Nanofiltration of glucose and sodium lactate solutions
Variations of retention between single- and mixed-solute solutions

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Abstract

The aim of this work was to investigate NF as a purification step, i.e. sugar removal, in the production process of lactic acid from sodium lactate fermentation broth. Experiments were carried out with the Desal 5 DK membrane and solutions of increasing complexity, i.e. single-solute solutions of sodium lactate and glucose and mixed-solute solutions containing both solutes. Concentrations close to those of a fermentation broth were chosen. Experimental results were used to get the variations of the intrinsic retention versus the permeation flux in order to achieve comparisons without the interference of concentration polarization. Quite distinct retentions were obtained for glucose and sodium lactate in single-solute solutions so that the purification was expected to be feasible. However, it is pointed out that glucose retention is significantly lower in mixed-solute solutions, i.e. when sodium lactate is present. This decrease is such that the retentions of both solutes become comparable so that any purification is unachievable. Experiments were also performed with a salt of a different nature (mineral salt, NaCl). Again, it was found that the presence of NaCl tends to decrease glucose retention. Moreover, the phenomenon is shown to be related to the salt concentration in both cases, i.e. with sodium lactate and NaCl. Some possible explanations of this effect are provided in this paper. Further investigations are still in progress to improve the knowledge of the mechanisms involved.

Keywords: Nanofiltration Lactic acid; Intrinsic retention; Salt and sugar retention; Hydration

1. Introduction

Nanofiltration (NF) is known to be a separation technique lying between ultrafiltration (UF) and reverse osmosis (RO) which presents a selectivity governed both by steric hindrance effects and electrostatic repulsions. Most NF membranes have therefore, the particularity to strongly retain compounds of molecular weight up to 150–250 g mol^{-1} and charged species, especially multivalent ions.

Due to these interesting separation properties, NF begins to be used in a wide range of applications in the food industry such as dairy by-product treatment [1,2], fruit juice production [3], or sugar beet press water clarification [4]. Moreover, according to the numerous works published in the last few years, the use of NF as a downstream operation in organic acids production processes is expected to be a large and new application field of this technology [5–10].

Organic acids (acetic, lactic, gluconic acids. . .), which are increasingly used in food industries, are mainly produced by fermentation. This fermentation generates a broth containing the dissociated form of the acid (sodium, ammonium or calcium salt) and different impurities, such as residual sugars and mineral salts. Different operations of purification concentration and conversion are then required in order to get the acid in a suitable form [11,12]. The integration of NF in the process can be investigated at different stages depending on the organic acid. On one hand, for high molecular weight organic acids, NF can be considered as a concentration step. For example, the concentration of model solution of ammonium fumarate by NF or RO has already been achieved [5]. It was also pointed out that the use of NF to concentrate or-

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ganic acid salts, such as sodium citrate or gluconate, could allow to overcome the concentration upper limit reached by RO [6,7]. On the other hand, NF can constitute a purification step in the case of low molecular weight organic acids. It was shown for instance that NF is an appropriate method for the downstream processing of sodium acetate fermentation broths thanks to its ability to let permeate the acetate while retaining nutrients, like glucose, that can be recycled in the fermentation tank [8].

In this paper, the possibility of using NF to achieve the purification of a sodium lactate fermentation broth, i.e. a partial glucose elimination, is investigated. The originality of such a study rests on the nature of the fluid which is a mixed-solute solution of an electrolyte (sodium lactate) and a non-electrolyte (glucose). This kind of mixture was indeed rarely studied in NF. Moreover, in the few references available, differences were reported between retentions obtained with each solute taken separately and those obtained with mixtures (effect called "interaction" or "coupling" between retentions). A decrease in salt retention in the presence of a neutral solute was generally observed [13–15]. Some attempts were made to explain these observations, such as an increasing viscosity near the membrane surface being due to the presence of the neutral solute leading to a higher concentration polarization of the salt [13]. Conversely, the results concerning the effect of a charged solute on the retention of a neutral solute are much more contradictory. Indeed, while a decrease of lactic acid or glucose retention was reported in the presence of NaCl [16,17], other authors found an opposite effect with solutions of lactose/NaCl and lactic acid/NaCl [14,15,18]. Unfortunately, it is hardly feasible to draw any general tendency from these results since they were obtained in different conditions, i.e. with different membranes and at varying concentrations.

Accordingly, this paper aims not only to determine if the glucose/sodium lactate separation is possible but also if such effects of "interaction" or "coupling" between retention occur in this case. The experimental investigation reported here was consequently performed with solutions of increasing complexity, i.e. single-solute solutions of glucose and sodium lactate on one hand and mixed-solute (binary) solutions on the other hand.

2. Experimental materials and methods

2.1. Membrane and chemicals

The Desal 5 DK, supplied by Osmonics as flat sheets, was used. This membrane is a 3-layer membrane (polyamide/Osmonics proprietary layer/polysulfone, [19]) and is negatively charged at pH greater than 4 [20]. Its average characteristics, provided by the supplier, are an average molecular weight cut-off of 150–300 g mol^{-1}, a 98% retention of Mg_2SO_4 (at $[Mg_2SO_4] = 2\,g\,l^{-1}$ and $\Delta p = 6.9$ bar), and a hydraulic permeability of approximately $5.5\,l\,h^{-1}\,m^{-2}\,bar^{-1}$.

