Production processes of fermented organic acids targeted around membrane operations: design of the concentration step by conventional 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 generate big amount of effluents, are then traditionally used to get the acid in a suitable form. To lower the impact on the environment, the implementation of cleaner operations are investigated. In this context, a

the description of the solute and solution fluxes through the membranes is developed. Dedicated procedures are proposed to determine the different contributions, i.e. electromigration and diffusion, to these fluxes so as to feed the model. This approach is then applied to the concentration of sodium lactate solutions. The preponderance of electromigration is thus demonstrated as well as the existence of a maximum achievable concentration, the predicted value of which is confirmed experimentally. Comparison between EDC of sodium and ammonium lactate solutions shows that the counter ion has negligible influence on the transport of lactate. The influence of the membrane characteristics is also drawn from comparison with previously published results. Finally, the predictions of the model are compared with the experimental results concerning the concentration of a fermentation broth and a good agreement is stated. The approach proposed in this paper can be used as well to design EDC concentration of any other organic acid salt than lactate.

Keywords: Organic acids; Electrodialysis; Mass transfer; Process design

1. Introduction

Organic acids, like lactic, succinic, gluconic or citric acid, are increasingly used in the food, detergent or biodegradable plastics industries [1]. Their production at the industrial scale is mainly achieved by mean of fermentation from molasses, starch hydrolysates or sugars. Several unit operations are then required to get the acid having the properties in accordance with its future use. Traditional processes are designed around one or several precipitation stages which produce large amounts of effluents with a high salt content [2]. For example, 1 kg of citric acid produced by precipitation results in the production of 2 kg of gypsum, which constitutes an effluent difficult to recycle or to treat. In order to reduce this

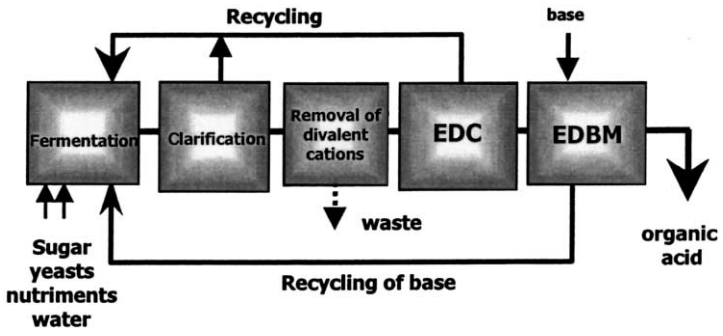

Fig. 1. Example of a process targeted around electromembrane operations for the production of organic acid from fermentation, EDC (concentration), EDBM (conversion).

environmental impact, the design of alternative production schemes has recently been investigated. In the literature, extraction [3], adsorption [4], and membrane technologies, like electrodialysis [5] or reverse osmosis [6], were proposed to replace precipitation. However, as far as the reduction of the environmental impact is concerned, the use of extraction or adsorption steps for organic acid recovery from fermentation media still remains problematic. Therefore, membrane operations, like electrodialysis for instance, appear very attractive since the generation of effluents or by products can be significantly reduced.

A complete production scheme, targeted around membrane operations for clarification, concentration and conversion, was studied (Fig. 1). The heart of the process is constituted by a conversion step carried out by bipolar electrodialysis (EDBM). Former operations are required to get a fluid having appropriate properties to carry out EDBM in proper conditions.

The fermentation broth is first clarified by cross flow microfiltration. Divalent cations, that constitute a poison in the configuration used, are then removed from the clarified broth [7]. Conventional electrodialysis (EDC) is further used prior to EDBM in order to increase the concentration of ionic species, comprising the organic acid salt. In this manner, the area of bipolar membrane required for the conversion is lowered so that the economical profitability of the EDBM step is improved. To some extent, EDC can also simultaneously increase the purity of the target acid salt, since residual sugars or other impurities can be removed [8].

Results concerning cross flow microfiltration and bipolar membrane electrodialysis are published elsewhere [9,10].

In this paper, we focus on the study of the concentration of organic acid salts carried out by conventional electrodialysis. Lactic acid is retained as case study. This work is carried out by associating a theoretical approach with an experimental study.

A model, based on the description of the different mass transfer phenomena involved in the system, is proposed. Expressions are established to give the variation of the concentration versus time. Experiments are then carried out with synthetic solutions of sodium lactate. Dedicated procedures are used to determine the contributions of the different transport phenomena.

The concentration of synthetic ammonium lactate solutions is then investigated in order to study the influence of the lactate counterion. Finally, predicted results are compared with the experimental ones obtained with an ammonium lactate contained in a clarified fermentation broth.

2. Mass transfer modeling

The principle of EDC is described in Fig. 2, in the case of a two-compartments arrangement used in this work. Other arrangements may be used such as a four-compartments configuration for the recovery of lactic acid from lactate salt solutions [11].

A model is proposed to describe the mass transfer of the charged species and of water through the

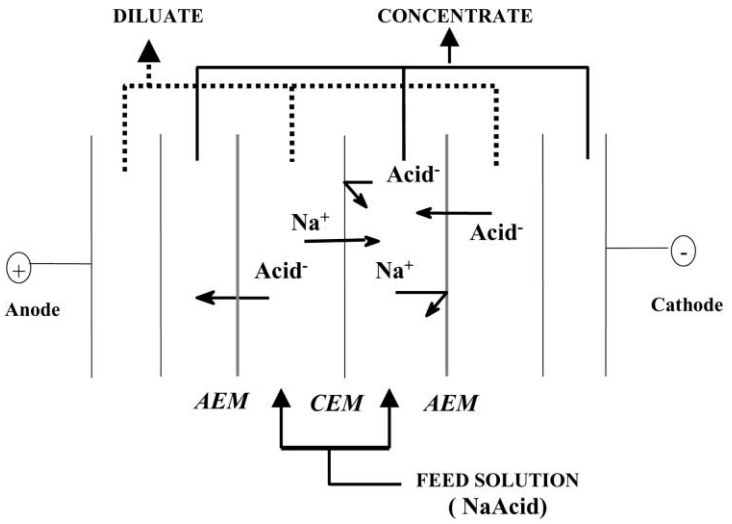

Fig. 2. Principle of EDC in a two compartment configuration — example of the concentration of a sodium organic acid salt, CEM: cation exchange membrane, AEM: anion exchange membrane.

membranes of the electrodialysis stack. It enables the calculation of the lactate concentration at any time during EDC, in both the concentrate and the diluate compartments.

