This is an author's version published in: http://oatao.univ-toulouse.fr/24598

**Official URL:**

https://doi.org/10.1016/S0011-9164(02)00863-9

**To cite this version:**

Roux-de Balmann, Hélène and Bailly, Mathieu and Lutin, Florence and Aimar, Pierre *Modelling of the conversion of weak organic acids by bipolar membrane electrodialysis.* (2002) Desalination, 149 (1-3). 399-404. ISSN 0011-9164.

# Modelling of the conversion of weak organic acids by bipolar membrane electrodialysis

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## Abstract

Organic acids are increasingly used for various industrial applications. Their production is mainly achieved by fermentation. Precipitation or extraction stages, which generates big amount of effluents, are then traditionally used to get the acid in a suitable form. Bipolar membrane electrodialysis (EDBM) can be used to achieve the conversion of the acid salt into its acidic form. Its introduction in replacement of precipitation can significantly lower the environmental impact of the process. This paper is focused on the modelling of the conversion of weak organic acid salts by EDBM The different mass transfer phenomena involved in the system are first identified. A model is then established to get expressions providing the evolution of the product and effluent lines with respect to the operating conditions. The physical meaning of the characteristic parameters involved in the model is also discussed.

*Keywords*: Electrodialysis; Bipolar membrane; Modelling; Mass transfer; Organic acids

## 1. Introduction

In many industrial application fields, increasing environmental constraints lead to the improvement of production processes in order to decrease their impact on environment. One of the concerned fields is the production of organic acids, which constitute essential agents in many applications like food, pharmaceutical or biodegradable polymers industries. The world-wide market of organic acids grows constantly by 4% every year. Moreover, in terms of yearly capacity, the acids mainly produced are citric acid (725,000 T/y), lactic acid

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*Presented at the International Congress on Membranes and Membrane Processes (ICOM), Toulouse, France, July 7 12, 2002.*

(90,000 T/y) and gluconic acid (45,000 T/y) [1]. The growing importance of lactic acid for biopolymers elaboration has also to be pointed out.

At the industrial scale, organic acids are mainly produced by fermentation from molasses, starch hydrolysats or sugars. Several unit operations, which constitute the clarification, extraction and purification pools, are then required to get the acid having the right specifications with respect to its further utilisation. One of them is the conversion of the acid salt, obtained from the fermentation, into its acid form. Traditional processes are designed around one or several precipitation stages which produce large amounts of effluents with a high salt content. In order to lower this environmental impact, alternative production schemes based on membrane operations were proposed.

Electrodialysis with Bipolar Membranes (EDBM) can be used as a conversion step. In that case, the neutralisation of the acid salt results from the production of protons coming from the bipolar membrane and the conversion can be achieved without requiring any addition or production of chemicals. A complete process, targeted around EDBM was studied, in which microfiltration (MF) and conventional electrodialysis (EDC) are used before EDBM for clarifying the fermentation broth and to concentrate the acid salt. Results concerning MF and EDC were presented elsewhere [2,3].

Different works were devoted to EDBM. The water dissociation mechanisms taking place in the bipolar membrane as well as the different factors limiting the use of bipolar membranes were investigated [4,5]. In most of these studies, EDBM was considered to regenerate water soluble salt solutions into their corresponding acid and base (regeneration of sodium chloride into hydrochloric acid and caustic soda for instance) [6]. Few results were published concerning the conversion of weak acid salts, like organic acids concerned in the present study, except experimental ones [7].

The present paper deals with the modeling of bipolar membrane electrodialysis (EDBM) as a conversion step of weak organic acid salts into their acid form. From this model, expressions are obtained providing the evolution of the two outlet streams, i.e. the acid and the base ones, vs. time.

