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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 solution of sodium lactate and glucose and mixed-solute solutions containing both solutes. Concentrations close to those found in a fermentation broth were chosen. Experimental results were used to get the variations of the intrinsic retention versus the filtration flux in order to achieve comparisons without 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 was pointed out that glucose retention is significantly lower in mixed-solute solutions, i.e. as far as lactate is present. This decrease is such that retentions of both solutes become comparable so that any purification is unachievable. Experiments at different salt concentrations and with a salt of different nature (mineral salt - NaCl) were also performed. Again, it was found that the presence of NaCl tends to decrease glucose retention. Moreover, the phenomenon is shown to be related to 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 involved mechanisms.

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

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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 $150\text{-}250\text{ g}\cdot\text{mol}^{-1}$ 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 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 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 acid salt (sodium, ammonium or calcium salt) and different impurities, like

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 such processes can be investigated at different stages depending on the organic acid considered. On the one hand, for high molecular weight organic acids, NF can be considered as a concentration step. The concentration of model solution of ammonium fumarate by NF or RO was already achieved [5]. It was also pointed out that the use of NF to concentrate organic acid salts, as sodium citrate or gluconate, could present the advantage 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 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 to the fermentation tank [8].

In the present work, the possibility of using NF to achieve the purification of a sodium lactate fermentation broth, i.e. a partial glucose elimination, is investigated. The specificity 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). Such a kind of mixture was rarely studied in NF. In the few references available, differences between retentions obtained with each solute taken separately and those obtained with mixtures were reported. A decrease of the salt retention in presence of a neutral solute was generally observed [13-15]. Some attempts were made to explain these observations, like an increasing viscosity near the membrane surface due to the presence of the neutral solute which leads 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 presence of NaCl [16, 17], other authors found an opposite effect with solutions of lactose / NaCl and lactic acid / NaCl [14, 15, 18]. 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 variable concentrations.

Nevertheless, it clearly demonstrates the necessity to carry out more systematic work, as that presented in this paper. The experimental investigation reported here was indeed performed with solutions of increasing complexity, i.e. single-solute solutions of glucose and sodium lactate on the one hand and mixed-solute (binary) solutions on the other hand. Experiments with mixtures of NaCl and glucose were also carried out to investigate the influence of the salt nature.

2. Experimental materials and methods

2.1. Membrane and chemicals

The Desal 5 DK NF membrane was used. Supplied by Osmonics as flat sheets, this membrane is made of polyamide (active layer) and polysulfone and is negatively-charged at pH greater than 4 [19]. Its average characteristics, provided by the supplier, are an average molecular weight cut-off of 150-300 g.mol⁻¹, a 98% retention of Mg₂SO₄ (at [Mg₂SO₄] = 2 g.l⁻¹ and $\Delta p = 6.9$ bar), and an hydraulic permeability of approximately 5.5 l.h⁻¹.m⁻².bar⁻¹.

Solutions were prepared using high purity sodium lactate (Prolabo - Merck Eurolab), sodium chloride (Prolabo - Merck Eurolab), glucose (Acros Organics) and lactic acid (Acros Organics) dissolved in ultra-pure water. The relevant characteristics of these compounds are listed in Table 1.

2.2. Analytical methods

Sodium lactate (NaLac), glucose (Glu) and lactic acid (HLac) concentrations for single-solute solutions were determined by refractometry (Atago RX-5000 refractometer). Sodium lactate, sodium chloride and glucose concentrations for mixed-solute solutions were determined by high-performance liquid chromatography using a Shodex SUGAR SH1011 column (Showa Denko) and a refractive index detector. 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 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 of 137 cm². The solution is pumped from a five litres 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.

The concentrations of the solutions used in the present study are listed in Table 2. Experiments were performed at cross-flow velocities varying from 0.33 to 1.33 m.s⁻¹ and at transmembrane pressures 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 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 NF membranes, need to be pre-treated at elevated pressure [20]. In this work, the membrane was compacted before each experiment by filtering high-purity water at 20 bar until reaching a constant permeation flux J_v . Then, the mean hydraulic permeability L_{p0} was calculated from n permeation fluxes $J_{v,i}$ obtained at n transmembrane pressures Δp_i from 2 to 20 bar according to this equation :

$$L_{p0} = \frac{\sum_{i=1}^n \frac{J_{v,i}}{\Delta p_i}}{n} \quad (1)$$

Fig.2 shows the variation of hydraulic permeability versus the number of experiments for six membrane samples used in this study. Two observations can be made regarding to these results. On the one hand, the initial hydraulic permeabilities (L_{p0} for the first experiment) of all samples are similar. Initial L_{p0} 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. However, it shows that no irreversible fouling occurred.

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} :

$$R_{obs} = 1 - \frac{c_p}{c_r} \quad (2)$$

$$R_{int} = 1 - \frac{c_p}{c_m} \quad (3)$$

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

Fig.3 shows the theoretical variations of R_{obs} and R_{int} with the permeation flux. 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 polarization and consequently changes with the hydrodynamic conditions near the membrane. Such a dependence is illustrated by the decrease of R_{obs} after reaching a maximum on Fig.3. The intrinsic retention R_{int} , also called the "real retention", deals directly with the concentration at the membrane surface c_m . Contrary to R_{obs} , R_{int} increases gradually with J_v until reaching a constant value R_∞ . Because it leaves the concentration polarization phenomenon out of account, R_{int} represents a relevant characteristic parameter of the system solute/solution/membrane in term of selectivity. It is then often preferred to R_{obs} as far as the investigation of the mass transfer mechanisms is concerned. Further results will consequently be presented as variation of the intrinsic retention versus permeation flux.

Since the direct calculation of R_{int} from equation (3) requires the knowledge of c_m , that cannot be obtained experimentally, different methods were proposed to calculate R_{int} from the observed retention. Among these methods, the "velocity variation method" is generally recognized as the most appropriate [21]. This method, which is used in this paper, is

summarized below. It is based on the description of the concentration polarization phenomenon by the film theory, which gives:

$$\ln\left(\frac{1-R_{obs}}{R_{obs}}\right) = \ln\left(\frac{1-R_{int}}{R_{int}}\right) + \frac{J_v}{k} \quad (4)$$

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

$$Sh = \frac{kd_h}{D} = a Re^b Sc^{0.25} \quad (5)$$

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

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

$$k = \frac{1}{c} v^b \quad (6)$$

$$\text{with } c = \frac{1}{a} d_h^{(1-b)} D^{-0.75} \rho^{(0.25-b)} \mu^{(b-0.25)} \quad (7)$$

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

Combining equation (4) and (6), we obtain:

$$\ln\left(\frac{1-R_{obs}}{R_{obs}}\right) = \ln\left(\frac{1-R_{int}}{R_{int}}\right) + c \frac{J_v}{v^{0.875}} \quad (8)$$

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 and al. showed that this assumption can reasonably be made and leads to satisfactory results [21].