The concentration is given by the ratio of the mass of acid salt A, mA, over the volume of the solution, V, in the compartment. Following expressions are obtained.

The concentration is given by the ratio of the mass of acid salt A, m_A, over the volume of the solution, V, in the compartment. Following expressions are obtained for the concentration variation versus time:

$$C_A^C(t) = \frac{m_0^C + \int_0^t R_A \, dt}{V_0^C + \int_0^t R_V \, dt} \quad \text{with}$$

$$R_A = \frac{dm_A}{dt} \quad \text{and} \quad R_V = \frac{dV}{dt} \tag{1}$$

$$C_A^D(t) = \frac{m_0^D - \int_0^t R_A \, dt}{V_0^D - \int_0^t R_V \, dt} \tag{2}$$

where $C_A^j(t)$, m_0^j and V_0^j are respectively the concentration of A and the initial values of the acid mass and solution volume in the compartment j. R_A and R_V are respectively the mass flow of acid salt and the volume flow of solution through the membranes. By convention, these flows are positive while oriented from the diluate to the concentrate.

Two different kinds of phenomenon contribute to the solute and solution transfer. The first contribution to the solute transfer is diffusion, coming from the concentration difference existing across the membranes because of their selectivity with respect to ions. The resulting flux of diffusion is directed from the more concentrated compartment to the more diluted one. The second contribution to the solute transfer is the migration of charged species through the membranes due to the electrical current. Then diffusion and migration are oriented in opposite directions. In the same manner, the volumic flux of solution has two origins. The first one is osmosis, coming from the difference of osmotic pressure existing across the membranes. The resulting flux is directed from the lowest to the highest concentrated compartment. The other one, which is often referred to electroosmosis in the literature, is tied to the migration of charged species under the influence of the electrical current. Indeed, charged species migrating through the membranes are accompanied by a shell of molecules of solvent, which then takes part to the volume variation of both compartments. Then, osmosis and electroosmosis are oriented in the same direction, i.e. from the diluate to the concentrate. Fig. 3

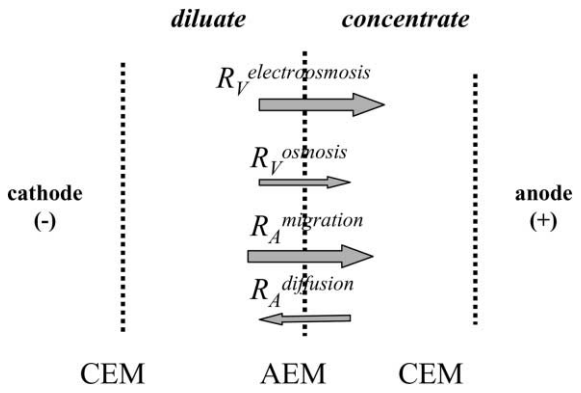

Fig. 3. Schematic drawing of the different contributions to the mass transfer.

gives a schematic representation of the different contributions, the origin of which was former explained.

The total volume flow of solution can be expressed as the sum of two contributions:

$$R_{\mathrm{V}} = R'_{\mathrm{V}} + L_{\mathrm{P}}\Delta\Pi = R'_{\mathrm{V}} + L_{\mathrm{P}}\sum_{k'}\sum_{k}\alpha_k \Delta C^k_{k'}(t) \tag{3}$$

where $\Delta\Pi$ is the osmotic pressure difference, L_{P} the membrane permeability ($\mathrm{m^3\,s^{-1}\,Pa^{-1}}$), $\Delta C_{k'}$ the concentration difference across the membrane ($\mathrm{kg\,m^{-3}}$) and R'_{V} the volume flow associated to the solute mass flux through the membrane ($\mathrm{m^3\,s^{-1}}$), i.e. the electroosmotic flow. In this relationship, k' is the number of species transported by diffusion; k varies between 0 and 3, and α_k are the virial coefficients. The general Eq. (1) then becomes (4):

$$C^{\mathrm{C}}_{\mathrm{A}}(t) = \frac{m^{\mathrm{C}}_0 + \int_0^t R_{\mathrm{A}}\,\mathrm{d}t}{V^{\mathrm{C}}_0 + \int_0^t \left(R'_{\mathrm{V}} + L_{\mathrm{P}}\sum_{k'}\sum_{k}\alpha_k \Delta C^k_{k'}(t)\right)\mathrm{d}t} \tag{4}$$

Assuming that the osmotic contribution to the solvent flux is negligible (i.e. $R_{\mathrm{V}} = R'_{\mathrm{V}}$), and that R_{V} and R_{A} do not depend on time, a simplified expression of (4) is obtained:

$$C^{\mathrm{C}}_{\mathrm{A}}(t) = \frac{m^{\mathrm{C}}_0 + R_{\mathrm{A}}t}{V^{\mathrm{C}}_0 + R_{\mathrm{V}}t} \tag{5}$$

These assumptions have to be verified experimentally.