Solutions were prepared using high purity sodium lactate (Prolabo–Merck Eurolab), and glucose (Acros Organics) dissolved in ultra-pure water. Glucose concentrations ranging from 0.05 to 0.1 M and sodium lactate concentrations ranging from 0.1 to 1 M were used. Experiments with mixed-solute solutions of glucose and pure NaCl (Prolabo–Merck Eurolab) were also performed (see Section 3.3). The relevant characteristics of these different compounds are listed in Table 1.

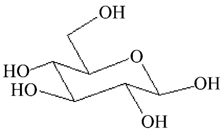
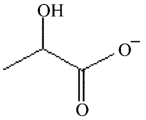
2.2. Analytical methods

Sodium lactate (NaLac) and glucose (Glu) concentrations for single-solute solutions were determined by refractometry (Atago RX-5000 refractometer). Sodium lactate, NaCl and glucose concentrations in mixed-solute 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 N sulfuric acid at a flow rate of 1 ml min^{-1}. Mixtures of the two solutes (glucose/NaLac or glucose/NaCl) at different concentrations were used for the calibration.

2.3. Experimental procedure

Fig. 1 is a schematic diagram of the cross-flow filtration unit used in this work. Experiments were carried out with the Osmonics Sepa CF II cell which uses flat sheet membranes

Table 1
Principal characteristics of the investigated compounds

Compounds	Formula	Molecular weight (g mol^{-1})	Diffusivity D (10^{-10} m^{2} s^{-1})	Stokes radius r_s (nm)
Glucose		180.16	6.9	0.365
Na^+	–	22.99	13.3	0.184
Lactate		89.07	10.6	0.23
Cl^-	–	35.45	20.3	0.121

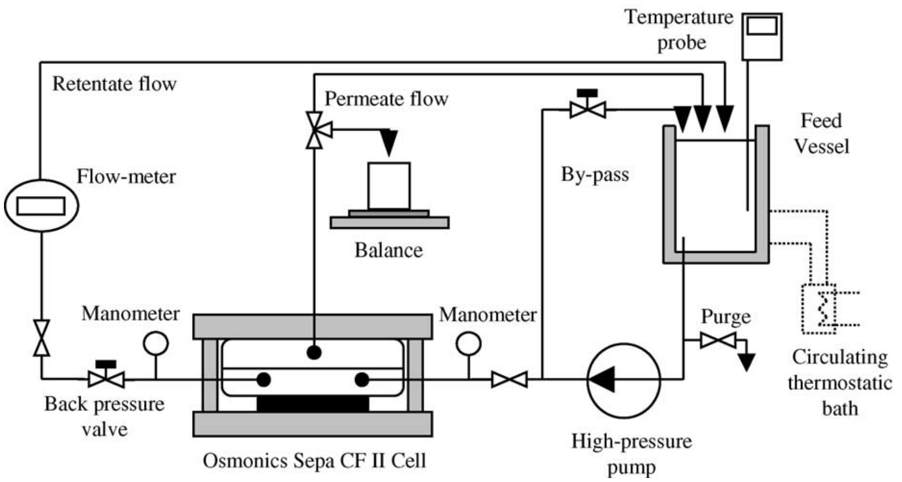


Fig. 1. Schematic diagram of the membrane system used.

of 137 cm^2. The solution is pumped from a 5 l feed vessel, kept at 25 ± 0.5 °C, into the cell and flows tangentially to the membrane. A stainless steel control valve is mounted on the retentate outlet to control the transmembrane pressure which is monitored through two digital manometers located on the inlet and outlet of the cell. The retentate and the permeate were recycled into the feed vessel in order to work at constant feed concentration. Permeate samples were taken through a by-pass mounted on the permeate outlet.

Experiments were performed at cross-flow velocities varying from 0.33 to 1.33 m s^{-1} and at transmembrane pressures ranging from 2 to 20 bar. A volume of 5 ml of permeate was collected for each pressure and timed to estimate the permeation flux The permeate concentrations c_p were determined by the analytical methods previously presented while the retentate concentrations c_r were calculated from a mass balance by considering the feed concentration as constant.

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

2.4. Membrane pre-treatment

In order to get an adequate reference state before each experiment, Desal 5 DK, like most of the NF membranes, needs to be pre-treated at high pressure [21]. In this work, the membrane was compacted before each experiment by filtering high-purity water at 20 bar until it reached a constant permeation flux J_v. The mean hydraulic permeability L_{p_0} was then calculated from the slope of the plot of J_v versus Δp (calculation subject to a maximum standard deviation of ±5%).

Fig. 2 shows the variation of hydraulic permeability versus the number of experiments for the three membrane samples used in this study (called A, B and C). Two observations can be made regarding these results. On one hand, the initial hydraulic permeabilities (L_{p_0} determined before the first experiment) varies from 5 to 7 l h^{-1} m^{-2} bar^{-1}, which is in accordance with the value given by the supplier. On the other hand, all samples showed an increase of the hydraulic permeability as experiments were carried out. This increase is of different magnitude depending on the sample but no correlation was stated with the type of solution investigated.