Consequently, at a given flux $J_{v,i}$, the variation of $\ln\left(\frac{1-R_{obs}(J_{v,i})}{R_{obs}(J_{v,i})}\right)$ as a function of $\frac{J_{v,i}}{v^{0.875}}$ (i.e. at different cross-flow velocities v) should provide a straight line of slope c , from the y-intercept of which $R_{int}(J_{v,i})$ 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.4 taking the results obtained with a 0.25 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.5 provides the experimental variations of R_{obs} versus the flux J_v together with that calculated for R_{int} from the results presented in Fig.4.

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

3. Results and discussion

Experiments were carried out with solutions of different composition, i.e. single-solute ones, containing sodium lactate or glucose, and mixed-solute ones, containing variable proportions of both. The different membrane sheets used are first of all characterized in term of charge density and mean pore radius using relevant single-solute retention results. The glucose and sodium lactate retentions obtained with single- and mixed-solute solutions are

then successively presented in details. Any possible interaction 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.6 presents the R_{int} plots obtained for a single-solute solution of glucose 0.1 M with three different membrane samples D, E and F. We can observe that the retention differs significantly from one membrane to another. For instance at $J_v = 2.5 \times 10^{-5} \text{ m}^3 \cdot \text{m}^{-2} \cdot \text{s}^{-1}$, the retention varies from 0.7 (membrane E) to 0.9 (membrane F). Since glucose is considered as a "neutral" solute, its retention comes from steric effects only. Glucose retention depends consequently on its hydrodynamic radius (\approx Stokes radius) and on the mean pore size of the membrane. Such variations as those shown on Fig.6 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 rejection data obtained with an uncharged solute. For nanofiltration, Bowen and al. recently introduced a simplified model obtained from the finite difference linearization of pore concentration gradient [22]. In the case of an uncharged solute, it presents the advantage of using r_p as the only independent parameter. The values of the mean pore radius obtained from the glucose retention (Fig.6) for the different membrane samples are reported in Table 3. One can observe that r_p varies from 0.52 nm (membrane F) to 0.63 nm (membrane E). These values are systematically higher than those reported by Wang, Bowen and Straatsma for the same membrane, i.e. respectively 0.40, 0.43 and 0.46 nm [22-24].

Such variations of the solute retention from a membrane sample to another are still more visible regarding sodium lactate results. Fig.7 shows the retentions obtained for a 0.5 M sodium lactate solution with the three membranes D, E and F. One can observe that retention difference can reach up to 600 % from membrane F to membrane D ($J_v = 0.5 \times 10^{-5} \text{ m}^3 \cdot \text{m}^{-2} \cdot \text{s}^{-1}$). Sodium lactate is a dissociated specie, i.e. a negatively charged solute. Then, 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 [22] 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 . Because 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 3). Electrostatic repulsions can be described through a Donnan potential term, combined or not with a dielectric exclusion term [25]. Because it led in most cases in an overestimation of the retention, dielectric exclusion was not taken into account in our calculations. Anyway, it is impossible to obtain the accurate contribution of dielectric exclusion to electrostatic repulsions without complementary experiments [22]. It is to be noted here that the X_d values reported in Table 3 do not correspond to an intrinsic characteristic of the membrane. It is indeed known that the membrane charge density depends on the considered salt and on its concentration [24, 25], and also on the pH of the solution (See [26] for instance). However, for a same given solution, i.e. NaLac at 0.5 M, Table 3 reveals that each membrane samples show different charge densities from -378 to -2258 $\text{mol} \cdot \text{m}^{-3}$.

Because of the variabilities pointed out here, the results obtained on different membranes samples have to be distinguished (see section 3.2 and 3.3). As a matter of fact, such results show that different membrane samples, even corresponding to a unique given commercial reference, can exhibit quite large disparities in terms of physical properties (pore

radius and charge density). As far as a process evaluation is investigated, such variabilities have to be considered carefully.

3.2. *Single-solute solutions*

Fig.8 shows the variations of the intrinsic retentions of glucose versus J_V for two different concentrations, i.e. 0.05 and 0.1 M. One can state that the intrinsic retention is almost independent from the glucose concentration. This classical behaviour of an uncharged solute in membrane filtration comes from the fact that only steric-hindrance effects are responsible of the retention. On the other hand, Fig.9 shows the sodium lactate retention curves obtained with solutions at different concentrations on the same membrane. One can state that in that 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. For a low solute concentration compared to the membrane charge density, electrostatic repulsion are predominant so that high retentions are obtained. As the feed concentration increases, electrostatic interactions become weaker and the retention decreases. The lowest retention value is thus reached when electrostatic repulsions become negligible compared to steric-hindrance effects. Such a dependence of the retention of charged solute versus the concentration was already reported by different authors [27-30] and is generally explained according to the Donnan theory [31]. The retention obtained with a 0.25 M lactic acid solution is also reported on Fig.9. Because lactic acid is the uncharged form of sodium lactate, its retention represents the lower limit of the sodium lactate one.

All these tendencies, obtained on membrane D, were also found on membrane E and F (results not shown). Moreover, these single-solute retention results show that, despite the

variabilities pointed out in section 3.1, glucose retention is in all cases larger than sodium lactate one at concentrations of a fermentation broth (between 0.5 and 1 M of NaLac).

3.3. *Mixed-solute solutions*

Experiments were carried out and mixed-solute solutions of NaLac and glucose at concentrations listed in Table 2. Fig.10 and 11 shows respectively the variations of the sodium lactate and glucose retentions versus J_V obtained at a given mixture composition for the three membranes D, E and F. The results obtained with the single-solute solutions at the same concentrations are also shown for comparison.

As far as sodium lactate is concerned, one can observe (Fig.10) that quite identical values are obtained with membranes D and F for the single and mixed solutions. A slight variation, which is not significant, is observed with membrane E. Consequently, the retention for sodium lactate is not influenced, at least for the conditions investigated, by the presence of glucose.

On the contrary, Fig.11 shows that the retention of glucose is strongly affected by the presence of sodium lactate. Indeed, for any membrane, the retention obtained with the mixed-solution is lower than that obtained with the single-solute solution of glucose. This decrease is more or less important depending on the membrane. As a matter of fact, glucose retention, which seemed high enough according to single-solution results, is finally not sufficient to permit a partial purification. Comparison between Fig.10 and 11 shows that, for each membrane sample, glucose retention is too close to sodium lactate one to get an efficient separation.

In order to check to what extent such a variation of glucose retention in the presence of a salt can be generalised, experiments were carried out with solutions containing NaCl instead

of sodium lactate at the same concentrations. The results obtained for the glucose retention are plotted in Fig.12. One can state that, at least with membranes D and F, 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 comes out with membrane E. One can observe that this membrane is that for which the lowest decrease was obtained with sodium lactate (See Fig.11).