From Eq. (5) one can determine the concentration when $t \to \infty$. This limiting value $C^{\mathrm{C}}_{\mathrm{max}}$, given by Eq. (6), represents the theoretical maximum concentration that can be achieved.

$$C^{\mathrm{C}}_{\mathrm{max}} = \lim_{t\to\infty} C^{\mathrm{C}}_{\mathrm{A}}(t) = \frac{R_{\mathrm{A}}}{R_{\mathrm{V}}} \tag{6}$$

From previous relationships, the flux densities of acid salt J_{A} and solution J_{V} can be obtained as indicated in Eqs. (7) and (8), where S is the total active membrane area involved in the system.

$$J_{\mathrm{A}} = \frac{R_{\mathrm{A}}}{S}\ (\mathrm{kg\,m^{-2}\,s^{-1}}) \tag{7}$$

$$J_{\mathrm{V}} = \frac{R_{\mathrm{V}}}{S}\ (\mathrm{m^3\,m^{-2}\,s^{-1}}) \tag{8}$$

These flux densities can be used to design a concentration step by EDC.

Former equations involve several parameters like R_{A}, R_{V} and α_k. In order to make the model predictive and to get a simulation tool, these parameters have to be quantified as functions of the operating conditions, i.e. the current density, the initial acid salt concentration, the membranes used or the properties of transported species. This is the aim of the experimental section described above.

3. Experimental

3.1. Equipment and operating conditions

3.1.1. Electrodialysis pilot

Experiments are performed with an EUR 2D-10 electrodialysis pilot, supplied by Eurodia Industrie (France). The membranes used (AEM and CEM Neosepta) are supplied by Tokuyama Corp. (Japan). The stack comprises 10 cells (AEM/CEM). For each type of membrane, the total active area is $0.2\,\mathrm{m^2}$, i.e. $0.02\,\mathrm{m^2}$ per cell.

3.1.2. Experimental procedures and operating conditions

All the experiments are operated in a batch mode (complete recycling of diluate and concentrate). Two types of experiments are performed with synthetic solutions of lactate.

The first type aims at quantifying the contribution of diffusion and osmosis to the solute and solution transfer, respectively. Experiments are carried out at zero current density ($i = 0$) with different concentration differences across the membranes, ranging from 50 to 300 kg m^{-3}. One compartment is fed with the lactate solution at the appropriate concentration, while the other one is fed with distilled water. The experiment duration is fixed at 80 min.

The second kind of experiment aims at quantifying the model parameters as functions of operating conditions, when a current is applied. Both compartments (concentrate and diluate) are initially fed with the same solution, i.e. lactate salt at the desired concentration. Concentrations ranging from 50 to 95 kg m^{-3} in lactate are used. Electrode compartments are fed with a sodium chloride solution at a concentration of 10 kg m^{-3}.

Experiments are carried out at a constant current density, in a range between 0 and 300 A m^{-2}, corresponding to an intensity range of 0–6 A. The voltage evolution as a function of time is recorded to estimate the stack electrical resistance.

For any set of experiments, the feed flow rates are set at constant values of 180 l h^{-1} for the diluate and the concentrate and 150 l h^{-1} for the electrode solution. A heat exchanger is used to maintain the temperature between 33 and 36°C.

During the experiments, solution conductivities, temperature, current and voltage are measured in real-time. Conductivity and pH are measured with a HI933100 conductimeter (Hanna Instruments, Portugal) and a pH340 pH-meter (WTW, Germany), respectively. Then, the organic acid salt concentration, and the volume variation are followed in the two compartments as a function of time. The experiment duration is determined according to the conductivity in the diluate. EDC is stopped as soon as this conductivity reaches 1 mS cm^{-1}. Consequently, different experiment durations are obtained with respect to the operating conditions.

For each experiment, the limiting current density is determined by the Cowan and Brown method, i.e. by determining the minimum of the curve representing the variation of U/I as a function of 1/I [12]. This is done at the end of each run, when the concentration in the diluate is the lowest and so the electrical resistance is the highest. In this manner, the limiting current density is underestimated. The operating current was set at 80% of the measured limiting current, as this is the rule on industrial ED plants.

For the fermentation broth, the same procedure is used. However, in that case, since the removal of residual sugars is also investigated (results not shown), the concentrate is initially fed with a diluted (5 kg m^{-3}) synthetic solution of ammonium lactate, while the diluate is initially fed with the clarified broth. The current density is fixed at 250 A m^{-2}.

3.2. Feed solutions

3.2.1. Synthetic solutions

The solutions were prepared by diluting sodium lactate (60 wt.%, Prolabo, France) or ammonium lactate (20 wt.%, Aldrich Chemical Company Inc., USA) in distilled water to obtain the desired concentration.

3.2.2. Fermentation broth

A clarified fermentation broth was used to check the model validity. Its characteristics are listed in Table 1. The results concerning the clarification step, carried out by cross flow microfiltration, were published elsewhere [10].

3.3. Analytical methods

Samples of diluate and concentrate were analysed at different time intervals in order to follow the

Table 1
Characteristics of the clarified fermentation broth

Compounds	
Lactate	72 kg m^{-3} (0.8 mol l^{-1})
Mineral cations	
NH_4^+	13.8 kg m^{-3} (0.77 mol l^{-1})
K^+	4.8 kg m^{-3}
Na^+	0.64 kg m^{-3}
Divalent (Mg^{2+}, Ca^{2+}, ...)	60 ppm
Mineral anions	
SO_4^{2-}	5 kg m^{-3}
Cl^-	2 kg m^{-3}
Residual sugars	10 kg m^{-3}
Physico-chemical characteristics	
Conductivity	50 mS cm^{-1}
pH	8

variation of the acid salt concentration as a function of time. According to the concentration range, two different methods were used to determine the lactate concentration. For low concentrations, ion exchange chromatography (IEC, Dionex, France) with a CD20 conductimetric detector and an Ionpac AS11 column was used. For high concentrations, refractometry (Digital RX-5000, Atago Co., Ltd., Japan) was preferred.

4. Results and discussion

Experimental results obtained with synthetic solutions of sodium lactate are first presented and discussed. Then, the influence of the lactate counter ion is investigated by comparing the transport of lactate from sodium or ammonium lactate solutions. These results are compared to those reported in the literature. Finally, we present the qualification of the model by studying the electrodialytic concentration of a fermentation broth containing ammonium lactate.

