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> **To link to this article**: DOI:10.1016/J.PROCBIO.2010.01.015 URL: <u>http://dx.doi.org/10.1016/J.PROCBIO.2010.01.015</u>

**To cite this version**: Umpuch, Chakkrit and Galier, Sylvain and Kanchanatawee, Sunthorn and Roux-de Balmann, Hélène (2010) Nanofiltration as a purification step in production process of organic acids: Selectivity improvement by addition of an inorganic salt. *Process Biochemistry*, vol. 45 (n°11). pp. 1763-1768. ISSN 1359-5113

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# Nanofiltration as a purification step in production process of organic acids: Selectivity improvement by addition of an inorganic salt<sup> $\approx$ </sup>

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### ABSTRACT

The aim of this study is to investigate to what extend the addition of an electrolyte (NaCl or Na<sub>2</sub>SO<sub>4</sub>) can improve the selectivity of the sodium lactate/glucose separation by nanofiltration. Experimental results were used to get the variation of the observed retentions versus the permeation flux and to evaluate the separation efficiency from the separation factor. In presence of NaCl, both glucose and lactate retentions slightly decrease and remain very close except at low permeation fluxes where the addition of NaCl has more effect on lactate retention than on glucose one. On the contrary, whilst the addition of Na<sub>2</sub>SO<sub>4</sub> has no influence on glucose retention, a strong effect was pointed out on the lactate one, especially for high electrolyte concentrations for which negative retentions were obtained at low permeation fluxes. Then, the separation was much more improved by the addition of Na<sub>2</sub>SO<sub>4</sub> compared to NaCl. A maximum separation factor of 1.9 was obtained with Na<sub>2</sub>SO<sub>4</sub> at 0.25 M added to the glucose (0.1 M)/sodium lactate (0.1 M) solution whereas the separation was impossible without the addition of salt.

# 1. Introduction

Organic acids (acetic, lactic, gluconic acids, etc.) are increasingly used in food (preservative, taste), pharmaceutical (buffer solutions), and chemical (biodegradable polymer) industries as well as in cosmetics (moisturizers, skin-lightening or anti-acne agents). They are mainly produced by fermentation generating a broth containing the dissociated form of the acid (as a sodium, ammonium, or calcium salt) and different impurities, such as residual sugars and mineral salts. Further operations are thus required to get the organic acid with the desired purity and concentration.

Due to the environmental constraints, the development of processes able to replace the traditional operations like liquid/ liquid extraction and precipitation is considered since few years. In this context, membrane operations, such as electrodialysis [1] or nanofiltration [2], appear very attractive since the generation of effluents or by products is expected to be significantly reduced. A

two stage process, including conventional and bipolar electrodialysis, was thus proposed [3,4]. The integration of nanofiltration in this process was also investigated [2,5]. Different stages were considered, before and after the conversion step carried out by bipolar electrodialysis. Indeed, it was demonstrated that nanofiltration can remove the divalent ions and the remaining sugars, before and after the conversion step, respectively [5]. But, the expected partial elimination of sugars before the conversion step was found to be unachievable. Although a good selectivity was expected from single solute solutions, since the retentions of glucose and sodium lactate were about 80 and 20%, respectively, the separation was found to be very poor because of the decrease of the glucose retention in presence of sodium lactate [2].

Such an effect of the presence of charged species on the retention of neutral ones was reported in different situations, with organic as well as inorganic membranes and with different kind of solutes. The main results are summarized in Table 1. In any case, it was pointed out that an increasing salt concentration results in lowering the neutral solute retention and that this decrease depends on the nature of the added salt. For instance, it was observed that the retention of glucose decreases more with the addition of sodium lactate than with that of sodium chloride at the same concentration [2]. The effect on the glucose retention was also found to be more important with Na<sub>2</sub>HPO<sub>4</sub> than with NaCl and Na<sub>2</sub>SO<sub>4</sub> [9]. Concerning the addition of some inorganic ions (NaCl, KCl, CaCl<sub>2</sub>) it was observed that the lowest the salt retention the

<sup>\*</sup> Presented at the SFGP 2009 congress (Bioprocess Engineering), Marseille, October 14–16.

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Table 1

Influence of salt on the retention of neutral compounds.