Then, from the qualitative point of view, former results show that the retention of glucose decreases in the presence of salt. This decrease depends on the nature of the salt as well as on the membrane characteristics. From the quantitative point of view, it can be evaluated using the following variable α , which depends on the flux, defined as :

$$\alpha(J_v) = 1 - \frac{R'_{int,Glu}(J_v)}{R_{int,Glu}(J_v)} \quad (9)$$

where R_{int} and R'_{int} stand respectively for the retentions obtained in single- and mixed-solute solutions. α is maximum for the lowest fluxes and decreases with increasing flux. The range of variation does not exceed 20 %. Then, for comparison, the values obtained for a given flux are provided in Table 4. This table clearly highlights that, for any salt, the glucose retention decrease is the more important with membrane D and the less important for membrane E. Membrane F shows an intermediate behaviour. Moreover, the alpha values obtained with a same membrane are always larger for mixed-solute solutions containing sodium lactate. This illustrates the fact, already pointed out, that the phenomenon is less marked with NaCl.

In order to study the influence of the fluid composition on the NF performances, 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, Fig.13 and 14 show the variation of the glucose retention versus

the flux obtained for a given glucose concentration at different salt concentrations. One can state that in any case, glucose retention decreases with increasing salt concentration. The corresponding alpha values are reported in Table 4.

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. This difference is probably due to the type of solutes and concentrations used. The charged solute used by these authors is indeed the sodium chloride NaCl and it was shown here that sodium lactate has a stronger effect on glucose retention than this mineral salt. Moreover, it was shown that a high concentration of charged solute induces a stronger decrease of glucose retention and Wang and al. [17] used relatively low NaCl concentrations compared to the present study (0.1 M against 0.5 to 1 M here). Furthermore, the conclusions of these previous works 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 it is done in the present study.

The observed phenomenon can be explained by several hypothesis. It was shown here that the intrinsic retention of glucose (retention at no concentration polarization) decreases in the presence of a salt. An explanation based on interactions in the polarization layer, like the

one proposed by Vellenga and al. for instance [13], is therefore inappropriate to 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.

Pore swelling (increase of pore radius) may be qualitatively explained by variations of membrane charge density through the following hypothesis. As already pointed out in section 3.1, the charge density of nanofiltration membranes depends on many parameters (pH, salt nature and salt concentration). As the pH was sensibly constant in all the solutions used (between 6.5 and 7), only the presence of a salt may be responsible for the change in membrane charge density in our case. It is indeed known that adding a salt in solution leads to an increase of membrane charge density [19] and consequently an increase of the counter-ions concentration in the electrical double-layer at the pores surface. This phenomenon, by inducing higher repulsions forces inside the pores, may result in pore swelling. Moreover, absolute membrane charge density generally increases with salt concentration (it can be related to the salt concentration through a Freundlich isotherm for instance [24]). This could explain why glucose retention still decreases when salt concentration increases. To some extent, the higher retention decrease encountered with sodium lactate compared to sodium chloride could also be explain by this type of analysis (i.e. a same concentration of sodium lactate leads to a higher charge of the membrane compared to NaCl). However, the relations between salt nature and 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). Glucose, therefore less hydrated, may consequently present a lower

apparent volume than in absence of a salt and permeates more freely through the membrane. In the same manner as previously, this hypothesis is 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 is all the more important as the 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. The fact that glucose is more retained in presence of sodium lactate than in presence of sodium chloride 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 by nanofiltration was carried out with membrane Desal 5 DK. A first series of experiments was done with single-solute solutions of each solute. The effect of concentration on their retention was investigated. It was shown that, despite the variabilities existing between different membrane samples, glucose retention is in all cases 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 that the separation becomes more difficult and even unachievable. Further experiments at different salt concentrations and with a salt of different

nature (NaCl) were also performed. It was shown that the glucose retention decrease is more important in presence of the organic salt and increases with salt concentration.

The decrease of a neutral solute retention in presence of a charged one is probably a general problem in nanofiltration of complex fluids (like those of the food industry). It is thus absolutely necessary to identify the involved mechanisms. Some possible explanations are presented in this paper. Further investigations are in progress in order to completely understand the 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 ($\text{m}^2.\text{s}^{-1}$)
d_h	hydraulic diameter (m)
J_v	permeation flux ($\text{m}^3.\text{m}^{-2}.\text{s}^{-1}$)
k	mass transfer coefficient (m.s^{-1})
L_p	hydraulic permeability ($\text{m.s}^{-1}.\text{bar}^{-1}$)
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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Table 1: Principal characteristics of investigated compounds.

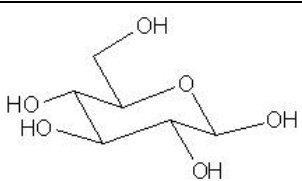
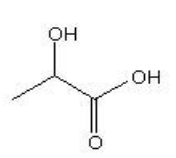
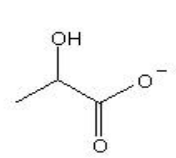
Compounds	Formula	Molecular weight (g.mol ⁻¹)	Diffusivity D (10 ⁻¹⁰ m ² .s ⁻¹)	Stokes radius r _s (nm)
Glucose		180.16	6.9	0.365
Lactic acid		90.08	11	0.22
Na ⁺	-	22.99	13.3	0.184
Lactate		89.07	10.6	0.23
Cl ⁻	-	35.45	20.3	0.121

Table 2: Solutions used ($M = \text{mol.L}^{-1}$).

Single-solute solutions	Glucose (Glu)	0.05 M - 0.1 M
	Sodium lactate (NaLac)	0.1 M - 0.25 M - 0.5 M - 1 M
	Lactic acid (HLac)	0.25 M
Mixed-solute solutions	Glu / NaLac	0.1 M / 0.5 M - 0.1 M / 1 M
	Glu / NaCl	0.1 M / 0.5 M - 0.1 M / 1 M

Table 3: Mean pore radius (r_p) and membrane charge density (X_d) obtained from the linearized transport model [22, 25].

	One-parameter model	Two-parameter model - without dielectric exclusion
	r_p (nm)	X_d (mol.m ⁻³)
Membrane D	0.57	-378
Membrane E	0.63	-1511
Membrane F	0.52	-2258

Table 4: Glucose retention decrease (α , defined by eq.(9)) in presence of a sodium salt (NaLac or NaCl) at two concentrations by comparison with glucose retention in single-solute solutions at $[\text{Glu}] = 0.1 \text{ M}$.

	+ NaLac 0.5 M		+ NaLac 1 M		+ NaCl 0.5 M		+ NaCl 1 M	
	α_{\min}	α_{\max}	α_{\min}	α_{\max}	α_{\min}	α_{\max}	α_{\min}	α_{\max}
Membrane D	0.73	0.89	-	-	0.53	0.7	-	-
Membrane E	0.15	0.25	-	-	0	0.01	-	-
Membrane F	0.27	0.46	0.42	0.52	0.07	0.13	0.18	0.33

Figure Captions

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

Fig.2. Variation of the initial hydraulic permeability Lp_0 measured before each successive experiment. Results obtained on six membrane samples A to F.

Fig.3. Theoretical variation of the observed retention (R_{obs}) and the intrinsic retention (R_{int}) versus permeation flux J_v .

Fig.4. Use of the "Velocity Variation Method" to determine the intrinsic retention R_{int} . Example of its application with the retention results obtained with a 0.25 M sodium lactate solution on membrane sample A.