## 2. Principle of EDBM for the conversion of weak organic acids

EDBM can be used with a two- or three-compartment arrangement. The most common three-compartment configuration is operated to recover acid and base streams from a salt solution. The two compartments configuration used for the conversion of weak acid salts into their acid form is depicted in Fig. 1. The membrane stack is constituted by an alternance of cation-exchange membranes (CEM) and bipolar membranes (BM). Thanks to BM, water is split into $OH^-$ and $H^+$. The acid compartment, called diluate, is fed with the acid salt solution. This stream constitutes then the product line. On the other hand, the base compartment, called concentrate, is fed with a diluted base solution corresponding to the counter ion of the acid salt (caustic soda for sodium acid salt for example). This stream is the effluent line. Due to the production of $H^+$ in the acid compartment, the pH decreases and the acid salt is converted into its acid form. At the same time,

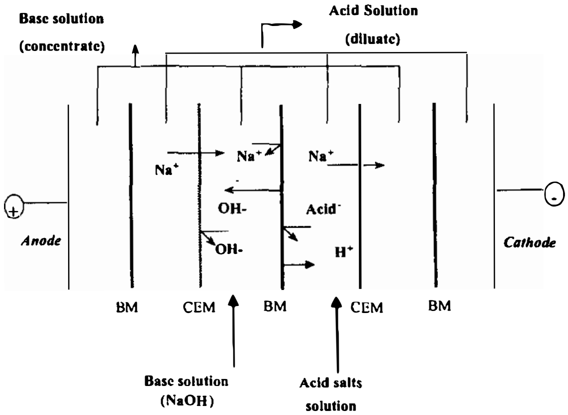

Fig. 1. Principle of EDBM for the conversion of weak organic acid salts — example of a sodium salt. CEM: cation exchange membrane; BM: bipolar membrane.

cations migrate through the CEM from the diluate to the concentrate to combine with $OH^-$produced by the other layer of BM, leading then to an increase of the base concentration in this compartment. The charged species migrating from the diluate to the concentrate carry with them a shell of solvent molecules. This flux, here called electroosmotic flux, is directed from the diluate to the concentrate. Then, the acid concentration in the diluate increases during the conversion.

## 3. Mass transfer modelling

### *3.1. Model establishment*

Equations presented hereafter are established in the case of the conversion of sodium lactate (NaLac) into lactic acid (HLac). However, they can be used to describe the conversion of any weak monoacid salt without any modification.

Fig. 2 provides a schematic drawing of the different fluxes and reactions, the origin of which was described in section 2. Then, these different fluxes and reactions taking place in the system are considered, as presented hereafter, to obtain a set of equations.

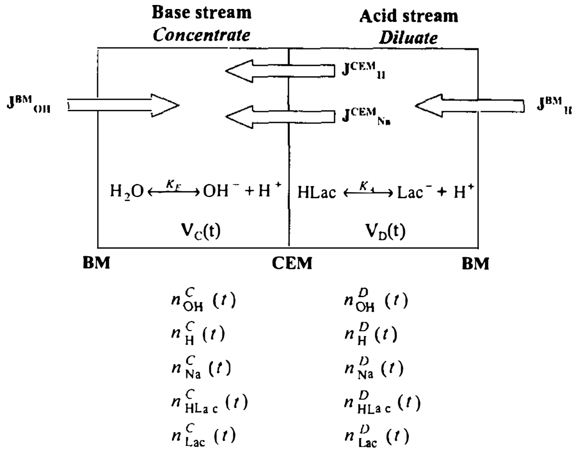

Fig. 2. Schematic drawing of the fluxes and reactions considered for the model establishment, $J_H^{BM}$ and $J_{OH}^{BM}$ (mol/s): molar flux of $H^+$ and $OH^-$ produced by the bipolar membrane; $J_{Na}^{CEM}$ and $J_H^{CEM}$ (mol/s): molar flux of $Na^+$ and $H^+$ through the CEM; $n_i^j$ (mol): number of moles of $i$ in the compartment $j$; $V_j$: volume in the compartment $j$.