2.5. Data treatment–concentration polarization

Because of concentration polarization, two different parameters can be used to describe the membrane retention, i.e. the observed retention, R_{obs}, and the intrinsic retention, R_{int}:

$$R_{obs} = 1 - \frac{c_p}{c_r} \tag{1}$$

$$R_{int} = 1 - \frac{c_p}{c_m} \tag{2}$$

where c_p and c_r stand for the permeate and retentate concentrations, respectively and c_m the concentration at the membrane surface.

The observed retention R_{obs} is an experimentally measured value, providing the filtration performance for a given run. R_{obs} is, however, strongly dependent on concentration

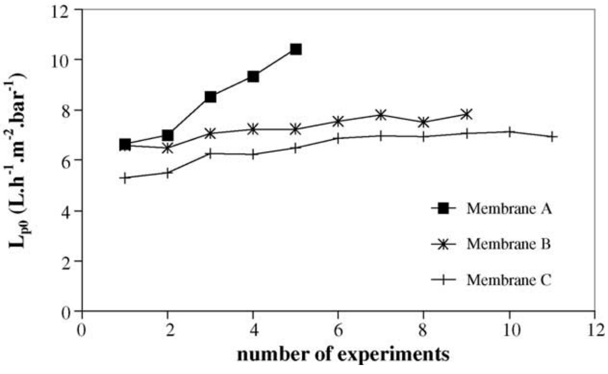


Fig. 2. Variation of the hydraulic permeability L_{p_0} measured before each successive experiment. Results obtained with three membrane samples A, B and C.

polarization and consequently changes with the hydrodynamic conditions near the membrane. The intrinsic retention R_{int}, also called the “real retention”, deals directly with the concentration at the membrane surface c_{m}. As the concentration polarization phenomenon is not taken into account, R_{int} represents a relevant characteristic parameter of the system solute/solution/membrane in terms of selectivity. Further results are thus presented as the variation of the intrinsic retention versus permeation flux.

Because of the high solute concentrations used in this work, it was not possible to reach a cross-flow velocity sufficient to guarantee a negligible concentration polarization for which $c_{\mathrm{m}} \approx c_{\mathrm{r}}$ and $R_{\mathrm{obs}} \approx R_{\mathrm{int}}$. Accordingly, R_{int} had to be estimated from the observed retention using a relevant method. The “velocity variation method” is generally recognized as the most appropriate [22]. This method is based on the description of the concentration polarization phenomenon by the film theory, which gives:

$$\ln\left(\frac{1-R_{\mathrm{obs}}}{R_{\mathrm{obs}}}\right) = \ln\left(\frac{1-R_{\mathrm{int}}}{R_{\mathrm{int}}}\right) + \frac{J_{\mathrm{v}}}{k} \tag{3}$$

The mass transfer coefficient k can generally be calculated from Sherwood’s relations of the type:

$$Sh = \frac{k d_{\mathrm{h}}}{D} = a\, Re^{\mathrm{b}}\, Sc^{0.25} \tag{4}$$

with d_{h} as the hydraulic diameter and D the diffusivity of the involved solute. The adjustable parameters a and b are equal to 0.023 and 0.875, respectively, for turbulent conditions (Deissler expression).

This relation shows a dependence between the mass transfer coefficient k and the cross-flow velocity v that can be expressed as:

$$k = \frac{1}{c} v^{b} \tag{5}$$

with

$$c = \frac{1}{a} d_{\mathrm{h}}^{(1-b)} D^{-0.75} \rho^{(0.25-b)} \mu^{(b-0.25)} \tag{6}$$

where ρ and μ are the solution density and the dynamic viscosity, respectively. As variations of properties in the polarization layer exist (increase of viscosity and changes in diffusivity and density as a result of increasing concentration near the membrane), these values correspond to the mean concentration in the polarization layer.

Combining Eqs. (3) and (5), we obtain:

$$\ln\left(\frac{1-R_{\mathrm{obs}}}{R_{\mathrm{obs}}}\right) = \ln\left(\frac{1-R_{\mathrm{int}}}{R_{\mathrm{int}}}\right) + c\frac{J_{\mathrm{v}}}{v^{0.875}} \tag{7}$$

It is then assumed that c is independent of the polarization level and can be considered as independent of the cross-flow velocity and permeation flux. Van den Berg et al. showed that this assumption can reasonably be made and leads to satisfactory results [22].

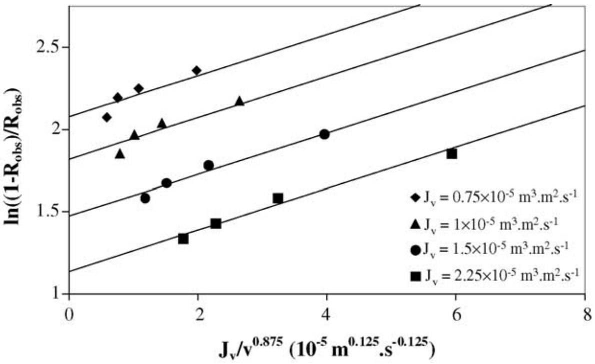


Fig. 3. Use of the “velocity variation method” to determine the intrinsic retention R_{int}. Example of its application with the retention results obtained with a 0.5 M sodium lactate solution. Membrane sample A.

