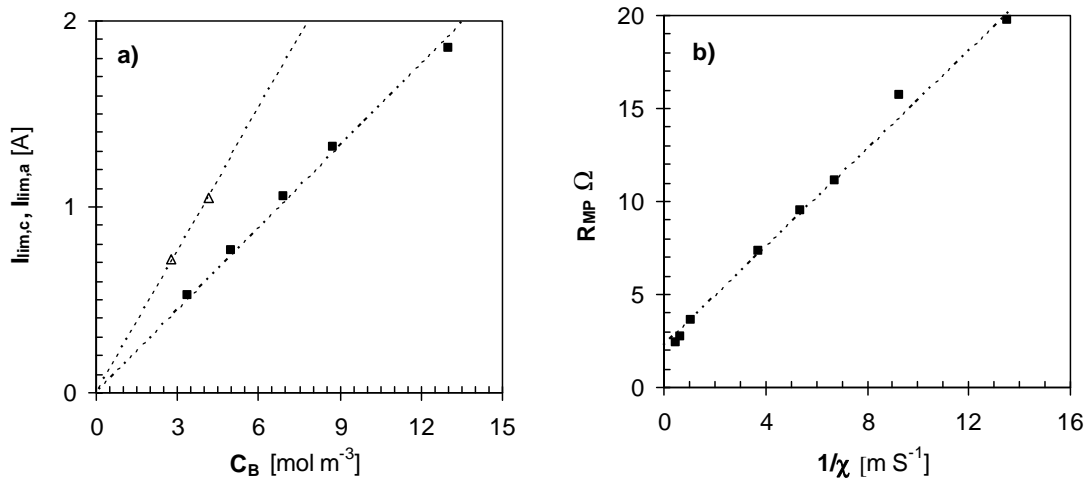


Figure 3: Main results of limiting current tests referred to CMV (\blacksquare) or AMV (\triangle) membranes: (a) limiting current ($I_{lim,k}$) vs. salt molar concentration (C_B) and (b) electrical resistance of cationic membrane pack (R_{MP}) vs. the reciprocal of conductivity (χ).

By correlating E against I in the ohmic region of the curves shown in Fig. 2, the least squares method allowed (i) to assess that all E - I curves exhibited a constant intercept (i.e. $E_{el} \approx 2.1 \text{ V}$) and (ii) to estimate accurately the resistance of the membrane pack (R_{MP}). After that, by neglecting the contribution of E_j , E_D and R_{fs} in Eq. (4), the apparent resistance (R_{MP}) of the membrane pack consisting of only cationic or anionic membranes was related to the reciprocal of the bulk solution electric conductivity (χ) as follows:

$$R_{MP} = \frac{E - E_{el}}{I} - \frac{2h_{ERS}}{a_E \chi_{ERS}} = R_k N_k + \frac{h(N_k - 1)}{a_{me} \chi} \quad (5)$$

where R_k and N_k are the resistance and overall number of the k -th membrane used, for $k = a$ or c . As shown in Fig. 3b, R_{MP} for the cationic membrane pack was a linear function of the inverse of the electrical conductivity (χ) of the bulk solution, its intercept and slope being proportional to the membrane resistance (R_c) and gap per unit effective membrane surface area (h/a_{me}), respectively. By using the least squares method, such unknown parameters were assessed as $R_c = 0.15 \pm 0.06 \Omega$; $a_{me} = 50.34 \text{ cm}^2$ ($r^2 = 0.95$).

It can be noted that a_{me} was $\sim 13\%$ greater than the exposed surface area of electrodes ($a_E = 44.6 \text{ cm}^2$) and significantly different from the geometrical membrane surface area ($a_{mg} = 72 \text{ cm}^2$), but in line with the values recently reported for the same electro dialyzer by Fidaleo and Moresi (2004, 2005ab, 2006b, 2009, 2010). Once the membrane gap per unit effective membrane surface area (h/a_{me}) had been assessed, Eq. (5) allowed the resistances of the anionic (R_a) or cationic (R_c) membranes to be calculated. Whereas R_c data scattered around the value given above, R_a exhibited a logarithmic decrease from 3.6 to 0.9Ω as χ was increased from 0.06 to 2.2 S m^{-1} (Fig. 4). The least squares fitting of R_a -vs.- $\ln(\chi)$ data yielded the following empirical equation: $R_a = (1.6 \pm 0.11) - (0.76 \pm 0.06) \ln(\chi)$ ($r^2 = 0.95$).