Fig.5. Variation of the observed retentions R_{obs} and of the calculated intrinsic retention R_{int} with permeation flux J_v - Membrane sample A - 0.25 M sodium lactate solution.

Fig.6. Intrinsic retention versus permeation flux for a single-solute solution of glucose (0.1 M). Dashed lines : best-fit curves obtained from the linearized transport model [22].

Fig.7 Intrinsic retention versus permeation flux for a single-solute solution of NaLac (0.5 M). Dashed lines : best-fit curves obtained from the linearized transport model.

Fig.8. Intrinsic retention versus permeation flux for single-solute solutions of glucose - Membrane sample D. Influence of glucose concentration.

Fig.9. Intrinsic retention versus permeation flux for single-solute solutions of sodium lactate - Membrane sample D. Influence of NaLac concentration.

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

Fig.11. Glucose intrinsic retention versus permeation flux for mixed-solute solutions - 0.5 M sodium lactate and 0.1 M glucose. Comparison with glucose retention in single-solute solution.

Fig.12. Glucose intrinsic retention versus permeation flux for mixed-solute solutions - 0.5 M sodium chloride and 0.1 M glucose. Comparison with glucose retention in single-solute solution.

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

Fig.14. Glucose intrinsic retention versus permeation flux for mixed-solute solutions of 0.1 glucose and sodium chloride at two concentrations (0.5 M and 1 M). Comparison with glucose retention in single-solute solution - Membrane sample F.