4.1. Concentration of synthetic solutions of sodium lactate

4.1.1. Quantification of diffusion and osmosis

The contribution of diffusion and osmosis to the solute and solution fluxes, respectively, is first investigated. Dedicated procedures depicted in Section 3.1.2 were used. Experimental results are plotted in Fig. 4, showing the variation of $R_A^{diffusion}$ and $R_V^{osmosis}$ versus the concentration difference across the membranes. Corresponding values are reported in Table 2. As previously explained, the diffusion flux $R_A^{diffusion}$ is directed from the concentrate to the diluate. Then, according to the convention, it is negative. Reported values are the absolute values of $R_A^{diffusion}$. Experimental data have been fitted and following expressions were obtained:

$$R_A^{diffusion} = -4 \times 10^{-12} \Delta C_A^2(t) + 3 \times 10^{-9} \Delta C_A(t) \,(kg\,s^{-1}) \quad (9)$$

$$R_V^{osmosis} = -2 \times 10^{-13} \Delta C_A^2(t) + 2 \times 10^{-10} \Delta C_A(t) \,(m^3\,s^{-1}) \quad (10)$$

In the range of concentration investigated, the maximum values of $R_A^{diffusion}$ and $R_V^{osmosis}$ are, respectively, equal to $6 \times 10^{-7}\,kg\,s^{-1}$ and $4.3 \times 10^{-8}\,m^3\,s^{-1}$. These values will be later compared to those obtained during EDC, i.e. when a current density is applied through the stack.

Table 2
Synthetic solutions of sodium lactate — contribution of diffusion and osmosis — experiments at $i = 0$

ΔC_A (kg m^{-3})	$R_A^{diffusion}$ (kg s^{-1})	$R_V^{osmosis}$ (m^3 s^{-1})
85	1.83×10^{-7}	1.38×10^{-8}
145	3.83×10^{-7}	2.5×10^{-8}
200	5×10^{-7}	3.3×10^{-8}
300	5.83×10^{-7}	4.3×10^{-8}

4.1.2. Validation of the model assumptions

A simplified expression of the lactate concentration was proposed from which C_{max} can be deduced. This part of the experimental study deals with the validation of the assumptions made to establish Eq. (5). These assumptions concern the lactate mass flow and the volume flow, which were considered to remain constant during EDC. Then, the variations of the volume and the lactate mass in the concentrate versus time are expected to be linear.

Experimental variations of the volume and the lactate mass in the concentrate are plotted versus time in Fig. 5. One can observe that for any experiment, the experimental points are actually aligned on a straight line. Then, the slopes of the corresponding straight lines provide the values of R_A and R_V.

4.1.3. Expression of R_A and R_V

Table 3 summarizes the values of R_A and R_V obtained for different current densities and initial lactate concentrations. For information, the limiting current density, determined according to the procedure described in Section 3.1.2, is also provided. The variations of R_A and R_V versus the current density are plotted in Fig. 6, for the different initial lactate concentrations. One can observe that these variations are linear. Moreover, the straight lines obtained for different concentrations are superimposed. For a current density tending towards zero, R_A and R_V tend toward

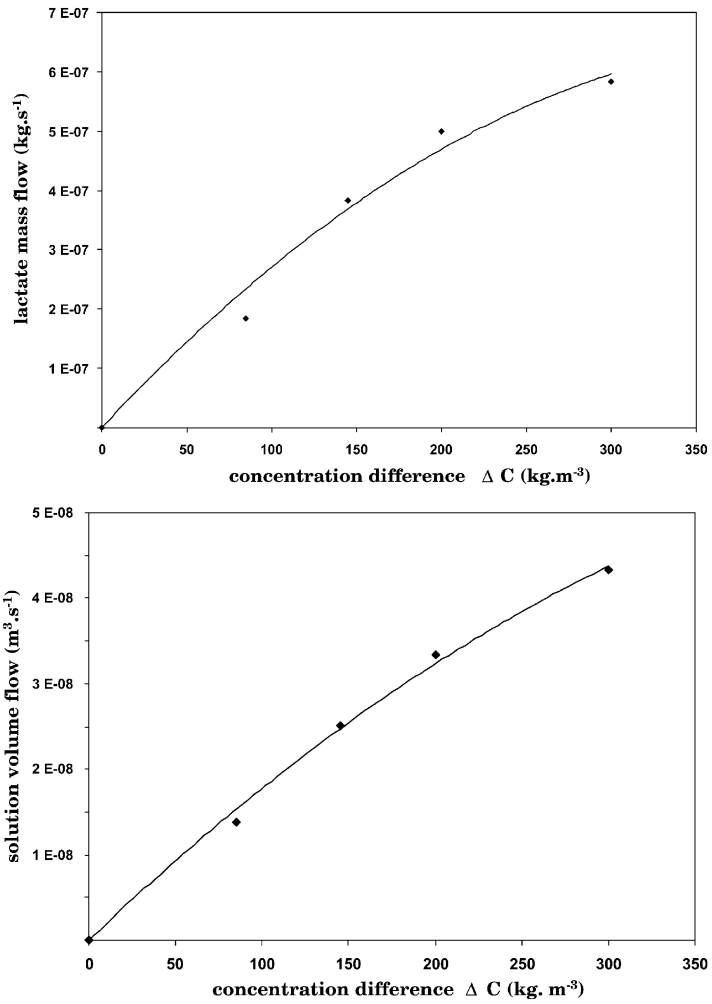

Fig. 4. Quantification of the contributions of diffusion and osmosis. Variations of the lactate mass flow $R_A^{diffusion}$ (top) and the solution volume flow $R_V^{osmosis}$ (bottom) vs. the lactate concentration difference ΔC across the membranes; operating conditions: $i = 0$.

