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Modeling of weak acid production by the EDB method

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Abstract

The electrodialysis with bipolar membrane (EDB) of organic acid salts is an alternative way of the production of organic acids. In this work a model of the basic EDB cell consisting of three compartments (acid, salt, base) is presented. The transport of ions through monopolar ion-exchange membranes is described by the extended Nernst–Planck equation, assuming the Donnan equilibrium at the boundary solution|membrane. The diffusion of undissociated acid and the electro-osmotic flow of water is taken into account. The model predicts how the efficiency of salt conversion, the resistance of cell, the volumes of acid, salt, and base solutions change with time for a given current density. The simulation results are presented for the acetic acid. The influence of nonideality of membranes and of the acid dissociation constant on the efficiency of acid production is shown.

Keywords: Electrodialysis; Bipolar membrane; Ion-exchange membrane; Organic acid; Current efficiency

1. Introduction

The production of organic acids using electrodialysis especially with bipolar membrane brings attention of many authors [1–13]. A wide spectrum of acids has been considered, e.g. acetic [1–4], propionic [3], gluconic [6], citric [6–9], lactic [3,12,13] acids. Some of the papers are also devoted to the modeling of that process, e.g. [11–13].

It is out of the scope of this paper to describe in detail the features and differences between the published models. In this work we present another approach to modeling of that process. It takes into account the basic transport occurring in the membranes in the ED module, i.e. the migration of ions in the external electric field, diffusion of dissociated and undissociated electrolyte, electro-osmotic transport of water. The influence of nonideality of membranes and of the acid dissociation constant on the acid production will be discussed. The differences between the current efficiency based on the number of ions and on the concentration also will be shown.

2. System

The transport of species taken into account in the model are schematically depicted in Fig. 1. The detailed description is given below. The electrode compartments will not be discussed.

2.1. Bipolar membrane

Because the theoretical description of the transport through a bipolar membrane is complicated (see, e.g. [14,15] and references therein), here we assume that the imperfection of that membrane results in the electrical transport of Na^+ ions, described by the transport number $\bar{t}_{B,Na^+}$, and the diffusion of acid HA. Thus the production of H^+ and OH^- ions is $1-\bar{t}_{B,Na^+}$ per 1 F of the passed electric charge. The number of moles of water needed for their production is $1-\bar{t}_{B,Na^+}$. It can come from both sides of membrane. Let us denote by $x_{B,w}$ the fraction of water which comes from the NaOH solution. Next, it is assumed that generally the electro-osmotic number of water, $\bar{t}_w$, is related to the transport numbers of ions by

$$\bar{t}_w = \sum_{i=1}^{n} \frac{\bar{t}_i}{z_i} h_i \tag{1}$$

where h_i is the number of water molecules dragged by ion i. Thus, for the B1 membrane the electro-osmotic flux of water directed towards the “a” compartment (without water to be splitted, Fig. 1) is given by

$$\bar{t}_{B1,w} = h_{Na^+}\bar{t}_{B1,Na^+} + h_{H^+}(1-\bar{t}_{B1,Na^+}) \tag{1a}$$

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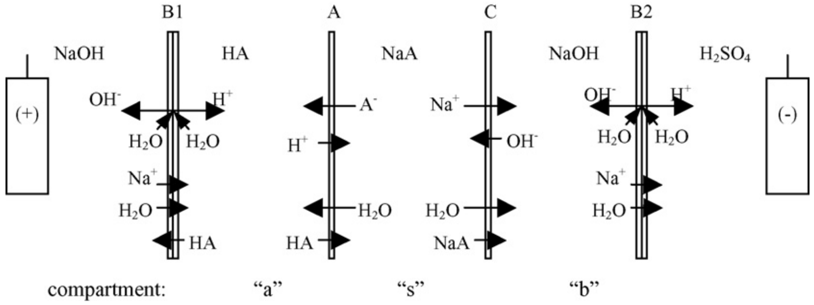

Fig. 1. Basic transport in the 3-compartment EDB module (the electrode compartments are not taken into account). B1, B2: bipolar membranes; A: anion-exchange membrane; C: cation-exchange membrane.

whereas for the B2 membrane—directed towards the "b" compartment is

$$\bar{t}_{\mathrm{B2,w}} = -h_{\mathrm{Na^+}}\bar{t}_{\mathrm{B2,Na^+}} + h_{\mathrm{OH^-}}(1-\bar{t}_{\mathrm{B2,Na^+}}) \tag{1b}$$

Further we assume that $\bar{t}_{\mathrm{B,Na^+}}$ and h_i are constant. The diffusion of organic acid through a bipolar membrane (Neosepta BP-1, Tokuyama Corp.) was measured by Wódzki and Nowaczyk [16]. From their data it results that the permeability coefficient of acetic acid is $P'_{\mathrm{B,HA}} = J_{\mathrm{B,HA}}/\Delta c_{\mathrm{HA}} \approx 5.3\times 10^{-8}\,\mathrm{m\,s^{-1}}$. As the concentration of undissociated HA on the anode side of the B1 membrane is 0 (solution of NaOH), the amount of diffused HA per 1 F of the passed electric charged, $y_{\mathrm{B1,HA}}$, can be expressed as

$$y_{\mathrm{B1,HA}} \equiv \frac{FJ_{\mathrm{B1,HA}}}{j} = \frac{P'_{\mathrm{B1,HA}}c_{\mathrm{a,HA}}F}{j} \tag{2}$$

where $c_{\mathrm{a,HA}}$ denotes the concentration of undissociated acid in the "a" compartment, j is the current density.