Neutral compound (MW g mol <sup>-1</sup> ) concentration	Electrolyte concentration	NF membrane	Neutral solute retention reduction <sup>a</sup>	Reference
Glucose (180) ~1 mM Sucrose (342) ~0.6 mM	NaCl 0.01–0.1 M	NF45 (Dow Chemical)	25% <8%	Wang et al. [6]
Glucose (180) ${\sim}0.01\text{M}$	NaCl 0.01-0.1 M	NF (Dow Chemical)	15%	Bargeman et al. [7]
Glucose (180) 0.1 M	NaCl 0.5 and 1 M NaLac 0.5 M	Desal 5DK (Osmonics)	20% 75%	Bouchoux et al. [2]
Lactose (342) in UF whey 0.1-0.15 M	Mineral salt in UF whey 0.05-0.10 M	Desal 5DL (Osmonics) NF200 (Dow Chemical)	<5%	Cuartas-Uribe et al. [8]
Glucose (180)	NaCl 0.01-0.1 M Na <sub>2</sub> SO <sub>4</sub> 0.01-0.1 M Na <sub>2</sub> HPO <sub>4</sub> 0.01-0.1 M	XN45 (Trisep)	Retention reduction (data not given) Negative retentions for [Na <sub>2</sub> HPO <sub>4</sub> ] >0.03 M	Mandale and Jones [9]
PEG (600) $\sim$ 3 mM	KCl 0.1–1 M LiCl 0.1–1 M MgCl <sub>2</sub> 0.1–1 M	NF ceramic membrane Filtanium® (Tami-Industries)	30% 60% 70%	Bouranene et al. [10]

PEG: polyethyleneglycol.

<sup>a</sup> The retention reduction is calculated from  $\frac{R_{Glu}(without salt) - R_{Glu}(with salt)}{R_{Glu}(without salt)} \times 100$ 

most the influence on the glucose retention [7]. Considering such results, it is difficult to predict the influence of the addition of a salt on the retention of a neutral solute.

The retention of a neutral solute comes from size exclusion, which is fixed by the solute and pore size. Then, a lower retention like that observed when adding a salt can be ascribed to an increase of the pore radius, to a decrease of the solute hydrodynamic radius, or more probably to a combination of both.

It was indeed suggested that, the addition of salt in solution can lead to an increase of the membrane charge density and to a higher concentration of counter-ions in the electrical double-layer at the pore surface [11,12]. Because of the stronger repulsion forces between the pore walls a pore swelling can appear if the membrane material behaves like an elastic polymer [2,7]. However, as already mentioned, the effect of salt on neutral solute transfer has also been observed with ceramic membranes, which are more rigid than organic ones and not expected to swell [10].

On the other hand, the apparent size of neutral solutes, like carbohydrates, is also expected to be influenced by the ionic composition. Indeed, it was established that glucose is less hydrated when NaCl is added into the solution [13]. Since this release of water makes the apparent size of the solute smaller, a lower retention can be expected. According to that, more hydrated salts in solution mean a higher dehydration, and thus a lower size and a lower retention of the sugar. This tendency was found to be in good agreement with experimental results obtained with different salts [2].

The retention of charged species is also expected to decrease for increasing salt concentrations. This well known phenomenon, called "screening effect", has been widely reported in the literature [14–16]. In fact, the retention of charged species depends on both steric effects and electrostatic interactions with the membrane. For solutes having the same charge as the membrane, electrostatic repulsions are dominant at low concentration, then high retentions are obtained. As the salt concentration increases, electrostatic interactions become weaker, and the retention decreases.

Both neutral and charged compounds retentions are thus affected by the ionic composition. However, the impact of the ionic composition may be different because the mechanisms governing the retention of both kinds of solutes are different.

Then, the objective of this paper is to evaluate to what extend the addition of an electrolyte can improve the selectivity of the sodium lactate/glucose separation. Indeed, a previous study has shown that this separation is hardly achievable because of the influence of the lactate salt on the glucose retention [2].

The influence of the addition of salts (NaCl and  $Na_2SO_4$ ) on both glucose and lactate retentions is first studied in binary solutions (glucose/electrolyte and sodium lactate/electrolyte). Then, the separation of glucose and lactate in ternary solutions (glucose/sodium lactate/electrolyte) of different compositions is investigated. The results are compared to those expected from binary solutions. The improvement due to the addition of salt is finally discussed.