Table 3
EDC of synthetic solutions of sodium lactate — influence of the operating conditions (initial lactate concentration C_0 and current density) on the values of the lactate mass flow R_A, the solution volume flow R_V and of the limiting current i_{lim}

Experiment number	C_0 (kg m^{-3})	i (A m^{-2})	i_{lim} (A m^{-2})	R_A (kg s^{-1})	R_V (m^3 s^{-1})
2	48	100	400	1.85×10^{-5}	6.52×10^{-8}
3	50	200	400	3.82×10^{-5}	13.5×10^{-8}
4	47	300	400	5.33×10^{-5}	20×10^{-8}
6	69	100	350	1.83×10^{-5}	7×10^{-8}
7	68	200	450	3.8×10^{-5}	14×10^{-8}
8	72	300	400	5.67×10^{-5}	20×10^{-8}
10	96	100	400	1.67×10^{-5}	6.3×10^{-8}
11	97	200	400	3.5×10^{-5}	12.5×10^{-8}
12	94	300	350	5.67×10^{-5}	20×10^{-8}

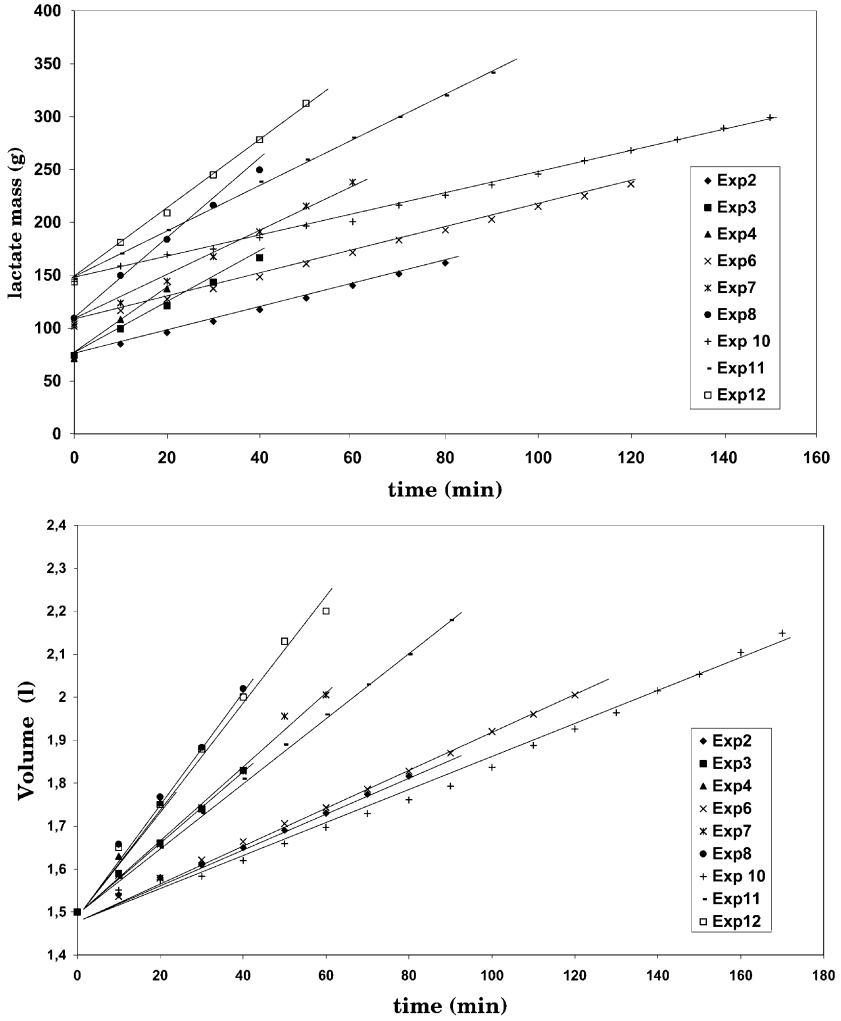

Fig. 5. EDC of synthetic solutions of sodium lactate — variations of the lactate mass (top) and the volume (bottom) in the concentrate vs. time; operating conditions: see Table 3.

$R_A^{\text{diffusion}}$ and R_V^{osmosis}, respectively. As far as values reported in Tables 2 and 3 are compared, one can conclude that the contributions of osmosis and diffusion are negligible. This is confirmed by the linear variation of the volume and the lactate mass in the concentrate versus time.

The data reported in Table 3 were fitted so as to get explicit relationships concerning the dependence of R_A and R_V versus the current density, since the influence of the initial lactate concentration was found to be negligible. The following expressions were obtained:

$$R_A = K_A^1 i + K_A^2 = 1.886 \times 10^{-7} i - 9.1 \times 10^{-7}\ (\text{kg s}^{-1}) \quad (11)$$

$$R_V = K_V^1 i + K_V^2 = 6.7 \times 10^{-10} i - 6.6 \times 10^{-10}\ (\text{m}^3\ \text{s}^{-1}) \quad (12)$$

where K_A^1, K_A^2, K_V^1 and K_V^2 are constants for the conditions used. Generally speaking, these parameters are