2.2. Monopolar membranes

The following ions will be considered:

- anion-exchange membrane separating HA and NaA solutions—H^+, Na^+ and A^-,
- cation-exchange membrane separating NaA and NaOH solutions—Na^+, OH^- and A^-.

All quantities in the presented below derivation refer to the pore solution of membranes, unless otherwise stated. The flux of ion i in the pores of a monopolar ion-exchange membrane, J_i will be approximated by the extended Nernst–Planck equation [17]:

$$J_i = -\bar{D}_i\left(\frac{\mathrm{d}\bar{c}_i}{\mathrm{d}x} + \bar{c}_i z_i \frac{\mathrm{d}\bar{\psi}^{\mathrm{r}}}{\mathrm{d}x}\right) + \bar{c}_i v \tag{3}$$

$\bar{D}_i$ denotes the diffusion coefficient of ion i. $\bar{\psi}^{\mathrm{r}}$ denotes dimensionless electric potential ($\bar{\psi}^{\mathrm{r}} \equiv \bar{\psi}F/RT$). The convection velocity v is given by

$$v = d_{\mathrm{h}}\left(\bar{X}_{\mathrm{m}}\frac{\mathrm{d}\bar{\psi}^{\mathrm{r}}}{\mathrm{d}x} - \frac{1}{RT}\frac{\mathrm{d}\bar{p}}{\mathrm{d}x}\right) \approx d_{\mathrm{h}}\bar{X}_{\mathrm{m}}\frac{\mathrm{d}\bar{\psi}^{\mathrm{r}}}{\mathrm{d}x} \tag{4}$$

where $\bar{X}_{\mathrm{m}} \equiv z_{\mathrm{m}}\bar{c}_{\mathrm{m}}$, $\bar{c}_{\mathrm{m}}$ is the concentration of fixed charges. For the sake of simplicity we neglect the internal pressure term, $\mathrm{d}\bar{p}/\mathrm{d}x$, in further derivations. One should remember that for low current density and high concentration difference that term can be significant.

Substituting Eqs. (3) and (4) into the equation for the current density j_{p} (referred to the pores):

$$j_{\mathrm{p}} = F\sum_{k=1}^{n} z_k J_k \tag{5}$$

solving for $\mathrm{d}\bar{\psi}^{\mathrm{r}}/\mathrm{d}x$:

$$\frac{\mathrm{d}\bar{\psi}^{\mathrm{r}}}{\mathrm{d}x} = -\frac{j_{\mathrm{p}}/F + \sum_{k=1}^{n} z_k \bar{D}_k \frac{\mathrm{d}\bar{c}_k}{\mathrm{d}x}}{\sum_{k=1}^{n}\bar{c}_k z_k^2\left(\frac{\bar{D}_k - d_{\mathrm{h}}\bar{X}_{\mathrm{m}}}{z_k}\right)} \tag{6}$$

and substituting back to Eqs. (3) and (4) we get

$$J_i = \frac{\bar{t}_i}{z_i}\frac{j_{\mathrm{p}}}{F} - \bar{D}_i\frac{\mathrm{d}\bar{c}_i}{\mathrm{d}x} + \frac{\bar{t}_i}{z_i}\sum_{k=1}^{n}\bar{D}_k z_k\frac{\mathrm{d}\bar{c}_k}{\mathrm{d}x}, \quad i = 1, 2, 3 \tag{7}$$

where $\bar{t}_i$ is the transport number of ion i:

$$\bar{t}_i \equiv \left(\frac{Fz_iJ_i}{j_{\mathrm{p}}}\right)_{\bar{c}} = \frac{\bar{c}_i z_i^2(\bar{D}_i - d_{\mathrm{h}}\bar{X}_{\mathrm{m}}/z_i)}{\sum_{k=1}^{n}\bar{c}_k z_k^2(\bar{D}_k - d_{\mathrm{h}}\bar{X}_{\mathrm{m}}/z_k)} \tag{8}$$

The coefficient d_{h} will be estimated in the following manner. The volume electro-osmotic flux (zero concentration gradient) is equal:

$$(v)_{\bar{c}} = \frac{j_{\mathrm{p}}}{F}\left(\bar{t}_{\mathrm{w}}\bar{v}_{\mathrm{w}} + \sum_{i=1}^{n}\frac{\bar{t}_i}{z_i}\bar{v}_i\right) \tag{9}$$

Combining Eqs. (1), (4), (6), (8) and (9) we get for d_{h}:

$$d_{\mathrm{h}} = \frac{\sum_{i=1}^{n} z_i\bar{D}_i(\bar{v}_i + h_i\bar{v}_{\mathrm{w}})\bar{c}_i}{\left(-1 + \sum_{i=1}^{n}(\bar{v}_i + h_i\bar{v}_{\mathrm{w}})\bar{c}_i\right)\bar{X}_{\mathrm{m}}} \tag{10}$$

The concentrations of ions inside the membrane must obey the electroneutrality condition:

$$\sum_{k=1}^{n} z_k\bar{c}_k + \bar{X}_{\mathrm{m}} = 0 \tag{11}$$