Consequently, at a given flux $J_{\mathrm{v,i}}$, the variation of $\ln\left(\frac{1-R_{\mathrm{obs}}(J_{\mathrm{v,i}})}{R_{\mathrm{obs}}(J_{\mathrm{v,i}})}\right)$ as a function of $\frac{J_{\mathrm{v,i}}}{v^{0.875}}$ (i.e. at different cross-flow velocities) should provide a straight line of slope c, from the y-intercept from which $R_{\mathrm{int}}(J_{\mathrm{v,i}})$ can be calculated. The variation of R_{int} with J_{v} can be obtained by repeating this procedure for different values of J_{v}.

This is illustrated in Fig. 3, taking the results obtained with a 0.5 M sodium lactate solution on membrane sample A as an example. Each set of points corresponds to experimental values of R_{obs} obtained at different cross-flow velocities and at a constant permeation flux. These sets are then fitted by straight lines of identical slope and R_{int} is calculated. Fig. 4 provides the experimental variations of R_{obs} versus J_{v} together with the R_{int} values determined for the example chosen.

This method was used to treat the results of both single- and mixed-solute solutions experiments. In the last case, it was applied to each solute independently.

3. Results and discussion

Experiments were carried out with solutions of different compositions, i.e. single-solute solutions containing sodium

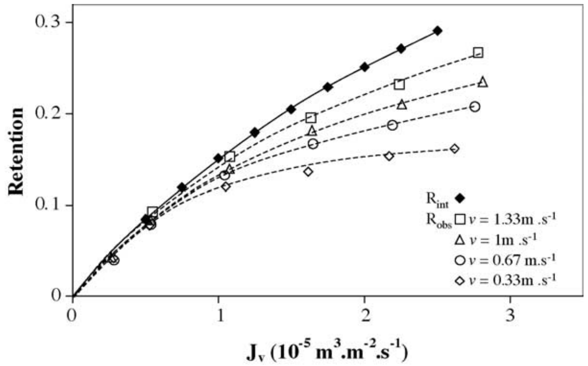


Fig. 4. Variation of the observed retentions R_{obs} and the calculated intrinsic retention R_{int} with permeation flux J_{v}. Membrane sample A. 0.5 M sodium lactate solution.

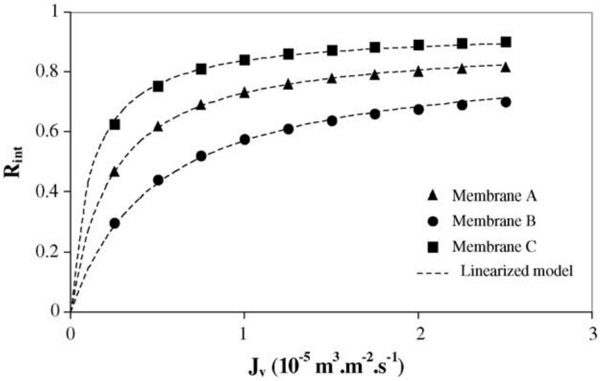


Fig. 5. Intrinsic retention vs. permeation flux for a single-solute solution of glucose (0.1 M). Dashed lines: best-fit curves obtained from the linearized transport model [23].

lactate or glucose, and mixed-solute solutions containing variable proportions of both solutes. Using relevant single-solute retention results, the different membrane sheets were first of all characterized in terms of charge density and mean pore radius. These results are presented in part 3.1. The glucose and sodium lactate retentions obtained with single- and mixed-solute solutions are then presented in details in parts 3.2 and 3.3. Any possible interactions between the solutes in mixed-solute solutions are investigated by comparing the two series of experiments. As previously explained, all the results are provided as variations of the intrinsic retention, R_{int}, versus the permeation flux J_v.

3.1. Membrane characterization

Fig. 5 presents the R_{int} values obtained for a single-solute solution of glucose 0.1 M with the different membrane samples A, B and C. We can observe that the retention differs significantly from one membrane to another. For instance, at $J_v = 2.5 \times 10^{-5}$ m^3 m^{-2} s^{-1}, the retention varies from 0.7 (membrane B) to 0.9 (membrane C). Since glucose is considered as a "neutral" solute, only steric effects are responsible for its retention. Glucose retention depends consequently on its hydrodynamic radius (≈Stokes radius) and on the mean pore size of the membrane. The variations shown on Fig. 5 are therefore due to variations of the mean pore size between the membrane samples. Different models were developed to calculate the mean pore radius r_p from the retention data obtained with an uncharged solute. In the present study, we chose to use the model recently introduced by Bowen et al. in [23]. This model, based on the extended Nernst–Planck equation, is obtained through the finite difference linearization of the concentration gradient inside the membrane. In the case of an uncharged solute, it has the advantage of using r_p as the sole independent parameter. The values of the mean pore radius obtained from the glucose retentions of Fig. 5 using this model are reported in Table 2. It can be observed that r_p varies from 0.52 nm (membrane C) to 0.63 nm (membrane B). These values are systematically higher than those reported by Wang, Bowen and Straatsma for the same membrane, i.e. 0.40, 0.43 and 0.46 nm respectively [23–25].