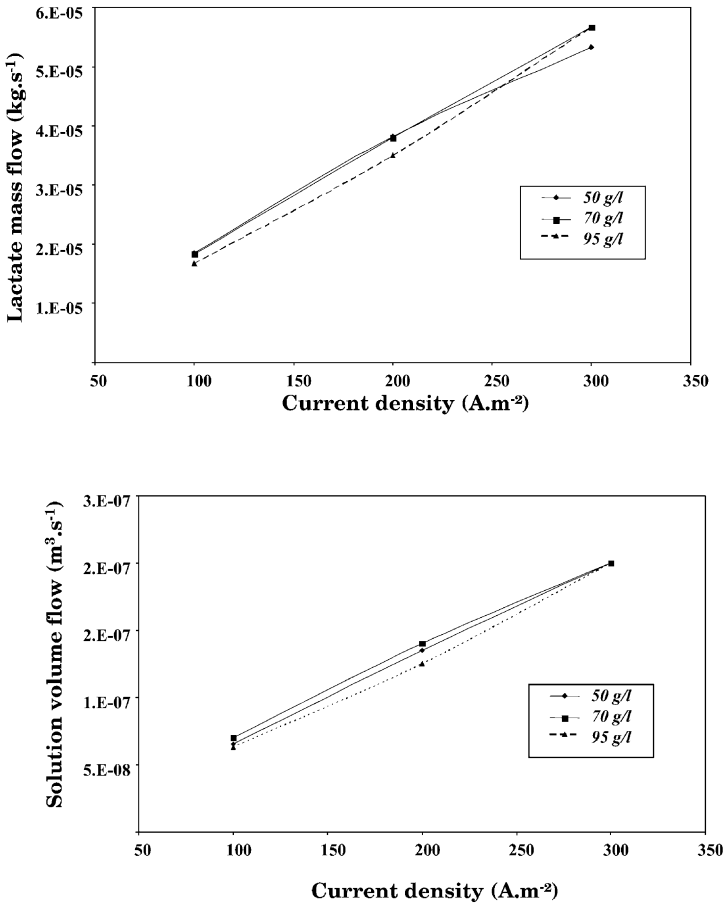

Fig. 6. EDC of synthetic solutions of sodium lactate — variation of R_A (top) and R_V (bottom) vs. the current density for different initial lactate concentrations.

dependent on the membrane characteristics as well as on the transported species. Moreover, as soon as a current density of $100\,A\,m^{-2}$ is applied, the constants K_A^2 and K_V^2 become negligible compared to $K_A^1 i$ and $K_V^1 i$. This shows that during EDC, phenomena related to the electrical current, i.e. the solute migration and electroosmosis, are preponderant upon diffusion and osmosis. Then, expressions of R_A and R_V can be simplified as

$$R_A = K_A^1 i = 1.886 \times 10^{-7} i\ (kg\,s^{-1}) \tag{13}$$

$$R_V = K_V^1 i = 6.7 \times 10^{-10} i\ (m^3\,s^{-1}) \tag{14}$$

The flux densities across the membranes can be further deduced from the previous relationships and expressed as in Eqs. (15) and (16):

$$J_A = \frac{R_A}{S} = \frac{K_A^1}{S} i = 9.43 \times 10^{-7} i\ (kg\,m^{-2}\,s^{-1}) \tag{15}$$

$$J_V = \frac{R_V}{S} = \frac{K_V^1}{S} i = 3.35 \times 10^{-9} i\ (m^3\,m^{-2}\,s^{-1}) \tag{16}$$

Whereas experiments were run batch-wise, these fluxes permit as well to characterize the transport of lactate for an electrodialytic step of concentration in feed-and-bleed mode, i.e. continuous mode.

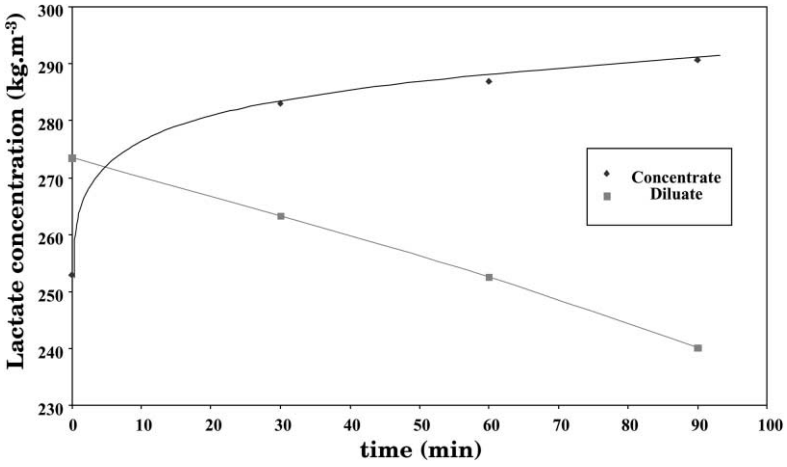

Fig. 7. EDC of synthetic solutions of sodium lactate — experimental validation of the maximum concentration — variation of the lactate concentration vs. time. Operating conditions: $i = 200\,\mathrm{A\,m^{-2}}$.

By combination of Eqs. (1), (13) and (14), the following expression is obtained for the concentration of lactate versus time:

$$C_{\mathrm{A}}^{\mathrm{C}}(t) = \frac{m_0^{\mathrm{C}} + 1.886 \times 10^{-7} it}{V_0^{\mathrm{C}} + 6.7 \times 10^{-10} it}\,(\mathrm{kg\,m^{-3}}) \tag{17}$$

4.1.4. Maximum concentration

From Eq. (17), the maximum sodium lactate concentration theoretically achievable by EDC can be calculated:

$$C_{\mathrm{max}}^{\mathrm{C}} = \frac{R_{\mathrm{A}}}{R_{\mathrm{V}}} = 282\,(\mathrm{kg\,m^{-3}}) \tag{18}$$

An experimental verification of this maximum concentration was searched. The electrodialysis compartments were fed with a concentrated sodium lactate solution (about $260\,\mathrm{kg\,m^{-3}}$) in order to reach the limit in one single batch. Fig. 7 shows the variation versus time of the lactate concentration in the two compartments. One can observe that the concentration in the concentrate increases to reach a constant plateau value. This value, about $290\,\mathrm{kg\,m^{-3}}$, is very close to that predicted by the model. Moreover, the values of R_{A} and R_{V} derived from the experimental data are $3.6 \times 10^{-5}\,\mathrm{kg\,s^{-1}}$ and $1.2 \times 10^{-7}\,\mathrm{m^3\,s^{-1}}$, respectively. These values are comparable to those predicted at the corresponding current density, i.e. $200\,\mathrm{A\,m^{-2}}$, by Eqs. (13) and (14), i.e. $3.7 \times 10^{-5}\,\mathrm{kg\,s^{-1}}$ and $1.3 \times 10^{-7}\,\mathrm{m^3\,s^{-1}}$, respectively.