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 $I=0.75 \text{ A}$, $v_s = 5.9 \text{ cm s}^{-1}$ and $T = 20 \text{ }^\circ\text{C}$. As shown in Fig. 5, for $I < (2/3 I_{lim,c})$ the agreement between the time courses of the experimental and calculated E_{MP} values appears to be quite satisfactory.

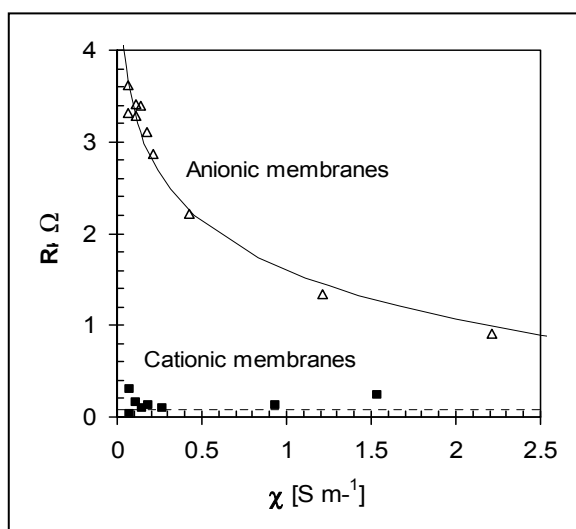


Figure 4: Plot of the resistance (R_k) of AMV (Δ) and CMV (\blacksquare) membranes against the bulk solution electric conductivity (χ) under constant superficial velocities (5.9 cm s^{-1}). The continuous line was calculated using the logarithmic regression reported in the text, while the broken line represents the average value of the cationic membrane resistance (R_c).

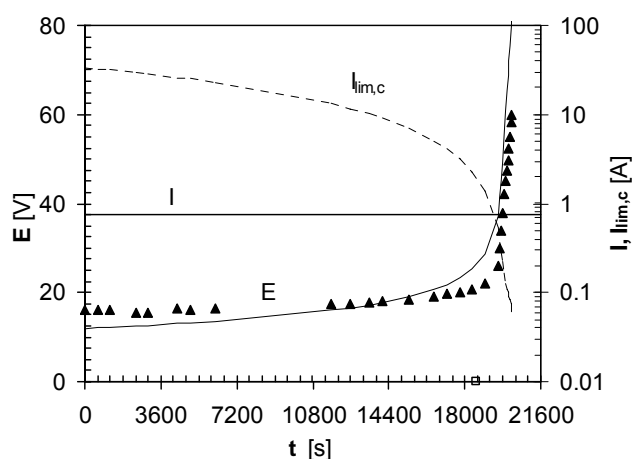


Figure 5: Time course of the applied current (I), estimated limiting current ($I_{lim,c}$) in D compartment, and experimental (\blacktriangle) voltage applied to the ED stack (E) throughout a desalination run carried out at $I = 0.75 \text{ A}$, $v_s = 5.9 \text{ cm s}^{-1}$ and $T = 20 \text{ }^\circ\text{C}$. The continuous line was calculated via Eq. (4) with the parameters reported in the text. The arrow shows the time at which I is equal to $(2/3 I_{lim,c})$.

4. Conclusions

The Nernst–Planck approach was applied to model the electro dialytic recovery of the trisodium salt of citric acid. When this strong electrolyte is dissolved in water and submitted to ED, the two prevailing ions in solutions, Na^+ and R^{3-} , transferred their electric charge through the CMV and AMV membranes, respectively. The most relevant difference in the recovery of this trivalent anion with respect to that of the univalent ones previously tested appeared to be related to the pattern of the voltage-current curves for the anionic membrane pack. In fact, the ohmic region was clearly observed at $I < 0.2 \text{ A}$ whatever the solution

electric conductivity. Moreover, for $\chi > 0.09 \text{ S m}^{-1}$ the curve pattern deviated from linearity and exhibited an extended downward concavity, this making impossible to assess the limiting current. In these tests, the controlling limiting current was that related to the cationic membranes ($I_{\text{lim,c}}$). Finally, the anionic resistance (R_a) was not constant and independent of the solute concentration, but a logarithmic function of the solution electric conductivity.

Provided that the electric current applied was less than 2/3 of $I_{\text{lim,c}}$, the basic engineering parameters estimated by the conventional experimental procedure were capable of reconstructing the time course of the voltage applied to the ED stack with an mean percentage error of 17.5%.

Further work is needed to assess the validity of the process and design parameters estimated here by varying the flow conditions and current applied.

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