#### 2. Experimental materials and methods

#### 2.1. Membrane and chemicals

A Desal 5DK membrane supplied by Osmonics as flat sheets was used. It was a composite membrane (polyamide/Osmonics proprietary layer/polysulfone) negatively charged at pH higher than 4 [17]. The main characteristics, provided by the supplier, were an average molecular weight cut-off of 150–300 g mol<sup>-1</sup>, and a hydraulic permeability of approximately  $5.5 L h^{-1} m^{-2} bar^{-1}$ .

Solutions were prepared using glucose (Acros Organics) and three types of sodium salts, sodium lactate (NaLac), sodium chloride (NaCl) and sodium sulphate (Na<sub>2</sub>SO<sub>4</sub>) (Prolabo-Merck Eurolab), dissolved in ultra-pure water. The relevant characteristics of these solutes are listed in Table 2. The compositions of feed solutions in binary and ternary solutions are reported in Table 3. For any set of operating conditions, the pH of the solutions was between 6 and 7, so the membrane is negatively charged.

#### 2.2. Analytical methods

NaLac, NaCl, Na<sub>2</sub>SO<sub>4</sub> and glucose concentrations in binary solutions were determined by high-performance liquid chromatography using a Shodex SUGAR SH1011 column (Showa Denko) and a refractive index detector. The column temperature was set to 50 °C and the mobile phase was 0.01 M sulphuric acid at a flow rate of 1 mL min<sup>-1</sup>.

#### Table 2

Principal characteristics of the investigated compounds.

Compounds	Molecular weight (gmol <sup>-1</sup> )	Diffusion coefficient $(10^{-10} \text{ m}^2 \text{ s}^{-1})$	Stokes radius (nm)
Glucose	180.16	6.9	0.365
Lactate	89.07	10.6	0.23
Na <sup>+</sup>	22.99	13.3	0.184
Cl-	35.45	20.3	0.121
$SO_4^{2-}$	96.1	10.6	0.23

Table 3

Compositions of binary and ternary solutions.

Solutions	Glucose	NaCl	Na <sub>2</sub> SO <sub>4</sub>	NaLac
Binary solution	0.1 M	0.1–1 M		
	0.1 M		0.05-0.5 M	
		0.1-1 M		0.1 M
			0.05-0.5 M	0.1 M
Ternary solutions	0.1 M	0.1–1 M		0.1 M
5	0.1 M		0.05-0.5 M	0.1 M

Ternary solutions were analysed by HPLC with a Dionex system. Glucose concentrations were determined using a CarboPac<sup>TM</sup> PA1 column with an electrochemical ED40 detector. The mobile phase was a 150 mM NaOH solution and the flow rate was 1 mL min<sup>-1</sup>. The column temperature was set at 30 °C. The ion concentrations were determined using a CD20 conductimetric detector with an lonpac AS11 column (mobile phase: 5 mM NaOH at 1 mL min<sup>-1</sup>) and an lonpac CS12 column (mobile phase: 20 mM CH<sub>4</sub>O<sub>3</sub>SO<sub>4</sub> at 1 mL min<sup>-1</sup>) for anions and cations, respectively.

#### 2.3. Filtration unit and experimental procedure

#### 2.3.1. NF set-up

NF experiments were carried out using a cross-flow filtration system depicted in Fig. 1. This system has been described in details in a previous paper [2]. A membrane sheet of 137 cm<sup>2</sup> was placed in the Osmonics Sepa CF II cell. Feed solution was contained in a 5 L feed vessel maintained at a constant temperature of  $25 \pm 0.5$  °C by a circulating thermostatic bath. A high-pressure pump was used to pull feed solution to the membrane cell. The transmembrane pressure was controlled by a back pressure valve (stainless steel control valve), mounted on the retentate outlet. The pressure was monitored through two digital manometers located on the inlet and outlet of the cell. The retentate and permeate streams were recycled back into the feed vessel in order to work at constant feed concentration.

Experiments were performed at a constant cross-flow rate of  $400 \text{ L} \text{ h}^{-1}$ , i.e. a cross-flow velocity of 1.33 m s<sup>-1</sup>, with increasing transmembrane pressures from 2 to 18 bar. A volume of 5 mL of permeate was collected for each pressure and timed to estimate the permeation flux. The flux values reported later are those obtained at steady state. The feed and permeate concentrations were determined by the analytical methods previously presented.