Table 2
Mean pore radius (r_p) and membrane charge density (X_d) obtained from the linearized transport model [23,26]

	One-parameter model, r_p (nm)	Two-parameter model - without dielectric exclusion, X_d (mol m^{-3})
Membrane A	0.57	−380
Membrane B	0.63	−1510
Membrane C	0.52	−2260

Such variations of solute retention from one membrane sample to another are still more visible concerning sodium lactate. Fig. 6 shows the retentions obtained for a 0.5 M sodium lactate solution with the three membranes A, B and C. In this case, the retention difference can reach up to 600% between membrane C and membrane A (for $J_v = 0.5 \times 10^{-5}$ m^3 m^{-2} s^{-1}). Sodium lactate is a dissociated species composed of two charged solutes. Therefore, its retention comes from the combination of steric effects and electrostatic repulsions due to the charges carried by the membrane. According to the former model [23] the retention of a charged solute can be described using two independent parameters, the pore radius r_p and the effective membrane charge density X_d. Since the model does not require any numerical integration, X_d can easily be calculated from the retention results by using the previously calculated mean pore radii (see Table 2). Electrostatic repulsions are given by a Donnan potential term, combined or not with a dielectric exclusion term [26]. Because it led, in most cases, to an overestimation of the retention, dielectric exclusion was not taken into account in our calculations. Moreover, it is impossible to obtain the accurate contribution of dielectric exclusion to electrostatic repulsions without complementary experiments [23]. It is to be noted here that the X_d values reported in Table 2 do not correspond to the intrinsic characteristic of the membrane. It is indeed known that the membrane charge density depends on the salt, its concentration [25,26], and also on the pH of the solution (see [27] for instance). However, for a same solution, i.e. NaLac at 0.5 M, Table 2

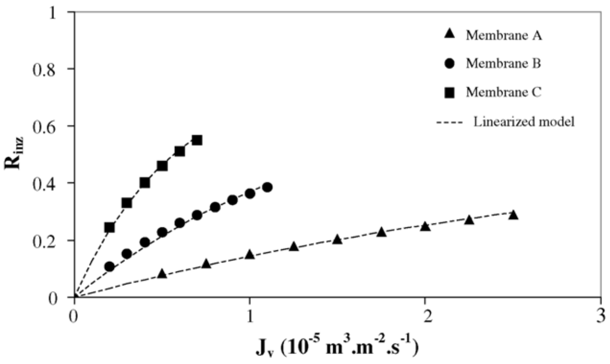


Fig. 6. Intrinsic retention vs. permeation flux for a single-solute solution of NaLac (0.5 M). Dashed lines: best-fit curves obtained from the linearized transport model.

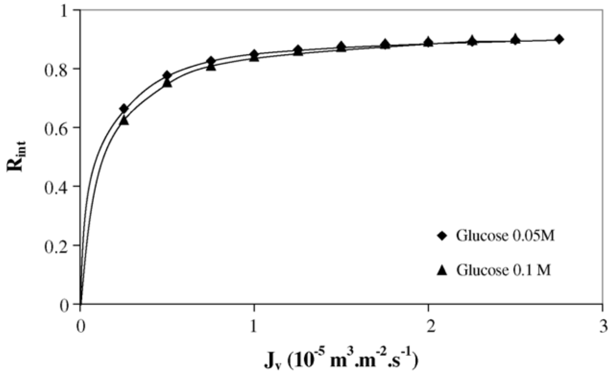


Fig. 7. Intrinsic retention vs. permeation flux for single-solute solutions of glucose. Membrane sample C. Influence of glucose concentration.

reveals that each membrane sample shows quite different charge densities ranging from -380 to $-2260\,\mathrm{mol\,m^{-3}}$.

As a result, the samples used, which correspond to a unique commercial reference, have to be considered as different membranes. Therefore, the results obtained with the different samples will be distinguished in the continuation of the article (Sections 3.2 and 3.3).

3.2. *Single-solute solutions*

Fig. 7 shows the variations of the intrinsic retentions of glucose versus J_v for two different concentrations, i.e. 0.05 and 0.1 M (membrane C). It can be observed that the intrinsic retention is quite independent of the glucose concentration. This classical behavior of an uncharged solute in membrane filtration comes from the fact that only steric-hindrance effects are responsible for the retention. On the other hand, Fig. 8 shows the sodium lactate retention curves obtained with solutions at different concentrations on the same membrane. In this case, decreasing retentions are obtained for increasing concentrations. Indeed, in such conditions, the retention of sodium lactate, which is negatively charged, results from the combination of steric effects and electrostatic interactions between the membrane and the solute. At low solute concentrations, electrostatic repulsions are predominant so that high retentions are obtained. As the feed concentration increases, electrostatic interactions become weaker and the retention decreases. Such a dependence on the retention of a charged solute versus the concentration was already reported by different authors [28–31] and is generally explained according to the Donnan theory [32].