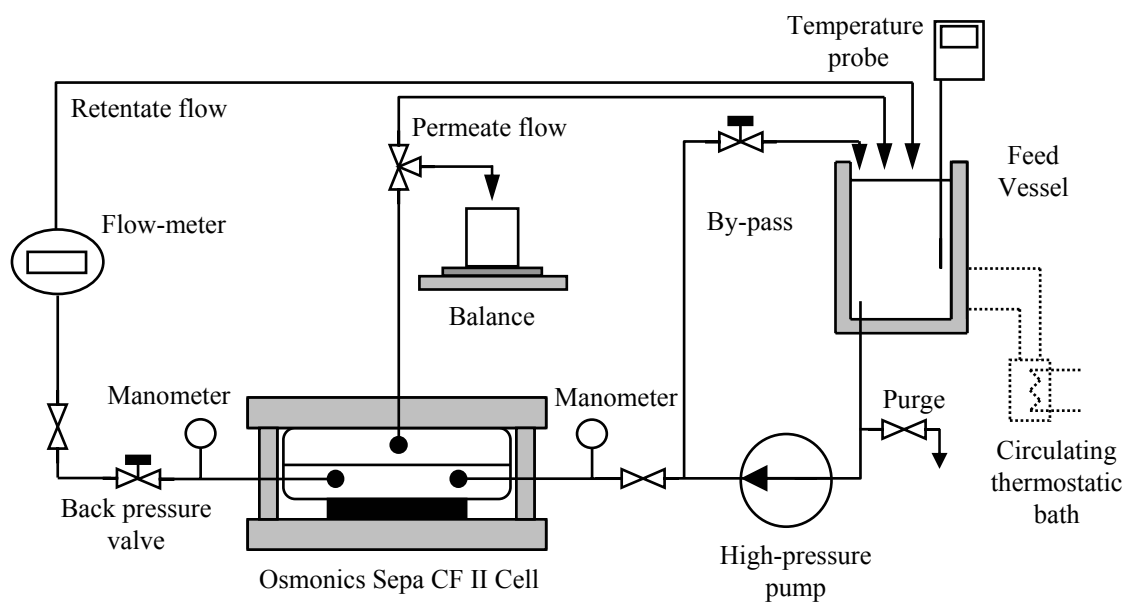


Figure 1

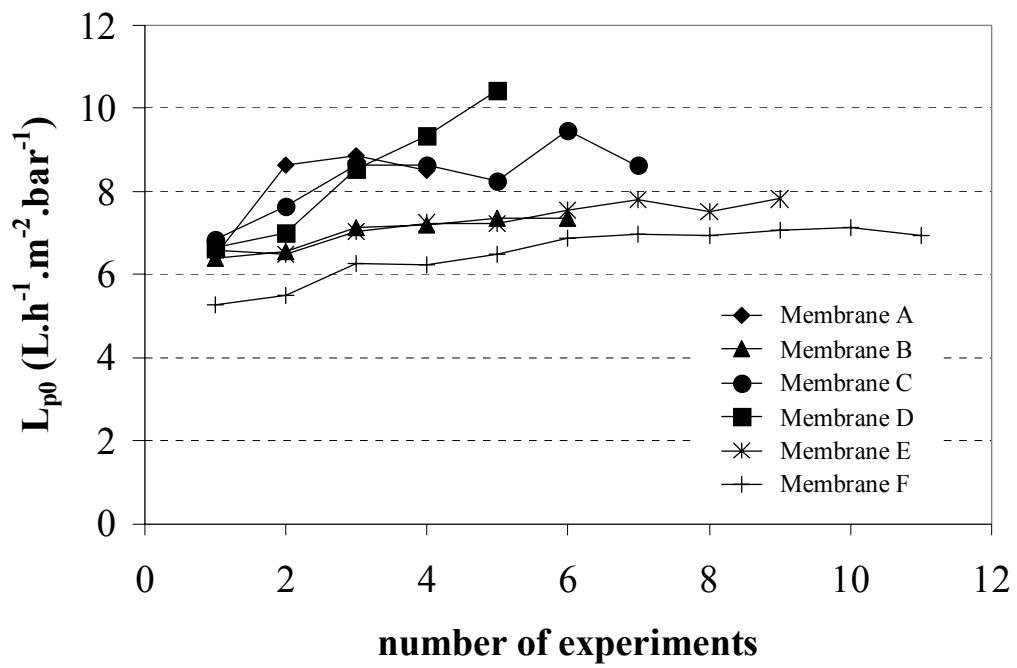


Figure 2

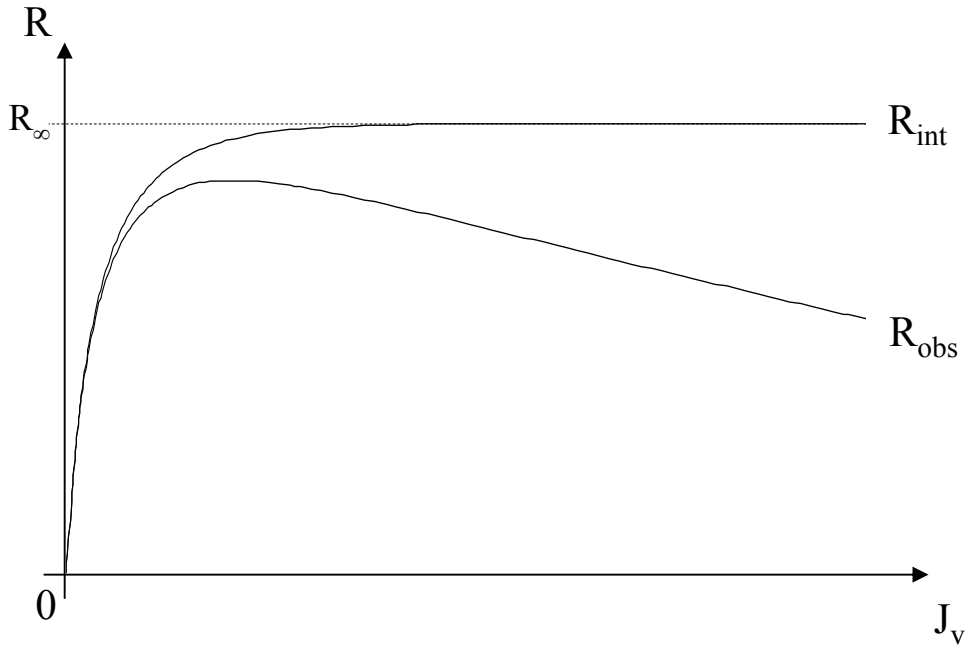


Figure 3