#### 2.3.2. Membrane pre-treatment and water permeability

The membrane pre-treatment and cleaning procedures are crucial to obtain the adequate reference state before each experiment.

The virgin membrane was first compacted by filtering ultra-pure water at 20 bar and a constant cross-flow rate of  $400 \text{ L} \text{ h}^{-1}$ , until the water flux ( $J_v$ ) remains constant (usually within 1 h).

After each experiment, the membrane was rinsed by circulating reverse osmosis water followed by ultra-pure water at 25 °C, 10 bar, and 150 L h<sup>-1</sup>. This rinsing was repeated until the water conductivity was lower than 5  $\mu$ S cm<sup>-1</sup>.

The hydraulic permeability  $L_{p0}$  was determined before each experiment. To do this, the water flux was measured at increasing applied pressures ranging between 4 and 20 bar at 25 °C. The value of  $L_{p0}$  was then obtained as the slope of the plot of  $J_{\nu}$  versus  $\Delta P$  (calculation subject to a maximum standard deviation of  $\pm 5\%$ ). The average initial hydraulic permeability obtained for the membranes used in this work was 5.0 L h<sup>-1</sup> m<sup>-2</sup> bar<sup>-1</sup>. It was in accordance with those previously reported [2,12,18].



Fig. 1. Schematic diagram of the nanofiltration system set-up (from Bouchoux et al. [2]).

A membrane sample presenting an abnormally high water flux (more than 20% difference between two consecutive permeability measurements) was replaced by a new one.

#### 2.3.3. Retention and separation factor

In permeation experiments, the observed retention,  $R_{obs}$ , of each component is usually defined as:

$$R_{obs} = 1 - \frac{C_p}{C_r} \tag{1}$$

where  $C_p$  and  $C_r$  are the permeate and retentate (or feed) concentrations, respectively.

The observed retention,  $R_{obs}$ , depends on the hydrodynamic conditions that may influence the concentration polarization phenomenon. Experiments were thus first carried out at different flow rates, ranging from 100 to 400 L h<sup>-1</sup>, with single glucose solutions at 0.1 M. It was shown that the observed retention slightly increases when the flow rate increases from 100 to 200 before approaching a constant value for flow rates higher than 300 L h<sup>-1</sup> (results not shown). Consequently, the observed retention measured at 400 L h<sup>-1</sup> was further considered as a good approximation of the "intrinsic" or "real" retention which deals directly with the concentration at the membrane surface [2,10].

In order to estimate the lactate/glucose separation efficiency, one can also use another parameter, the lactate separation factor, *SF*, which is expressed by the solute concentration ratio in the permeate divided by the concentration ratio in the retentate (or feed):

$$SF = \frac{(C_{lac}/C_{glu})_{permeate}}{(C_{lac}/C_{glu})_{retentate}}$$
(2)

The separation factor can be calculated from those of the lactate and glucose retentions as:

$$SF = \frac{1 - R_{obs(Lac)}}{1 - R_{obs(Glu)}}$$
(3)

SF values higher than 1, like those obtained in this work, mean that the NF permeate is a solution enriched in lactate, which is the target specie, compared to the feed. On the contrary, a value lower than 1 would correspond to an enriched retentate.

## 3. Results and discussion

Experiments were first carried out with binary solutions containing either glucose (0.1 M) and salts or sodium lactate (0.1 M) and salts in order to determine the influence of the salts (NaCl and Na<sub>2</sub>SO<sub>4</sub>) on the retention of neutral and charged solutes. Then, NF of ternary solution, i.e. containing glucose, lactate and different salt compositions, was investigated to evaluate the improvement that can be achieved by the addition of salt.

# 3.1. Influence of the ionic composition on glucose and lactate retentions

#### 3.1.1. *Glucose retentions*

The variations of the retention of glucose versus the permeate flux are plotted for different concentrations of NaCl and Na<sub>2</sub>SO<sub>4</sub> in Figs. 2 and 3, respectively.

Fig. 2 shows that the glucose retention slightly and continuously decreases with increasing NaCl concentrations. It decreases about 10% when NaCl concentration increases from 0 to 1 M. These results are in agreement with those already obtained in similar conditions [2] (see Table 1).