Yen and Cheryan investigated the recovery of lactate salt from fermentation broths by EDC [13]. From the experimental results they have reported, one can conclude that, as was observed in the present study, the lactate mass and volume transported are constant during EDC. Moreover, solution and lactate flux densities can be calculated. For the current density used, i.e. $180\,\mathrm{A\,m^{-2}}$, values of $1.14 \times 10^{-6}\,\mathrm{m^3\,m^{-2}\,s^{-1}}$ and $1.53 \times 10^{-4}\,\mathrm{kg\,m^{-2}\,s^{-1}}$ are obtained. In our system, according to Eqs. (15) and (16), at the same current density, J_{V} and J_{A} have respective values of $6 \times 10^{-7}\,\mathrm{m^3\,m^{-2}\,s^{-1}}$ and $1.7 \times 10^{-4}\,\mathrm{kg\,m^{-2}\,s^{-1}}$. The main reason for explaining this difference comes from the use of different membranes. The ones used by Yen and Cheryan are obviously more permeable to water than ours since for an identical solute flux, the electroosmotic flux is twice that observed in the present study. Consequently, the maximum lactate concentration achievable with their system is about two times lower than that achievable with the one used in this study, i.e. 135 compared to $280\,\mathrm{kg\,m^{-3}}$.

Lee et al. also studied the recovery of lactic acid by two-stage electrodialysis, i.e. both conventional and bipolar ED [14]. From their EDC experimental results, we have calculated the maximum lactate concentration, which is about $310\,\mathrm{kg\,m^{-3}}$. Whilst the membranes (Neosepta CM-1 and AM-1, Tokuyama

Corp.) were different from ours, this value is very close (within 10%) to that obtained in the present study. However, even small, this difference can be explained by the crosslinkage of each membrane pair. CM-1/AM-1 are indeed more crosslinked than the membranes used in the present study. Then, the number of water moles transported per mole of transported solute is probably lower. This will be further discussed in Section 4.3.

Finally, from a qualitative point of view, these studies also concluded that both lactate and solution transport are tied to the current density and non-dependent on the lactate concentration. Then, as far as weak organic acid salts are concerned, the contributions of osmosis and diffusion can be neglected with respect to those coming from electroosmosis and electromigration phenomena.

4.2. Influence of the counter ion

It was previously suggested that during EDC the counter ion of a given species could influence its transport [15]. In other words, a lower transport of the counter ion through the CEM could result in a lower transport of the target species, i.e. lactate in the present case, through the AEM. That means that to quantify the lactate mass flow, it is worth investigating that of its counter ion. This is done hereafter, where experimental results obtained during electrodialytic concentrations of sodium and ammonium lactate solutions are compared.

EDC experiments carried out with ammonium lactate solutions show that the variations of the volume and the lactate mass versus time are linear. Then, the experimental values of R_V and R_A were determined. These values are reported in Table 4 together with those calculated for the corresponding current densities thanks to Eqs. (13) and (14), established for EDC concentration of sodium lactate solutions. One can observe that the difference between experimental and predicted values never exceeds 13%. Consequently, in the case of single organic salt, for a given current density, the mass flow of organic salt is almost the same whatever its counter-ion. Different conclusions would be probably drawn with more complex solutions, containing a mixture of organic acids salts associated with different kinds of cations [15]. Finally, the influence of the counter ion on the volume flow will be further discussed in Section 4.3.

4.3. Relationship between R_A and R_V

Expressions established hereafter will be written for lactate salts. However, they can used for any monovalent organic acid salt.

Both lactate and the counter ion contribute to the water transport, as both carry a shell of water molecules. The resulting volume flow, R_V, of solution is then the sum of three contributions. The first two are due to the volume of lactate ions, R_V^{Lac}, and to that of its counter ions i, R_V^i, migrating from one compartment to the other. The third one is due to the volume of water molecules transported along by the migrating species, i.e. lactate and counter ion, R_W. Then, the volume flow R_V can be written as

$$R_V = R_V^{Lac} + R_V^i + R_W \tag{19}$$

R_V^{Lac} and R_V^i can be further related to R_i and R_A using the molar volumes v_i, and molecular weights M_{Lac} and M_i (for lactate and its counter ion i, respectively). Then Eq. (19) becomes

$$R_V = \frac{v_{Lac} R_A}{M_{Lac}} + \frac{v_i R_i}{M_i} + R_W \tag{20}$$

Moreover, because of electroneutrality, the molar flow of counter ion has the same value as the lactate one, since both are monovalent. That means that $R_A/M_{Lac} = R_i/M_i$. Then, Eq. (21) is obtained.

Table 4
EDC of synthetic solutions of ammonium lactate[a]

Experiment	Experimental R_A (kg s^{-1})	Experimental R_V (m^3 s^{-1})	R_A model (kg s^{-1})	R_V model (m^3 s^{-1})	Experimental C_{max} (kg m^{-3})	C_{max} model (kg m^{-3})
13	2.6×10^{-5}	0.87×10^{-7}	2.8×10^{-5}	10^{-7}	300	280
14	4.3×10^{-5}	1.5×10^{-7}	4.7×10^{-5}	1.7×10^{-7}	287	280

[a] Comparison between experimental and calculated values of R_A, R_V and C_{max}. Operating conditions — experiment 13: initial lactate concentration 80 kg m^{-3}; current density 150 A m^{-2}; experiment 14: initial lactate concentration 100 kg m^{-3}; current density 250 A m^{-2}.

$$R_W = R_V - \frac{R_A}{M_{Lac}}(v_{Lac} + v_i) \quad (21)$$

Combining Eqs. (21), (13) and (14), one gets a relationship that gives the amount of solvent accompanying the solutes migration:

$$R_W = \left(6.7 \times 10^{-10} - 1.886 \times 10^{-7}\left(\frac{v_{Lac} + v_i}{M_{Lac}}\right)\right) i \quad (22)$$

Then, the hydration number of the solute can be calculated thanks to

$$n_{Lac,i} = \frac{R_W M_{Lac} N_{H_2O}}{R_A} \quad (23)$$

The molar volumes of lactate v_{Lac}, sodium v_{Na} and ammonium v_{NH_4} are, respectively, 88, 22 and 14 $cm^3\,mol^{-1}$ [16]. The molecular weight of lactate M_{Lac} is $89 \times 10^{-3}\,kg\,mol^{-1}$ and one takes $N_{H_2O} = 55.2 \times 10^3\,mol\,m^{-3}$.