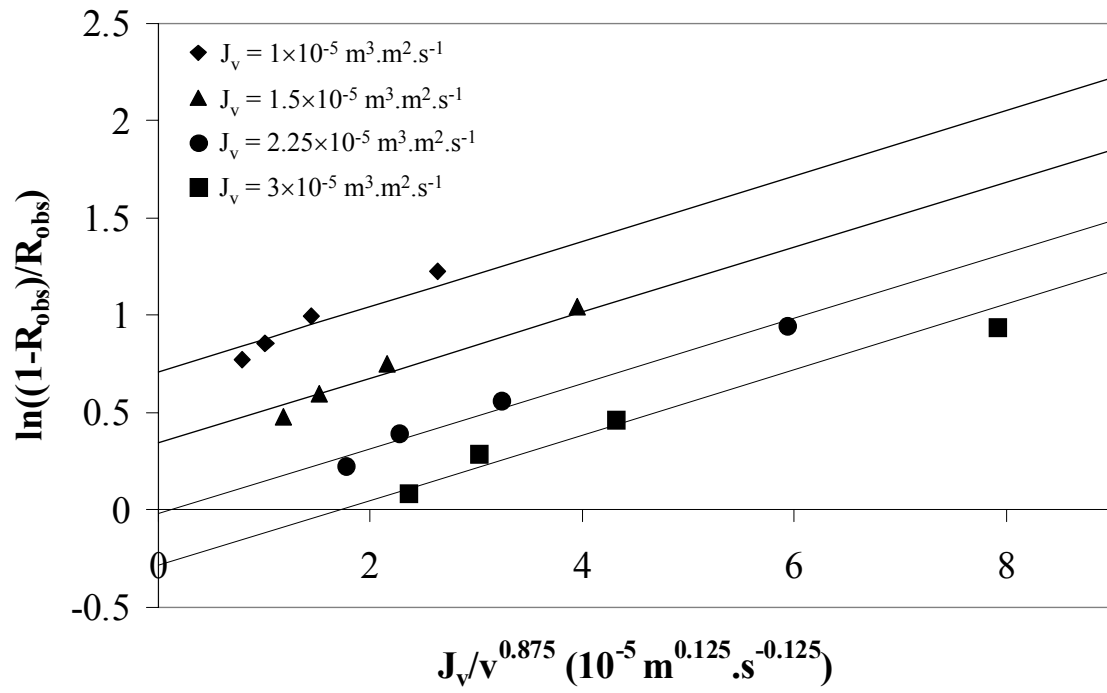


Figure 4

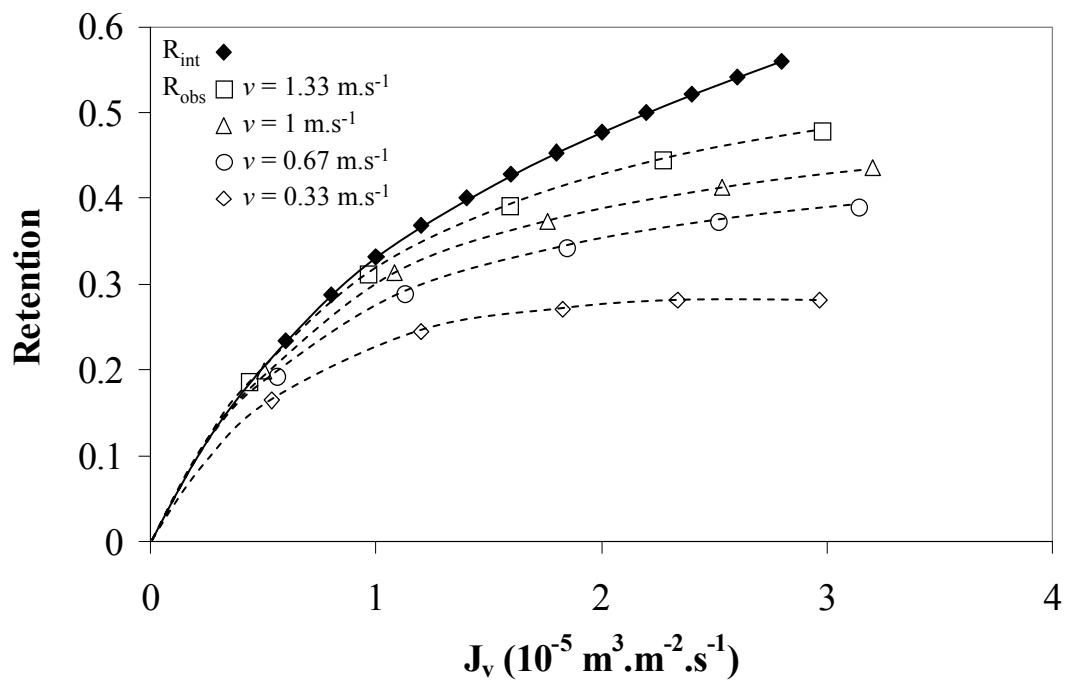


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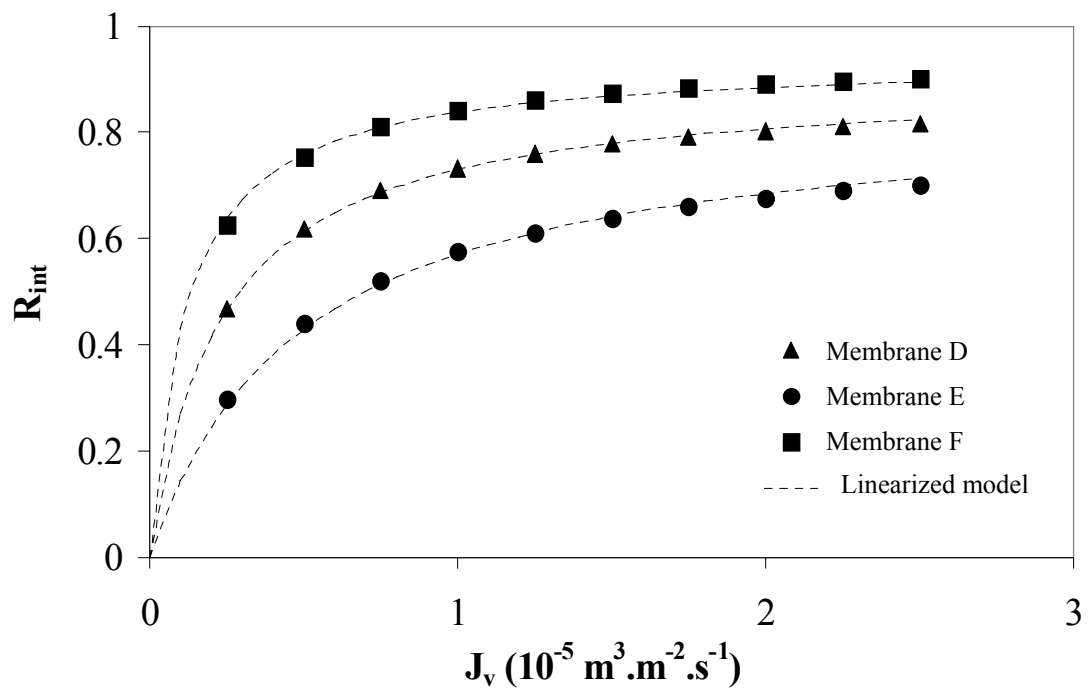


