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Demineralization of Glucose Solutions by Electrodialysis: Influence of the Ionic Composition on the Mass Transfer and Process Performances

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The aim of the present work was to investigate the influence of the ionic composition on the demineralization of a saccharide solution containing glucose. Experiments were carried out in order to evaluate the influence of the ionic composition on the solvent and solutes fluxes (glucose and electrolytes) through the membrane under different conditions (ionic compositions: NaCl, Na_2SO_4 and $CaCl_2$; with or without current). From diffusion experiments (without current), it was shown that the glucose diffusion flux decreases for increasing ion hydration. These results are in agreement with those obtained in a previous work showing that the transfer modification reflects changes in the membrane properties associated with the hydration of its counter-ion which is likely linked to swelling mechanisms at a microscopic scale.

From the experiments carried out in normal ED conditions (with current) an additional convective contribution was pointed out. This kind of result is rather scarce in the literature. The glucose flux was then the sum of two contributions: diffusion and convection, due to the electro-osmotic flux which is proportional to the electrical current. The contribution of the glucose convection flux on the overall glucose transfer was ranged between 70 and 90 % according to the electrolyte nature (NaCl, Na_2SO_4 and $CaCl_2$) and the electric current (150 or 300 A m^{-2}). The variation of the convective flux has been further correlated to the hydration of the ions. Indeed increasing convection fluxes were obtained for decreasing anion (or cation) hydration. It was shown that the saccharide transfer increases in presence of salts and that this increase was correlated to the saccharide dehydration in presence of electrolyte. Finally, the solvent, ions and glucose fluxes were used to calculate the glucose loss factor versus the demineralization factor to evaluate the influence of the electrolyte nature on the demineralization process performances. It was observed that, for a fixed demineralization factor, the glucose loss factor (comprised between 4 and 5 % for a demineralization factor of 90 %) increased with the ion hydration due to the higher contribution of the glucose convection flux.

Keywords: demineralization, electrodialysis, saccharide, electrolyte, hydration

INTRODUCTION

Efficient processes, like membrane operations and especially nanofiltration (NF) and electrodialysis (ED), are required for the treatment of complex fluids containing variable quantities of organic and mineral species to fit with environmental regulations as well as product quality constraints.

For such membrane processes, the applications move to the production and the treatment of food liquids, like organic acids from fermentation broths, sugar juices or whey, with the objective to recover all the valuable components present in the solution with high purity and yield while minimizing the consumption of water and energy. For instance, in food industries, ED is one of the more efficient technologies for the demineralization of molasses, syrups and sugar juices.[1,2] In biochemical industries or biorefinery applications, ED can be used for the desalination of solutions containing organic compounds such as carboxylic or amino acids.[3–7]

Another important application is the treatment of waste waters like brines or lixiviates. Again, the objective is to separate and recycle any valuable component present in the water. Indeed, as far as the reduction of the environmental impact of production process is concerned, the management of saline liquid wastes produced by chemical, pharmaceutical, food, and textile industries has a crucial importance. It is known that such liquid wastes are difficult to treat since high salt concentrations reduce the performances of the organic matter treatment processes (biological, advanced oxidation, etc.)[8–10] In such situations, the demineralization of waste water using electrodialysis as a pretreatment before the organic matter treatment processes appears very attractive.[11,12]

Whether for demineralization by electrodialysis of solutions containing valuable organic matter or saline waste waters containing organic contaminants, the process efficiency is characterized by the organic solute transfer, which has to be kept as low as possible, and the demineralization factor, which can be adapted to the specific requirements and reach quite high values. However, it was demonstrated that both parameters are linked and that the relationship between them depends on the ionic composition. For instance, it was reported during the demineralization of acetic acid solutions at different ionic compositions that the organic matter transfer, fixed by the diffusion of the acetic acid through the ion-exchange membranes, was more important in presence of sodium sulfate or calcium chloride than with sodium chloride.[11]

The influence of the ionic composition on the neutral solute transfer has been mainly observed in the case of NF, while studies relating these phenomena with ion-exchange membranes used in

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ED are rather scarce. Indeed, many recent investigations pointed out that the presence of electrolyte can change significantly the process performances because of the resulting modification of the neutral solutes transfer.[13–19] In any case, it was observed that an increasing electrolyte concentration results in a higher transfer and that this increase depends on the nature of the added electrolyte.

It was further shown that the modification of the organic solute transfer comes from the combination of two different contributions. On one hand, according to the ionic composition of the solution, the membrane structural properties can change (swelling phenomenon).[13,14,19] It was also demonstrated that the solute size can vary because of its lower hydration in presence of electrolyte.[15,20] More recently, the influence of the ionic composition on the diffusion transfer of saccharides through a cation-exchange membrane has been investigated.[21] It was shown that the transfer modification is mainly due to the influence of the electrolyte on the membrane properties, which is fixed by the membrane soaking. Moreover, a quantitative correlation has been established between the solute transfer and the hydration properties of the membrane counter-ion.

As explained previously, the influence of the ionic composition on the transfer of neutral solute through NF or ion-exchange membranes could be explained by a modification of the membrane properties, or by a solute dehydration induced by the electrolyte. The contributions of those two coupled phenomena can change with respect to the electrolyte composition and to the structural properties of the membranes. However, very few studies were devoted to investigating the impact of the ionic composition on the mass transfer and process performances during the ED demineralization of solutions containing neutral organic solutes.