On the contrary, Fig. 3 shows that the glucose retention is almost not affected by the presence of Na<sub>2</sub>SO<sub>4</sub>. Indeed, the variation due to the addition of Na<sub>2</sub>SO<sub>4</sub> is lesser than 4% for Na<sub>2</sub>SO<sub>4</sub> comprised between 0.05 and 0.5 M. The corresponding retentions of sulphate are also plotted on the same graph. Contrary to the retentions of lactate and chloride (results not shown), the values are very high and almost independent of the concentration. Then, although sulphate is a charged solute, its retention is mainly fixed by steric effects and the influence of electrostatic repulsions is negligible.



**Fig. 2.** Observed retention of glucose vs. permeation flux for binary solutions of glucose (0.1 M) and NaCl: influence of NaCl concentration.



**Fig. 3.** Observed retention of glucose (full symbols) and sulphate (empty symbols) vs. permeation flux for binary solutions of glucose (0.1 M) and Na<sub>2</sub>SO<sub>4</sub>: influence of Na<sub>2</sub>SO<sub>4</sub> concentration.

These results are in accordance with those obtained in a previous work, showing a correlation between the decrease of glucose retention and the retention of the added salt [7]. More precisely, the less the salt retention, the more the decrease of the glucose retention. In the same manner, the glucose retention was found to remain constant when adding a completely retained anion.

# 3.1.2. Lactate retentions

The variations of the lactate retention versus the permeate flux are plotted in Figs. 4 and 5 for different concentrations of NaCl and Na<sub>2</sub>SO<sub>4</sub>, respectively.

Fig. 4 shows a continuous decrease with increasing NaCl concentrations. It was previously demonstrated that, for the conditions investigated here, the retention of lactate is mainly fixed by to electrostatic repulsions [2]. Then, the addition of salt like NaCl results in a lower retention because of the screening effect that makes the electrostatic repulsion weaker. The lactate retention decreases about 30% at low permeation flux when the NaCl concentration increases from 0 to 1 M.

Fig. 5 shows the lactate retention in presence of Na<sub>2</sub>SO<sub>4</sub> versus the permeate flux. As expected following the high sulphate retention, the fluxes are lower than those obtained with single solution of lactate. One can thus observe that the lactate retention decrease is more important than that observed when adding NaCl. For instance, the lactate retention decreases about 50% at  $J_v = 0.2 \times 10^{-5} \text{ m}^3 \text{ s}^{-1} \text{ m}^{-2}$  when the Na<sub>2</sub>SO<sub>4</sub> concentration increases from 0 to 0.5 M.



**Fig. 4.** Observed retention of lactate vs. permeation flux for binary solutions of NaLac (0.1 M) and NaCl: influence of the NaCl concentration.



Fig. 5. Observed retention of lactate (full symbols) and sulphate (empty symbols) vs. permeation flux for binary solutions of NaLac (0.1 M) and Na<sub>2</sub>SO<sub>4</sub>: influence of Na<sub>2</sub>SO<sub>4</sub> concentration.

Moreover, negative values are obtained at low permeate flux for the highest Na<sub>2</sub>SO<sub>4</sub> concentrations. This means that in these conditions, the lactate concentration is higher in the permeate than in the feed. Negative values of the retention of ions were already reported during nanofiltration of model mixtures containing monoand divalent ions, mainly  $Cl^{-}$  and  $SO_4^{2-}$  [11,12,19]. It is due to the competition for permeation between the membrane co-ions (showing the same sign of charge as the membrane) which have different size and/or charge. Divalent ions such as sulphate are more retained than monovalent ones (chloride or lactate) through a negatively charged membrane. Then, in a solution containing NaLac and Na<sub>2</sub>SO<sub>4</sub>, the permeation of lactate increases in order to maintain electroneutrality on both sides of the membrane and negative retentions can be achieved. The permeation of lactate, which is the less retained co-ion, is facilitated by increasing the concentration of sulphate ions, which is the more retained co-ion. Indeed, Fig. 5 shows that the retention of sulphate remains very high and does not depend on the composition of the solution.