Figure 6

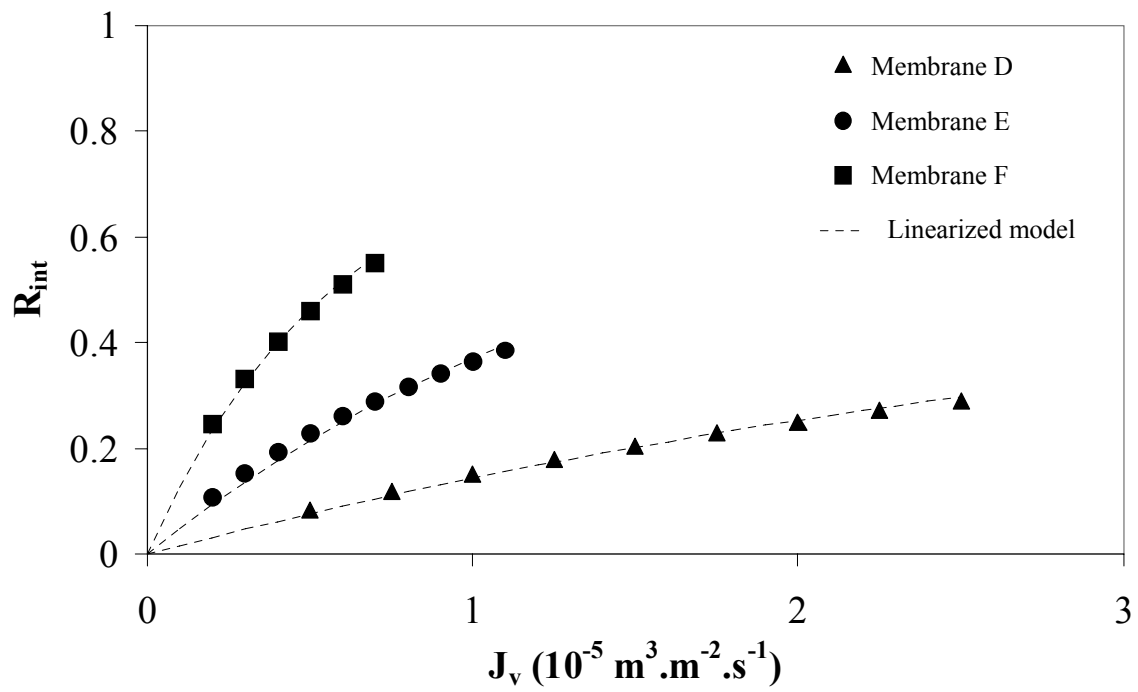


Figure 7

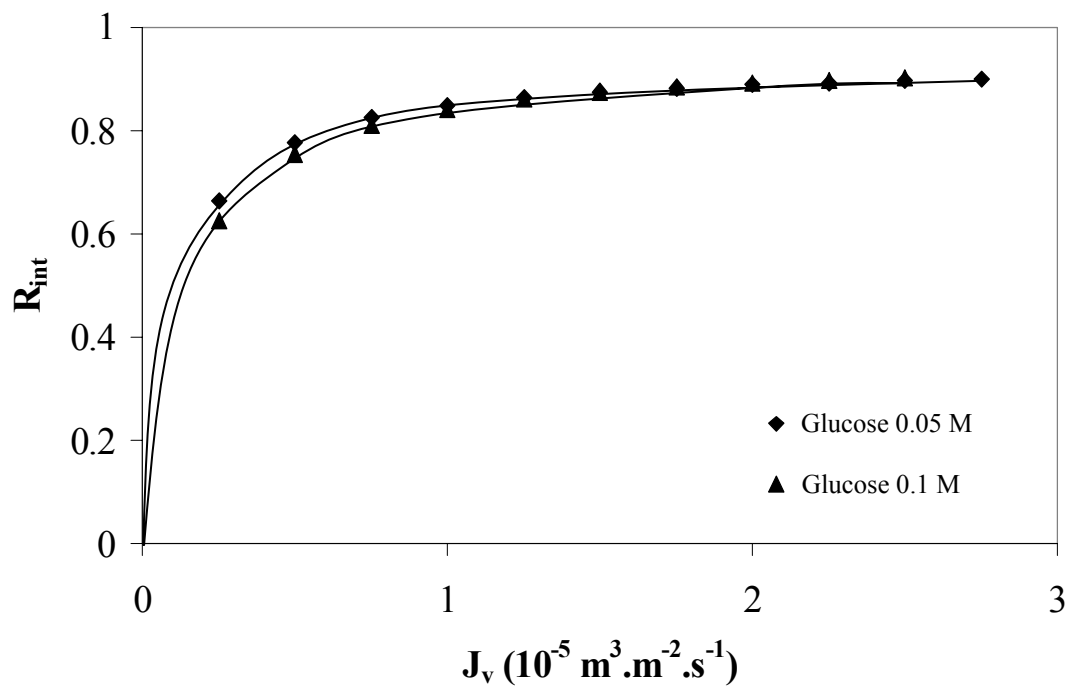


Figure 8

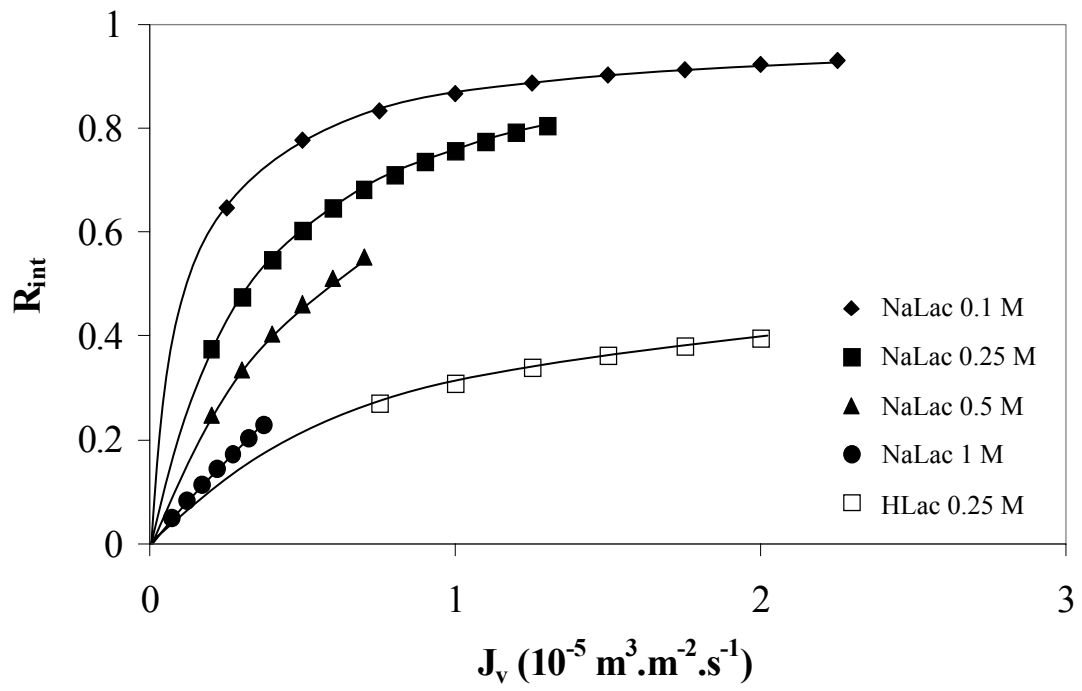


Figure 9

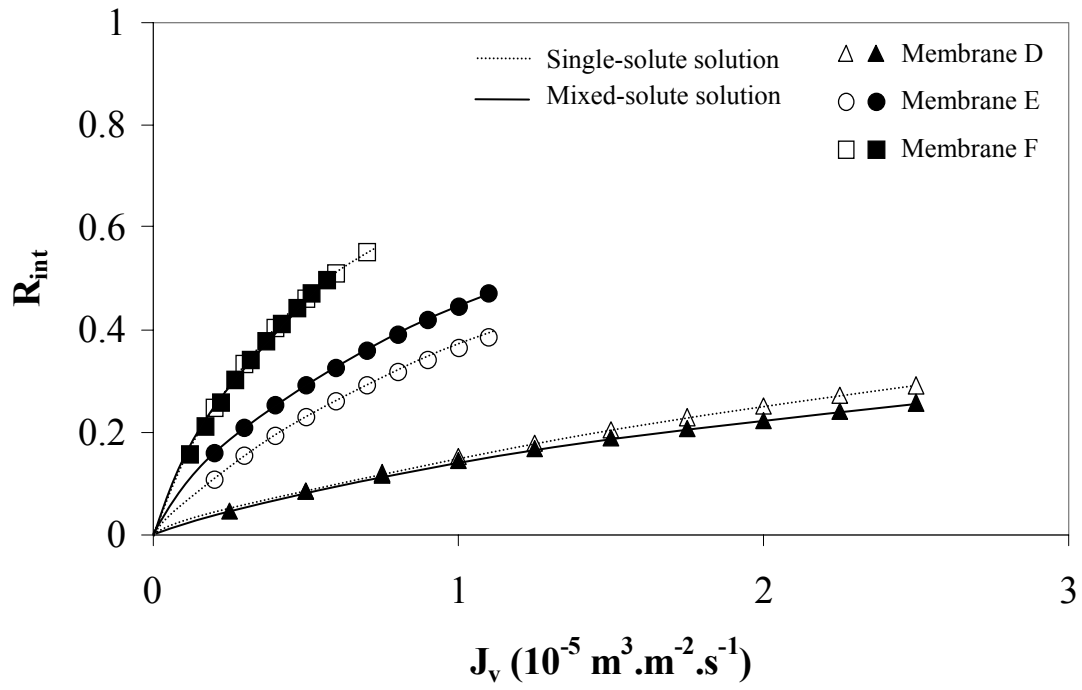


Figure 10