For each compartment, following reactions are considered

diluate: $HLac \longleftrightarrow Lac^- + H^+ \quad K_A$

concentrate: $H_2O \longleftrightarrow OH^- + H^+ \quad K_E$

where $K_A$ and $K_E$ are the equilibrium constants, tied to the molar concentrations of the species by the following expressions

$$K_A = \frac{n_H^D(t).n_{Lac}^D(t)}{V_D(t).n_{HLac}^D(t)} \tag{1}$$

$$K_E = \frac{n_H^C(t).n_{OH}^C(t)}{V_C^2(t)} \tag{2}$$

The proton balance in the diluate gives:

$$\frac{dn_H^D(t)}{dt} + \frac{dn_{HLac}^D(t)}{dt} = J_H^{BM} - J_H^{CEM} \tag{3}$$

Assuming that the water dissociation equilibrium is infinitely fast compared to the transfer of protons through the cation-exchange membrane on one hand and that the flux of hydroxyls issued from the bipolar membrane exceeds that of protons through the cation-exchange membrane on the other hand, one gets the variation of the OH-concentration in the concentrate:

$$\frac{dn_{OH}^C(t)}{dt} = J_{OH}^{BM} - J_H^{CEM} \tag{4}$$

Since the variation of the number of moles of sodium in the diluate, $n_{Na}^D$, is only due to the flux of sodium through the CEM, we have:

$$\frac{dn_{Na}^D(t)}{dt} = -J_{Na}^{CEM} \tag{5}$$

Then, the mass conservation equations for lactate and sodium are respectively:

$$\begin{aligned} &n_{HLac}^C(t) + n_{Hlac}^D(t) + n_{Lac}^C(t) + n_{Lac}^D(t) \\ &= n_{Lac,0}^D + n_{HLac,0}^D = n_0^D \end{aligned} \tag{6}$$

$$n_{\mathrm{Na}}^{D}(t)+n_{\mathrm{Na}}^{C}(t)=n_{\mathrm{Na},0}^{D}+n_{\mathrm{Na},0}^{C} \tag{7}$$

where $n_{i,0}^{j}$ represent the number of mole of *i* initially present ($t$ = 0) in the compartment *j*.

Finally, electroneutrality is written, for the diluate and the concentrate respectively:

$$n_{\mathrm{OH}}^{D}(t)+n_{\mathrm{Lac}}^{D}(t)=n_{\mathrm{Na}}^{D}(t)+n_{\mathrm{H}}^{D}(t) \tag{8}$$

$$n_{\mathrm{OH}}^{C}(t)+n_{\mathrm{Lac}}^{C}(t)=n_{\mathrm{Na}}^{C}(t)+n_{\mathrm{H}}^{C}(t) \tag{9}$$

On the other hand, in the case under study, all the ions are monovalent. Then, for a fixed current density, the molar flux of species through the different membranes is fixed. This is expressed for cations by the following relationship :

$$J_{\mathrm{H}}^{\mathrm{CEM}}+J_{\mathrm{Na}}^{\mathrm{CEM}}=J_{\mathrm{H}}^{\mathrm{BM}} \tag{10}$$

Moreover, the molar fluxes of sodium and protons through the cation-exchange membrane are tied by the following relationship:

$$\frac{J_{\mathrm{Na}}^{\mathrm{CEM}}}{J_{\mathrm{H}}^{\mathrm{CEM}}}=\frac{t_{\mathrm{Na}}^{\mathrm{CEM}}}{t_{\mathrm{H}}^{\mathrm{CEM}}}=\frac{u_{\mathrm{Na}}^{\mathrm{CEM}}C_{\mathrm{Na}}^{\mathrm{CEM}}}{u_{\mathrm{H}}^{\mathrm{CEM}}C_{\mathrm{H}}^{\mathrm{CEM}}} \tag{11}$$

where $u_i^{\mathrm{CEM}}$ and $C_i^{\mathrm{CEM}}$ represent the electrophoretic mobility and the concentration of *i* in the membrane. $t_i^{\mathrm{CEM}}$ is the transport number of *i* through the CEM, i.e. the ratio of the current transported by *i* over the total current. The concentrations in the membrane are besides tied to those in the solution. This can be expressed by a relationship of the following form:

$$\frac{J_{\mathrm{Na}}^{\mathrm{CEM}}}{J_{\mathrm{H}}^{\mathrm{CEM}}}=f\left(\frac{n_{\mathrm{Na}}^{D}}{n_{\mathrm{H}}^{D}}\right) \tag{11a}$$