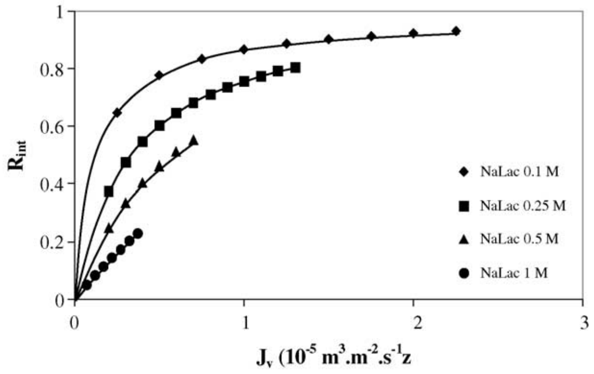


Fig. 8. Intrinsic retention vs. permeation flux for single-solute solutions of sodium lactate. Membrane sample C. Influence of NaLac concentration.

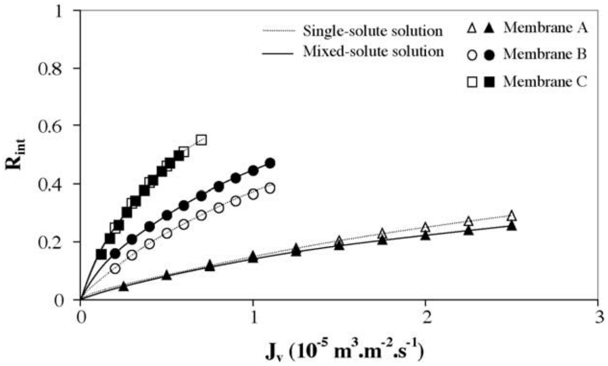


Fig. 9. Sodium lactate intrinsic retention vs. permeation flux for mixed-solute solutions of 0.5 M sodium lactate and 0.1 M glucose. Comparison with NaLac retention in single-solute solution.

All these classical tendencies, shown here on membrane C, were also found on membrane A and B (results not reported). As a matter of fact, these results, together with those reported in Section 3.1 (Figs. 5 and 6), show that glucose retention is in all cases (membranes A, B and C) greater than sodium lactate one at concentration of a fermentation broth, i.e. [NaLac] ≥ 0.5 M. Therefore, a glucose/sodium lactate separation lactate seems possible.

3.3. *Mixed-solute solutions*

Figs. 9 and 10 show, respectively, the variations of the sodium lactate and glucose retentions obtained with membranes A, B and C for one mixture composition. The results of the single-solute solutions experiments at the same concentrations are also shown for comparison.

Concerning sodium lactate retentions (Fig. 9), only slight variations are observed between single- and mixed-solute experiments with membrane A and membrane C (a mean difference of 2 and 8% can be calculated, respectively). A greater, but still relatively small, variation is observed with membrane B (mean difference of 20%). Consequently, we can assume that the retention of sodium lactate is not influenced at least for the conditions investigated, by the presence of glucose.

Conversely, Fig. 10 shows that the retention of glucose is affected by the presence of sodium lactate. Indeed, for any membranes, the glucose retention obtained with mixed-solute solutions is systematically lower than that obtained with single-solute solutions. This decrease is more or less important depending on the membrane.

In order to check the extent to which such a variation of glucose retention in the presence of a salt can be generalized, experiments were carried out with solutions containing NaCl instead of sodium lactate at the same concentrations. The

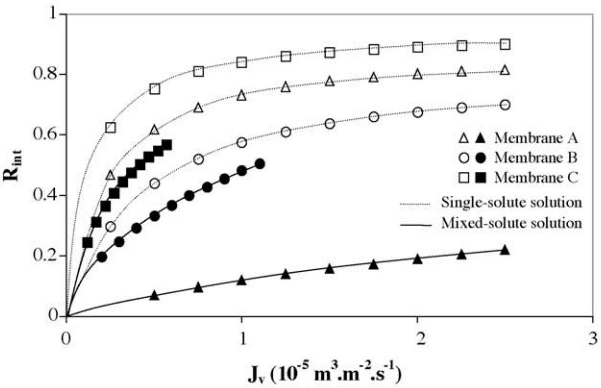


Fig. 10. Glucose intrinsic retention vs. permeation flux for mixed-solute solutions of 0.5 M sodium lactate and 0.1 M glucose. Comparison with glucose retention in single-solute solution.

results for the glucose retention are plotted in Fig. 11. It can be stated that, at least with membranes A and C, the glucose retention is lower in the presence of NaCl. This decrease is less pronounced than that obtained with sodium lactate. No visible influence of the presence of NaCl is apparent with membrane B. This membrane already showed the lowest glucose retention decrease when in presence of sodium lactate (see Fig. 10).

Accordingly, all these results show, in a qualitative way, that the retention of glucose decreases in the presence of a salt. This decrease depends on the nature of the salt as well as the membrane sample used. In a quantitative way, it can be evaluated using the following variable α, which depends on the flux defined as:

$$\alpha(J_v) = 1 - \frac{R'_{\text{int,Glu}}(J_v)}{R_{\text{int,Glu}}(J_v)} \tag{8}$$

where R_{int} and R'_{int} stand respectively, for the retentions in single- and mixed-solute solutions. The values obtained for a given flux are provided in Table 3. This table clearly highlights that, for any salt, the glucose retention decrease is the highest for membrane A and the lowest for membrane B. Membrane C shows an intermediate behavior. Moreover, the alpha values obtained with the same membrane are always higher for mixed-solute solutions containing sodium lactate. This illustrates the fact, already pointed out, that the phenomenon is less marked with NaCl.