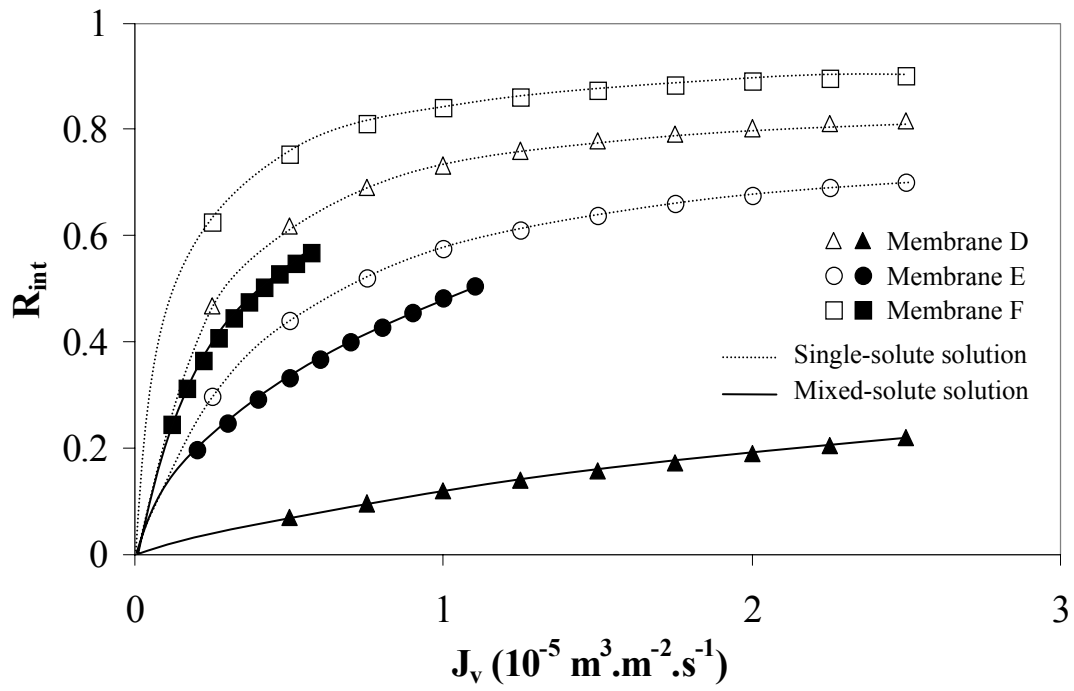


Figure 11

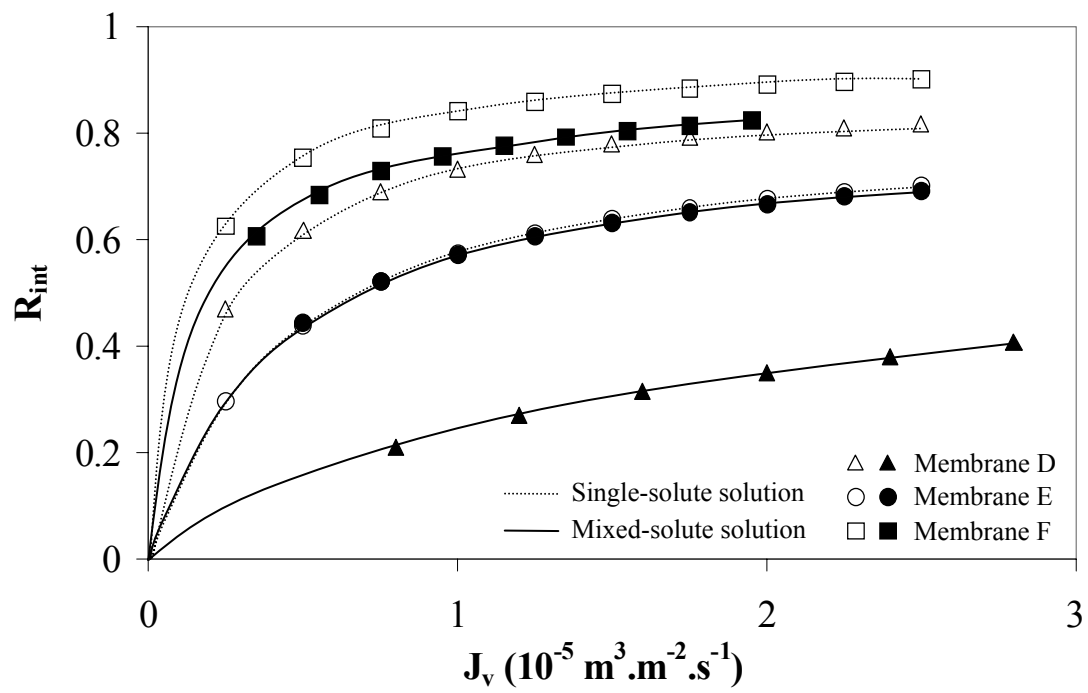


Figure 12

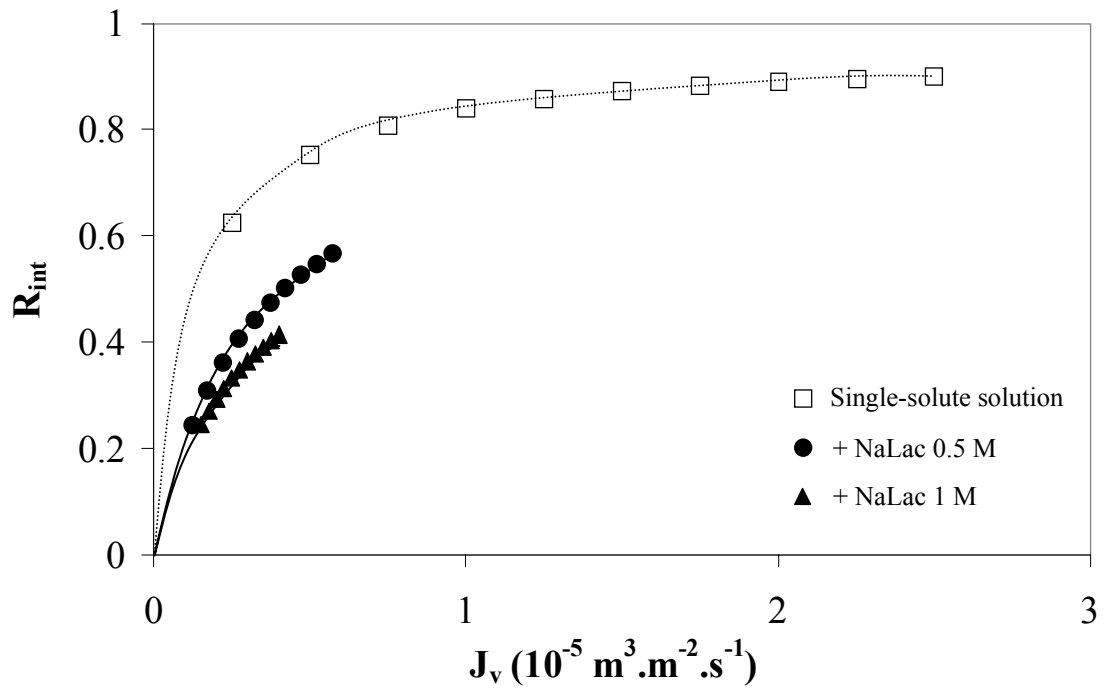


Figure 13

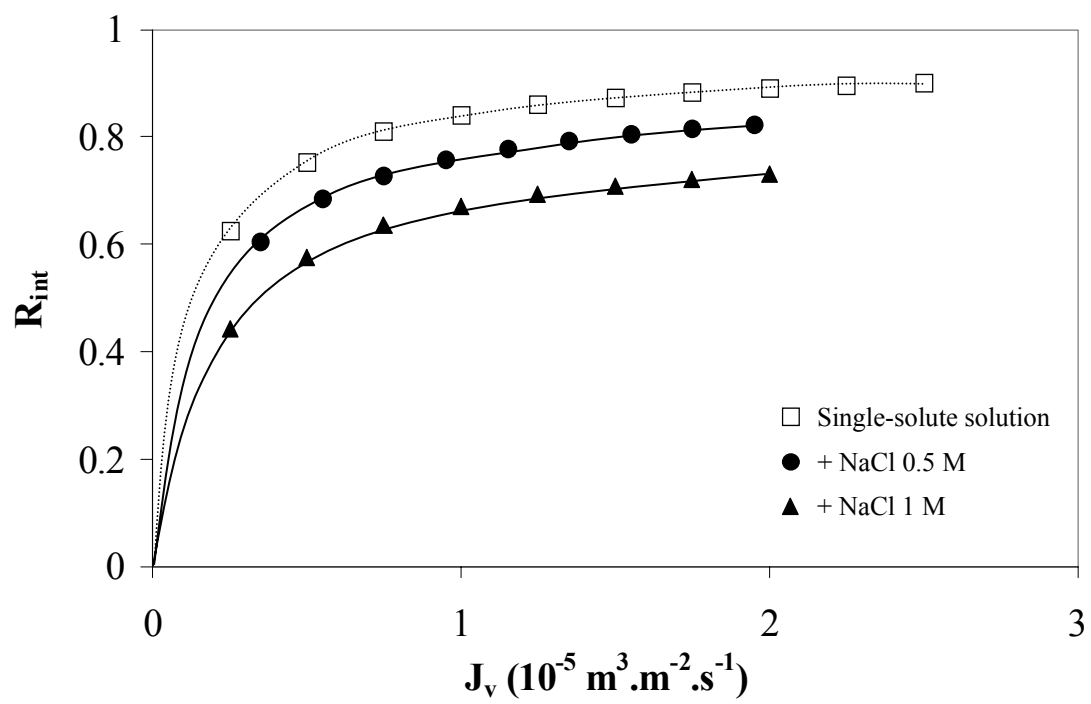


Figure 14