# 3.1.3. Discussion

These results show that the effect of the addition of NaCl or Na<sub>2</sub>SO<sub>4</sub> on the glucose and lactate retentions is quite different.

Glucose and lactate retentions slightly decrease with increasing NaCl concentrations (Figs. 2 and 4). In the high permeation flux region, the values are close and their decrease is similar. For instance, at  $J_v = 1.5 \times 10^{-5} \,\mathrm{m^3 \, s^{-1} \, m^{-2}}$ , both glucose and lactate retentions vary from 0.9 to 0.8 as NaCl concentration increases from 0 to 1 M. However, for lower permeation fluxes, the addition



Fig. 6. Observed retention of glucose vs. permeation flux for ternary solutions of glucose (0.1 M)/NaLac (0.1 M) and  $\text{Na}_2\text{SO}_4$  (0.05-0.5 M) (full symbols): comparison with binary solutions glucose  $(0.1 \text{ M})/\text{Na}_2\text{SO}_4$  (0.05-0.5 M) (empty symbols).

of NaCl has more effect on the lactate retention than on the glucose one. For instance, at  $J_v = 0.2 \times 10^{-5} \text{ m}^3 \text{ s}^{-1} \text{ m}^{-2}$ , the lactate retention decreases from 0.8 to 0.55 (retention decrease of 30%) whereas the glucose one varies from 0.7 to 0.63 (retention decrease of 10%) as NaCl concentration increases from 0 to 1 M. Consequently, the addition of NaCl to glucose (0.1 M)/sodium lactate (0.1 M) mixture is expected to improve the separation only at low permeation fluxes.

On the other hand, the addition of Na<sub>2</sub>SO<sub>4</sub> has no influence on the glucose retention. But a significant decrease of the lactate retention is observed especially for high electrolyte concentrations for which negative retentions are observed at low permeation fluxes (Figs. 3 and 5). Then, it is expected that the separation of glucose (0.1 M) and sodium lactate (0.1 M) could be improved by the addition of Na<sub>2</sub>SO<sub>4</sub>. This improvement could be more important compared to that expected by the addition of NaCl.

# 3.2. Influence of the addition of salt on the glucose/lactate separation

Experiments carried out with ternary solutions showed that the variations of glucose and lactate retentions versus permeate flux in presence of NaCl (results not shown) or Na<sub>2</sub>SO<sub>4</sub> (Figs. 6 and 7) at various concentrations, are similar to those obtained in binary solutions, glucose/electrolyte and NaLac/electrolyte. Indeed, both glucose and lactate retentions in ternary solutions deviate by less than 10% from retentions in binary solutions.



J<sub>v</sub>(10-5 m<sup>3</sup>s-1m-2)

**Fig. 7.** Observed retention of lactate vs. permeation flux for ternary solutions of glucose (0.1 M)/NaLac (0.1 M) and  $\text{Na}_2\text{SO}_4 (0.05-0.5 \text{ M})$  (full symbols): comparison with binary solutions glucose  $(0.1 \text{ M})/\text{Na}_2\text{SO}_4 (0.05-0.5 \text{ M})$  (empty symbols).



Fig. 8. Separation factor of NaLac purification from glucose vs. permeation flux for ternary solutions of glucose (0.1 M), NaLac (0.1 M) and NaCl: influence of the NaCl concentration.



Fig. 9. Separation factor of NaLac purification from glucose vs. permeation flux for ternary solutions of glucose (0.1 M), NaLac (0.1 M) and Na<sub>2</sub>SO<sub>4</sub>: influence of Na<sub>2</sub>SO<sub>4</sub> concentration.

The corresponding variations of the separation factor versus permeate flux for ternary solutions are plotted in Figs. 8 and 9, respectively. These results are compared with those obtained with the binary solution glucose (0.1 M)/NaLac (0.1 M) (dashed line).

One can first observe that the separation factor is higher than 1. This means that NF gives a permeate which is enriched in lactate compared to the feed solution.

Moreover, as expected, the separation factor increases by adding increasing concentrations of salt. This increase seems to level off for the highest salt concentrations. Higher lactate separation factors are also obtained with Na<sub>2</sub>SO<sub>4</sub> compared to NaCl.