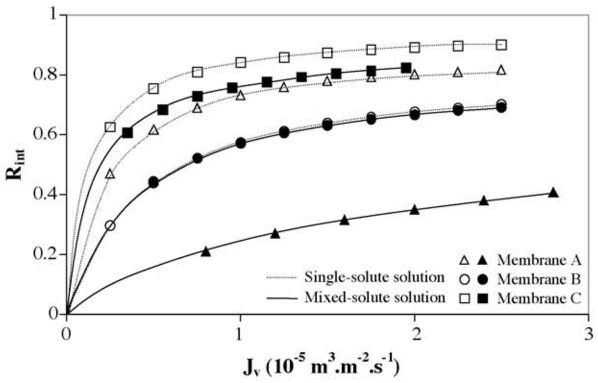


Fig. 11. Glucose intrinsic retention vs. permeation flux for mixed-solute solutions of 0.5 M NaCl and 0.1 M glucose. Comparison with glucose retention in single-solute solution.

Table 3
Glucose retention decrease (α, defined by Eq. (8)) in presence of a sodium salt (NaLac or NaCl) at two concentrations by comparison with glucose retention in single-solute solutions at [Glu] = 0.1 M

	+NaLac 0.5 M	+NaLac 1 M	+NaCl 0.5 M	+NaCl 1 M
Membrane A	0.89	–	0.76	–
Membrane B	0.25	–	0	–
Membrane C	0.30	0.42	0.13	0.25

Results obtained for $J_v = 0.5 \times 10^{-5}$ m^3 m^{-2} s^{-1}.

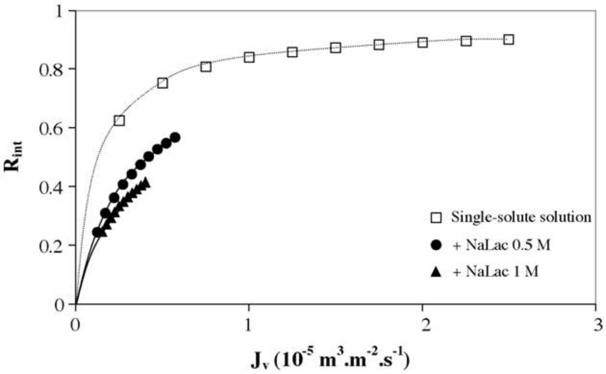


Fig. 12. Glucose intrinsic retention vs. permeation flux for mixed-solute solutions of 0.1 M glucose and sodium lactate at two concentrations (0.5 and 1 M). Comparison with glucose retention in single-solute solution. Membrane sample C.

In order to study the influence of the fluid composition, experiments were carried out with mixtures containing different concentrations of glucose and sodium lactate. For a given sodium lactate concentration, comparable glucose retentions were obtained for the two glucose concentrations investigated ([Glu] = 0.05 and 0.1 M, results not shown). On the other hand, Figs. 12 and 13 show the variation of glucose

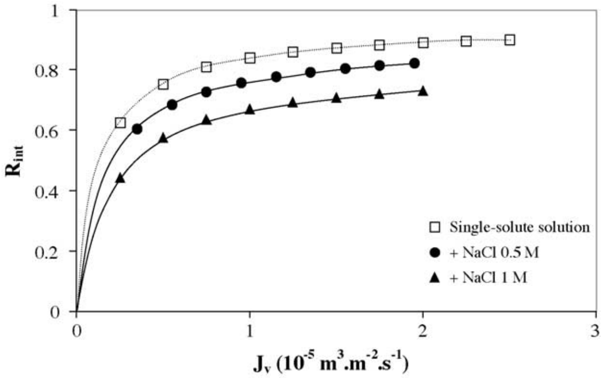


Fig. 13. Glucose intrinsic retention vs. permeation flux for mixed-solute solutions of 0.1 M glucose and NaCl at two concentrations (0.5 and 1 M). Comparison with glucose retention in single-solute solution. Membrane sample C.

retention versus permeation flux at different salt concentrations. In any case, glucose retention decreases with increasing salt concentration. The corresponding alpha values are reported in Table 3.

As a matter of fact, the results obtained with mixed-solute solutions show clearly that the glucose retention, which seemed high enough according to the single-solution results, is finally not sufficient to allow a partial purification of the fluid. By comparison between Figs. 9 and 10 and according to the concentration dependence shown in Fig. 12, glucose retention is indeed too close to (and even lower than, see membrane A) sodium lactate one to get a efficient separation at [NaLac] ≥ 0.5 M. The reasons for such a decrease of glucose retention are discussed in the next part.