Finally, assuming that the total volume remains constant, i.e. that the volume increase due the formation of water in the concentrate is negligible, the following expressions are obtained for the variations of the volume vs. time:

$$V_D(t)=V_0-\int_0 R_V.\mathrm{d}t \tag{12}$$

$$V_C(t)+V_D(t)=2.V_0 \tag{13}$$

where $R_V$(>0) is the volume flux of solution (m$^3$/s) and $V_0$ the initial volume, assumed to be the same in both compartments.

Previous relationships provide of a system of 13 equations with 14 variables. These variables are the 10 species $n_i^j$, the flux of solution $R_V$, the molar fluxes through the CEM, $J_{\mathrm{Na}}^{\mathrm{CEM}}$ and $J_{\mathrm{H}}^{\mathrm{CEM}}$, and the function *f* in Eq. (11a). In order to close this system, an additional equation is required. It can be obtained from the assumption that the bipolar membrane is ideal, i.e. that the fluxes of proton and hydroxyl produced by the BM are equal:

$$J_{\mathrm{H}}^{\mathrm{BM}}=J_{\mathrm{OH}}^{\mathrm{BM}} \tag{14}$$

The variations of the composition in both compartments versus time in a quite general case should be provided by the resolution of the system constituted by former Eqs. (1–14). One can observe that differential equations strongly non linear are involved, so that numerical methods are required. Moreover, the explicit expression of the function *f* involved in Eq. (11a) is to be determined. This requires the knowledge of quite inaccessible data. Consequently, a simplified approach was preferred in order to achieve a mathematical resolution providing analytical expressions.

Following assumptions were made with respect to experimental observations.

The contribution of diffusion to the transfer of target species, HLac and Lac, was first neglected. Then, the transfer of both species from the diluate to the concentrate is nil so that the number of mole of HLac and Lac in the concentrate remain constant vs. time and equal to zero, i.e. $n_{\mathrm{HLac}}^{C}(t)=n_{\mathrm{Lac}}^{C}(t)=0$. Then Eq. (6) becomes:

$$n_{\mathrm{HLac}}^{D}(t)+n_{\mathrm{Lac}}^{D}(t)=n_0^{D} \tag{6a}$$

The second assumption concerns the pH range in both compartments. It was considered that the pH in the diluate and in the concentrate are such that the terms $n_{\mathrm{OH}}^{D}(t)$ and $n_{\mathrm{H}}^{C}(t)$ in Eqs. (8) and

(9) can be neglected. Then, these equations become:

$$n_{\mathrm{H}}^{D}(t)+n_{\mathrm{Na}}^{D}(t)=n_{\mathrm{Lac}}^{D}(t) \tag{8a}$$

$$n_{\mathrm{OH}}^{C}(t)=n_{\mathrm{Na}}^{C}(t) \tag{9a}$$

Finally, for a given current density, the molar flux of sodium through the CEM is assumed to remain constant during the conversion. The constant and positive value of $J_{\mathrm{Na}}^{\mathrm{CEM}}$ is later represented by the parameter α.