From these data, we can calculate the number of water moles transported per mole of transported solute, i.e. the hydration number of the solute [Lac, i]:

$$n_{Lac,i} = 17.45 - 55200(v_{Lac} + v_i) \quad (24)$$

The values obtained for sodium lactate n_{LacNa} and ammonium lactate n_{LacNH_4} are then equal to 11.4 and 11.7, respectively.

The difference between n_{LacNa} and n_{LacNH_4} may be explained by a difference of hydration shell between sodium and ammonium ion.

Previous equations were used to calculate, from previously published data [14], the number of water moles transported per mole of transported solute. A value of 9.7 was obtained. This lower value explains the former discussed difference (Section 4.1) between the maximum concentrations obtained in both studies.

On another hand, these results show that once the hydration number of the solute in the membrane and the mass flux of each transported species are known, it is possible to calculate the volume flow and so the maximum achievable concentration.

4.4. Fermentation broth

In order to know to what extent the model developed from synthetic solutions could be applied to real conditions, the concentration of a clarified fermentation medium is carried out. This clarified broth is mainly composed of ammonium lactate, as shown in Table 1.

Again, experimental results show linear variations of the volume and the lactate mass versus time. Then, experimental values of the solution and lactate flows are determined.

These values are equal to $1.8 \times 10^{-7}\,m^3\,s^{-1}$ and $4.7 \times 10^{-5}\,kg\,s^{-1}$, respectively. For the corresponding current density, i.e. $250\,A\,m^{-2}$, the values predicted

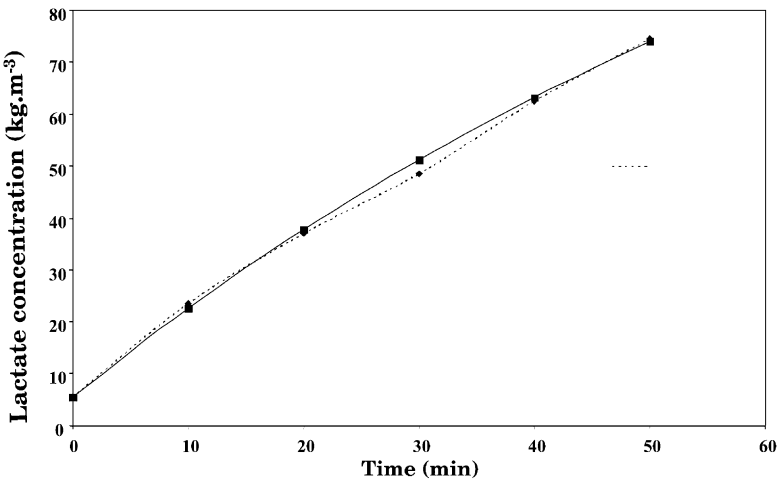

Fig. 8. EDC of the fermentation broth — comparison between experimental (dashed line) and calculated (full line) variations of the lactate concentration in the concentrate. Operating conditions: $i = 200\,A\,m^{-2}$; initial concentration $= 5\,kg\,m^{-3}$.

by the model are equal to 1.7×10^{-7} m^3 s^{-1} and 4.7×10^{-5} kg s^{-1}.

Finally, the experimental and calculated variations of the lactate concentration in the concentrate are plotted versus time in Fig. 8. One can observe that the model predicts the concentration with a good precision since the difference between experimental and predicted values never exceeds 5%.

5. Conclusion

This study aimed at proposing design tools for the concentration of weak organic acid salt by conventional electrodialysis.

A model, based on the description of the solute and solution fluxes through the membranes, was established. This model enables to calculate the variation of the target specie concentration in both compartments versus time from the knowledge of two characteristic parameters: the volume flow, R_V, and the target specie mass flow, R_A. Moreover, this model predicts the existence of a maximum concentration, the value of which can be calculated.

Experiments were performed with synthetic solutions of sodium lactate. Dedicated procedures were first used to quantify the two kinds of contributions involved, i.e. diffusion and electromigration for the solute transfer and osmosis and electroosmosis for the solution flow. It was thus demonstrated that, in most operating conditions, i.e. except for low values of the current density, the electromigration phenomena (transport of charged species and co-transport of solution) are preponderant compared to diffusion and osmosis. Thus, the assumptions made for the model establishment were verified. Then, the characteristic parameters, R_A and R_V, involved in the model were determined with respect to the operating conditions. In this manner, their physical meaning was checked. These values were compared to those deduced from previously published results. On the other hand, the existence of a maximum concentration C_{max} has been confirmed experimentally. Its value was found to be identical to that predicted by the model. Again, it was compared to those calculated from previous results.

The influence of the counter ion was also investigated, through the comparison of EDC concentration of sodium and ammonium lactate solutions. The counter ion was found to have negligible influence on the transport of the acid salt while slightly different values of the volumic flow were obtained. This was explained from the difference of the hydration number of the counter ion in the membrane. A relationship between R_A and R_V and this hydration number was established.

Finally, the model predictions were compared to the experimental results obtained during the concentration of an ammonium lactate fermentation broth and a good agreement was stated.

Since the methodologies proposed in this paper enable to quantify the different fluxes involved during the concentration by electrodialysis, they can be used as well for any other organic acid than that used in the present study.

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