One can observe that for any salt concentration, the separation factor passes through a maximum value. The flux corresponding to this maximum increases with the salt concentration, from 0.05 to  $0.2 \times 10^{-5}$  m<sup>3</sup> s<sup>-1</sup> m<sup>-2</sup> as NaCl concentrations increase from 0 to 1 M and Na<sub>2</sub>SO<sub>4</sub> from 0 to 0.25 M.

The maximum values of the separation factor obtained for ternary solutions containing NaCl and Na<sub>2</sub>SO<sub>4</sub> at two concentrations are reported in Table 4. The one obtained without adding a salt is also reported for comparison. The corresponding permeate fluxes are also given. As expected, the selectivity improvement at low NaCl concentration (0.1 M) is poor. But it can reach up to about 35% for the highest NaCl concentration. The maximum value of the separation factor obtained in the conditions investigated in this work is about 1.9. It is obtained at a flux about  $0.2 \times 10^{-5}$  m<sup>3</sup> s<sup>-1</sup> m<sup>-2</sup> with the addition of Na<sub>2</sub>SO<sub>4</sub> at 0.25 M. Higher concentrations of Na<sub>2</sub>SO<sub>4</sub> do not improve the separation any more.

#### Table 4

Maximum separation factor in binary and ternary solutions and their corresponding permeate fluxes for glucose 0.1 M and NaLac 0.1 M.

Solutions	Salt concentration	SF <sub>max</sub>	$J_{v} (\times 10^{-5} \mathrm{m}^{3} \mathrm{s}^{-1} \mathrm{m}^{2})$
Binary solution Glucose/NaLac	0	1.1	0.05
Ternary solution	0.1 M	1.2	0.1
Glucose/NaLac/NaCl	1 M	1.5	0.2
Ternary solution	0.05 M	1.3	0.05
Glucose/NaLac/Na <sub>2</sub> SO <sub>4</sub>	0.25 M	1.9	0.2

Then, besides improving the selectivity by adding  $Na_2SO_4$ , the permeate flux increases by a factor 4 at the maximum separation factor compared to that one obtained in binary solution. Consequently, the addition of  $Na_2SO_4$  also improves the productivity. It is also to be mentioned that such an addition of salt has a negligible influence on the salt composition in the permeate, which constitutes the enriched lactate solution, since sulphate is strongly retained by the nanofiltration membrane.

## 4. Conclusion

Previous studies had demonstrated that the separation of glucose and sodium lactate by nanofiltration was hardly achievable due to the influence of the lactate salt on the glucose retention. It was also observed that the influence of the addition of salt on the retention of both solutes was different due to different mechanisms.

The aim of this work was thus to determine to what extent the ionic composition could be changed to improve the selectivity of the glucose/lactate separation.

An experimental study was first carried out with binary solutions containing either glucose or sodium lactate and different electrolytes, NaCl (0.1-1 M) and Na<sub>2</sub>SO<sub>4</sub> (0.05-0.5 M).

The effects of the addition of NaCl or  $Na_2SO_4$  on both glucose and lactate retentions were found to be quite different. In presence of NaCl, both glucose and lactate retentions slightly decrease and remain very close except at low permeation fluxes. On the contrary, whilst the addition of  $Na_2SO_4$  has no influence on the glucose retention, a strong effect was pointed out on the lactate retention, especially for high electrolyte concentrations for which negative retentions were obtained at low permeation fluxes. Then, a better improvement of the separation of glucose (0.1 M) and sodium lactate (0.1 M) was expected to be achieved by the addition of  $Na_2SO_4$  compared to NaCl.

This was confirmed by the experiments carried out with ternary solute solutions, i.e. glucose/sodium lactate/electrolyte. Indeed, it was observed that the separation factor is higher when increasing salt concentrations are added. It was also confirmed that this improvement is more important when adding Na<sub>2</sub>SO<sub>4</sub> compared to NaCl due to the high retention of sulphate. Then, significant improvement of the separation can be achieved by the addition of strongly retained membrane co-ions like multivalent ones. For the conditions investigated in this study, a maximum separation factor of 1.9 was obtained with the addition of Na<sub>2</sub>SO<sub>4</sub>

at 0.25 M into to the glucose (0.1 M)/sodium lactate (0.1 M) solution when no separation was achievable with the salt free solution. Moreover, the flux corresponding to that maximum value is increased by a factor of 4. Finally, because of the high sulphate retention, the lactate enriched permeate remains almost free from sulphate ions.