Then, Eqs. (5) and (7) can be integrated between $t = 0$ and $t = t_{\mathrm{final}}$ to get

$$n_{\mathrm{Na}}^{D}(t)=n_{\mathrm{Na},0}^{D}-\alpha.t \qquad \text{for } 0\leq t\leq t_{\mathrm{final}} \tag{5a}$$

$$n_{\mathrm{Na}}^{C}(t)=n_{\mathrm{Na},0}^{C}+\alpha.t \qquad \text{for } 0\leq t\leq t_{\mathrm{final}} \tag{7a}$$

$$\frac{\mathrm{d}n_{\mathrm{Na}}^{C}(t)}{\mathrm{d}t}=\frac{\mathrm{d}n_{\mathrm{Na}}^{D}(t)}{\mathrm{d}t}=0 \qquad \text{for } t>t_{\mathrm{final}} \tag{7b}$$

where $t_{\mathrm{final}}$, the expression of which is provided by the following relationship,

$$n_{\mathrm{Na}}^{C}(t_{\mathrm{final}})=n_{\mathrm{Na},0}^{C}+n_{\mathrm{Na},0}^{D}$$

is defined as the particular time for which the sodium concentration in the diluate reaches zero.

Then, the mathematical resolution of the system is possible to get the expression of the number of moles of protons in the diluate from which that of the pH can be deduced. Combination of Eqs. (8a), (1) and (6b) gives:

$$n_{\mathrm{H}}^{D}(t)-\frac{n_{0}^{D}.K_{A}.V_{D}(t)}{(n_{\mathrm{H}}^{D}(t)+K_{A}.V_{D}(t))}+n_{\mathrm{Na}}^{D}(t)=0 \tag{15}$$

from which the following expression is obtained:

$$n_{H}^{D}(t)=\frac{-\left[n_{Na}^{D}(t)+K_{A}.V_{D}(t)\right]}{2}+\frac{\sqrt{\left[n_{Na}^{D}(t)+K_{A}.V_{D}(t)\right]^{2}+4K_{A}V_{D}(t)\left[n_{0}^{D}-n_{Na}^{D}(t)\right]}}{2} \tag{16}$$

Lastly, combining Eqs. (5a) and (16), it comes:

$$n_{\mathrm{H}}^{D}(t)=\frac{-g(t)+\sqrt{g(t)^{2}+4K_{A}.V_{D}(t).h(t)}}{2} \tag{17}$$

with $g(t)=n_{\mathrm{Na},0}^{D}-\alpha.t+K_{A}.V_{D}(t)$

and $h(t)=4.K_{A}.V_{D}(t).\left(n_{0}^{D}-n_{\mathrm{Na},0}^{D}+\alpha.t\right)$

where $V_D(t)$ is provided by Eq. (12). The expressions of the pH in the diluate, $\mathrm{pH}_D(t)$, and the corresponding conversion factor, $\tau(t)$, are then:

$$\mathrm{pH}_{D}(t)=-\log\left(\frac{n_{H}^{D}(t)}{V_{D}(t)}\right) \tag{18}$$

$$\tau(t)=\frac{1}{1+10^{(\mathrm{pH}_{D}(t)-pK_{A})}} \tag{19}$$

### *3.2. Discussion*

From previous expressions, the conversion of weak acid by EDBM can be characterized. Indeed, they provide the variations vs. time of the number of moles of sodium in the concentrate [Eqs. (7a) and (7b)] and the pH in the diluate from which the conversion factor can be calculated [Eqs. (12), (17–19)].

Three characteristic parameters are involved which are the volumic flux of solution, $R_V$, the molar flux of sodium through the cation exchange membrane, α, and the equilibrium constant, $K_A$, of the reaction between the acid and the acid salt.

$R_V$ and α are transfer parameters, related to the kinetics of the system, while $K_A$ is an equilibrium parameter, related to the thermodynamic properties of the organic acid solution. These parameters depend on the operating conditions and on the physico-chemistry of the system, in different manner. $R_V$ and α depend on the current density and on the membrane characteristics, while $K_A$ depends on the ionic strength of the solution and so on the concentration of considered species.