3.4. Summary and discussion

The experimental investigation shows that glucose retention is strongly affected by the presence of sodium lactate. From the qualitative point of view, the apparition of such a phenomenon is in accordance with former observations showing that the retention of a uncharged solute decreases in the presence of a charged one [16,17]. However, the phenomenon is clearly stronger in our case. The charged solute used by these authors is indeed sodium chloride, NaCl, and it was shown here that sodium lactate has a stronger effect on glucose retention than this mineral salt. Moreover, we have shown that a high concentration of charged solute induces a greater decrease of glucose retention. However, Wang et al. [17] used relatively low salt concentrations compared to the present study (0.1 M compared to 0.5–1 M here). Furthermore, the conclusions of these previous studies were drawn by considering the variations of retention versus the transmembrane pressure. This approach does not take into account the additional osmotic pressure due to the addition of a salt. It consequently does not permit a rigorous comparison between the retentions obtained at different fluid compositions. This comparison can only be done at a same permeation flux i.e. at a same convective flux as in the present study.

The observed phenomenon can be explained using different assumptions. Because it directly concerns the intrinsic retention, an explanation based on interactions in the polarization layer, such as the one proposed by Vellenga and Tragardh [13], cannot be used in our case. Plausible explanations are more probably related to glucose size exclusion. According to this postulate, the decrease of glucose retention can be imputed to an increase of membrane mean pore radius, a decrease of the glucose hydrodynamic radius, or a combination of the two phenomena.

Qualitatively, pore swelling (increase of pore radius) may be explained through the following hypothesis. As already pointed out in Section 3.1, the charge density of nanofiltration membranes depends on the solution pH (which showed little variations in our case, pH $\approx$ 6.5–7), and the presence of a salt (see [20] for instance). Adding a salt in solution leads to an increase of the membrane charge density. By inducing a greater counter-ions concentration in the electrical double-layer at the pores surface, this effect could result in pore swelling. Moreover, since the involved phenomenon is concentration-dependent (through a Freundlich isotherm for instance [25]), this explanation is consistent with our results. To some extent, the greater retention decrease encountered with sodium lactate compared to sodium chloride could also be explained by this type of analysis (i.e. the same concentration of sodium lactate leads to a higher membrane charge density compared to NaCl). However, the relations between the salt nature and the membrane charge density are still relatively unknown.

On the other hand, the decrease of glucose hydrodynamic radius may be described through direct interactions between the solutes in the bulk. In a mixed-solute solution of glucose and a salt, water will indeed preferentially solvate the salt to the detriment of glucose ("salting-out" effect, see Hofmeister's works recently translated by Kunz et al. [33]). Glucose, therefore less hydrated, may consequently present a lower apparent volume than in the absence of a salt and permeate more freely through the membrane. This second hypothesis is also in agreement with the variations of glucose retention as a function of the salt nature and concentration. This "salting-out" effect is indeed related to the salt concentration and becomes stronger when concentration increases. Moreover, because salts of different nature are more or less solvated by water, the corresponding salt effect is expected to differ from one salt to another according to the Hofmeister series (see [34] for instance). The fact that glucose is retained more in the presence of sodium chloride than in the presence of sodium lactate could therefore, be explained by a stronger hydration of lactate ion compared to chloride ion. Further investigations are, however, needed to confirm this last assumption.

4. Conclusion

The possibility of using NF to achieve a partial glucose elimination from a sodium lactate fermentation broth was investigated. The evaluation of the separation efficiency glucose/sodium lactate was carried out with membrane Desal 5 DK. The first series of experiments were done with single-solute solutions of each solute and the effect of concentration on their retention was investigated. Despite the variabilities existing between the different membrane samples used, it was shown that glucose retention is, in any case, larger than sodium lactate one at concentrations of a fermentation broth (0.05–0.1 M of glucose and 0.5–1 M of NaLac). A second series of experiments, carried out with mixtures of both solutes, provided quite different results. It was indeed observed that, as sodium lactate retention is unchanged, glucose retention strongly decreases. This decrease is such that the retentions of both solutes are comparable and the separation becomes more difficult and even unachievable. Further experiments at different salt concentrations and with a salt of a different nature (NaCl) were also performed. The glucose retention decrease is less important in presence of the mineral salt but also happens. Moreover, the magnitude of the phenomenon increases with salt concentration in all cases.

The decrease of a neutral solute retention in the presence of a charged one is probably a general problem in the nanofiltration of complex fluids (like those in the food industry). It is thus absolutely necessary to identify the mechanisms involved. Some possible explanations are presented in this paper. Further investigations are in progress in order to completely understand this phenomenon.

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Nomenclature

c_m	concentration at the membrane surface (mol m^{-3})
c_p	concentration in the permeate (mol m^{-3})
c_r	concentration in the retentate (mol m^{-3})
D	diffusivity (m^2 s^{-1})
d_h	hydraulic diameter (m)
J_v	permeation flux (m^3 m^{-2} s^{-1})
k	mass transfer coefficient (m s^{-1})
L_p	hydraulic permeability (m s^{-1} bar^{-1})
Δp	transmembrane pressure (bar)
Re	Reynolds number (dimensionless)
R_{int}	intrinsic retention (dimensionless)
R_{obs}	observed retention (dimensionless)
r_p	mean pore radius (m)
Sc	Schmidt number (dimensionless)
Sh	Sherwood number (dimensionless)
v	cross-flow velocity (m s^{-1})
X_d	membrane charge density (mol m^{-3})

Greek letters

α	glucose retention decrease (dimensionless)
μ	solution dynamic viscosity (Pa s)
ρ	density (kg m^{-3})

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