# Acknowledgements

The authors would like to thank ASEMDUO (Duo-Thailand and Duo France) program and the French government who provide the financial support for Chakkrit Umpush PhD scholarships.

# References

- Bailly M, Roux-de Balmann H, Aimar P, Lutin F, Cheryan M. Production processes of fermented organic acid targeted around membrane operations: design of the concentration step by conventional electrodialysis. J Membr Sci 2001;191:129–42.
- [2] Bouchoux A, Roux-de Balmann H, Lutin F. Nanofiltration of glucose and sodium lactate solutions. Variation of retention between single- and mixed-solute solutions. J Membr Sci 2005;258:123–32.
- [3] Lee EG, Moon SH, Keun Chang Y, Yoo IK, Nam Chang H. Lactic acid recovery using two stage electrodialysis and its modelling. J Membr Sci 1998;145:53– 66.
- [4] Bailly M. Production of organic acids by bipolar electrodialysis: realizations and perspectives. Desalination 2002;144:157–62.
- [5] Bouchoux A, Roux-de Balmann H, Lutin F. Investigation of nanofiltration as a purification step for lactic acid production processes based on conventional and bipolar electrodialysis operations. Sep Purif Technol 2006;52:266–73.
- [6] Wang XL, Zhang C, Ouyang P. The possibility of separating saccharides from NaCl solution by using nanofiltration in diafiltration mode. J Membr Sci 2002;204:271–81.
- [7] Bargeman G, Vollenbroek JM, Straatsma J, Schroen CGPH, Boom RM. Nanofiltration of multi-component feeds. Interactions between neutral and charged components and their effect on retention. J Membr Sci 2005;247:11–20.
- [8] Cuartas-Uribe B, Vincent-Vela MC, Alvarez-Blanco S, Alcaina-Miranda MI, Soriano-Costa E. Nanofiltration of sweet whey and prediction of lactose retention as a function of permeate flux using the Kedem-Spiegler and Donnan Steric Partitioning models. Sep Purif Technol 2007;56:38–46.
- [9] Mandale S, Jones M. Interaction of electrolyte and non-electrolytes in nanofiltration. Desalination 2008;219:262–71.
- [10] Bouranene S, Szymczyk A, Fievet P, Vidonne A. Influence of inorganic electrolytes on the retention of polyethyleneglycol by a nanofiltration ceramic membrane. J Membr Sci 2007;290:216–21.
- [11] Hagmeyer G, Gimbel R. Modelling the salt rejection of nanofiltration membranes for ternary ion mixtures and for single salts at different pH values. Desalination 1998;117:247–56.
- [12] Straatsma J, Bargeman G, van der Horst HC, Wesselingh JA. Can nanofiltration be fully predicted by a model? J Membr Sci 2002;198:273–84.
- [13] Zhuo K, Wang J, Yue Y, Wang H. Volumetric properties for monosaccharide (Dxylose, D-arabinose, D-glucose, D-galactose)-NaCl-water systems at 298.15 K. Carbohydr Res 2000;328:383-91.
- [14] Tsuru T, Urairi M, Nakao SI, Kimura S. Negative rejection of anions in the loose reverse osmosis separation of mono- and divalent ion mixtures. Desalination 1991;81:219–27.
- [15] Schaep J, Vandecasteele C, Mohammad AW, Bowen WR. Modelling the retention of ionic components for different nanofiltration membranes. Sep Purif Technol 2001;22–23:169–79.
- [16] Wang XL, Tsuru T, Togoh M, Nakao SI, Kimura S. Evaluation of pore structure and electrical properties of nanofiltration membrane. J Chem Eng Jpn 1995;28:189–92.
- [17] Tanninen J, Platt S, Weis A, Nystrom M. Long-term acid resistance and selectivity of NF membranes in very acid conditions. J Membr Sci 2004;240:11–8.
- [18] Bowen WR, Mohammad AW. Characterization and prediction of nanofiltration membrane performance—a general assessment. Int IChemE 1998;76:885–93.
- [19] Tsuru T, Urairi M, Nakao SI, Kimura S. Reverse osmosis of single and mixed electrolytes with charged membranes: experiment and analysis. J Chem Eng Jpn 1991;24:518–24.