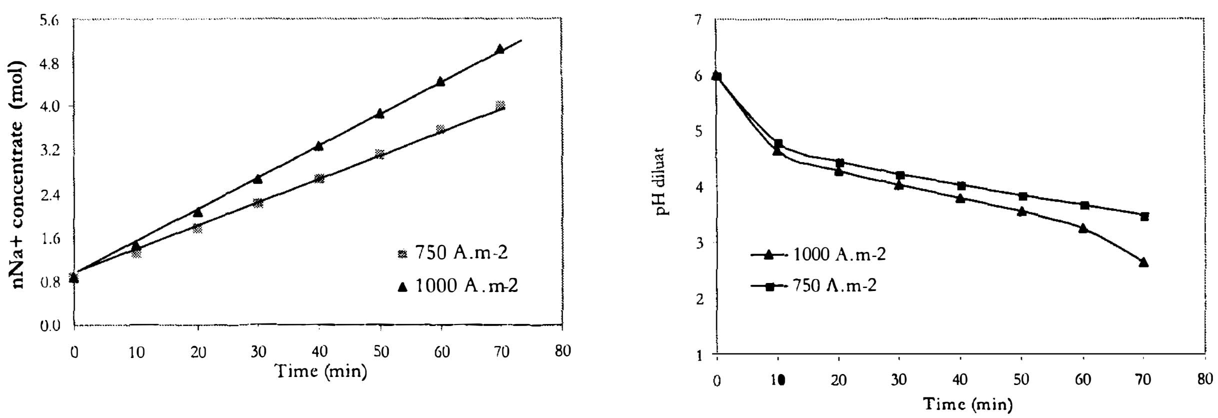

Fig. 3. Simulation of the conversion of sodium lactate — influence of the current density on the variations of the number of moles of sodium in the concentrate (top) and pH in the diluate (bottom). Characteristic parameters: $R_v = 8.10^{-11}*i$ ($m^3.s^{-1}$); $\alpha = 10^{-6}*i$ ($mol.s^{-1}$); $pK_A = 3.86$.

Fig. 3 provides an example of calculated variations of the number of moles of sodium and of the pH in the diluate vs.time for two different current densities. The values of the characteristic parameters $R_v$ and $\alpha$ are those determined from previous work dedicated to the concentration of sodium lactate by EDC [3].

## 4. Conclusions

This paper was devoted to the modelling of the conversion of weak organic acids by EDBM. The different transport phenomena involved in the system, i.e. a two compartment configuration using in alternance bipolar and cation exchange membranes, were studied. These were considered to establish a set of equations, the mathematical resolution of which was then carried out. Expressions were thus obtained providing the variations of the composition of the fluids, i.e. both product line and effluent line, during the EDBM conversion. These expressions require the knowledge of three characteristic parameters, the physical meaning of which was discussed. This will be checked by comparing the results calculated by the model with experimental ones obtained during the conversion of different kinds of organic acids.

## References

[1] P.-J. Sicard, Bio-industries: la nouvelle donne, Info chimie magazine, 415 (2000) 68–72.

[2] H. Carrère, F. Blaszkow and H. Roux-de Balmann, Modelling of the clarification of lactic acid fermentation broths by cross flow microfiltration, J. Membr. Sci., 186 (2001) 219–230.

[3] M. Bailly, H. Roux-de Balmann, P. Aimar, F. Lutin and M. Cheryan, Production processes of fermented organic acids targeted around membrane operations: design of the concentration step by conventional electrodialysis, J. Membr. Sci., 191 (2001)129–142.

[4] H. Strathmann, J.J. Krol, H.J. Rapp and G. Eigenberger, Limiting current density and water dissociation in bipolar membranes, J. Membr. Sci., 125 (1997) 123–142.

[5] J.L. Gineste, G. Pourcelly, Y. Lorrain, F. Perrin and C. Gavach, Analysis of factors limiting the use of bipolar membranes: a simplified model to determine trends, J. Membr. Sci., 112 (1996) 199–208

[6] K.N. Mani, Electrodialysis water splitting technology, J. Membr. Sci., 58 (1991) 117–138.

[7] E.G. Lee, S.-H. Moon, Y.K. Chang, I.-K. Yoo and H.N. Chang, Lactic acid recovery using two stage electrodialysis and its modelling, J. Membr. Sci., 145 (1998) 53–66.