In this context, the aim of the present work was then to investigate the influence of the ionic composition on the demineralization of a saccharide solution containing glucose. More precisely, laboratory scale experiments were carried out in order to evaluate the impact of the electrolyte nature on the solvent and solutes fluxes (glucose and ions) through the membrane under different conditions (ionic compositions, with or without current). From these values, the variation of the glucose loss factor versus the demineralization factor was determined in order to evaluate the impact of the ionic composition on the demineralization process performances.

TRANSPORT PHENOMENA

There are different contributions for the mass transfer through the membranes in the ED stack.[12,22,23]

Two different kinds of phenomena contribute to the solvent and charged species transfer. The first contribution to the charged species is diffusion, coming from the concentration gradient between both sides of the membrane. The corresponding solute flux is directed towards the decreasing concentration, i.e., from the more concentrated compartment to the less concentrated one. The second contribution is the migration of charged species through the membranes due to the electrical current. Diffusion and migration are oriented in opposite directions. Usually, the migration contribution is preponderant compared to that of diffusion. Then, the ion flux due to migration, proportional to the electric current, can be expressed as shown in Equation (1), in which the coefficient β relates the amount of electrolyte transferred and the electric current, I:[12]

$$j_i = \beta\, I. \tag{1}$$

In the same manner, the solvent flux through ion-exchange membranes is the sum of two terms. The first one, the osmotic flux, is the solvent flux due to the osmotic pressure existing across the membrane due to the concentration gradient. The other one, known as the electro-osmotic flux, is due to the shell of water molecules accompanying the migration of charged species under the influence of the electric current. Consequently, the electro-osmotic flux is proportional to the ion flux due to migration.[23] Usually, under ED conditions, i.e., when an electric current is applied, the osmosis contribution is negligible compared to that of electro-osmosis. Then, the solvent flux due to electro-osmosis is proportional to electric field. It can be expressed by using the electro-osmotic coefficient, α, to relate the electro-osmotic flux to the electric current, I:[12]

$$j_v = \alpha\, I. \tag{2}$$

Neutral solutes, like glucose in this work, can be transferred by diffusion caused by the concentration gradient. But from the theoretical point of view, a convective contribution can be expected for conditions that the solvent flow is significant.

The convective flux of a solute through a permeable membrane separating two well-mixed compartments can be expressed from the equation, derived from irreversible thermodynamics, proposed by Kedem et Katchalsky:[24]

$$j_{conv\,i} = \overline{C_i}(1-\sigma)j_v \tag{3}$$

where $\overline{C_i}$ is the mean solute concentration on either side of the membrane, and i and v refer to the solute and the solvent, respectively. σ is the reflection coefficient, which represents the relative restriction of the membrane the solute flux. It varies from 0 for a freely permeable molecule to 1 for a non-permeating solute.

MATERIALS AND METHODS

Chemicals

The organic neutral solute used in the experiments was glucose ($180.16\,g\,mol^{-1}$) from Acros Organics. Electrolytes containing ions of various hydrations were used, NaCl, Na_2SO_4 and $CaCl_2$ (Acros Organics). The corresponding ion hydration scale is given as follows:[25,26]

$$\text{Anions}: Cl^- < SO_4^{2-} \qquad \text{Cations}: Na^+ < Ca^{2+}$$

Ultra-pure water (Milli-Q RG, Millipore) was used to prepare the solutions. Glucose and electrolyte concentrations were fixed at $1\,mol\,L^{-1}$ and $1\,eq\,L^{-1}$, respectively. The pH of the various solutions was about (6 ± 0.5) without any adjustment.

Analytical Methods

For any set of experiments, the glucose concentration was analyzed by HPLC with a Dionex ICS 3000 system, using a CarboPac PA1 column with an electrochemical ED40 detector. The mobile phase was a 150 mM NaOH solution at a flow rate of $1\,mL\,min^{-1}$. The column temperature was set as 30 °C. The injection volume was 25 μL.

The electrolyte concentration, and more precisely the anion concentration, was also analyzed with the Dionex ICS 3000 system, using a Ionpac AS11 column with a AG11 guard column, ASRS-ultra at 300 mA suppressor and a CD20 conductivity detector. The

mobile phase was a 5 mM NaOH solution at a flow rate of 1 mL min^{-1}. The column temperature was set as 30 °C. The injection volume was 25 μL.

Electrodialysis Set-up

A schematic diagram for an ED stack is shown in Figure 1 representing the demineralization of a solution containing an electrolyte M^+X^- and glucose. It is composed of a number of identical cell pairs in parallel. Each pair consists of alternating cation-exchange membranes (CEM) and anion-exchange membranes (AEM). When an electric current is applied across the stack, the cations migrate towards the cathode. They can pass through the CEM, while they are retained by the AEM. Meanwhile, the anions migrate towards the anode. They can pass through the AEM but are stopped by the CEM. Consequently, the alternating compartments between consecutive membranes become increasingly enriched (concentrate), and depleted (diluate) in electrolyte.

ED experiments were performed with EUR 2B-10 (stack supplied by Eurodia industrie) equiped with AMX and CMX ion exchange membranes (Neosepta, Tokuyama Corp. Japan).[12,22] The stack comprised 10 cells (AMX/CMX). For each type of membrane, the total active area is 0.2 m^2, i.e., 0.02 m^2 per cell. The flow channel width between two membranes is 0.5 mm.

The ED experiments were operated in batch mode (complete recycling of diluate, concentrate and electrode rinse solution). The set-up consists of three separated circuits, concentrate, diluate and electrode rinse solution, with three 4 L vessels.

The diluate vessel was initially fed with 2 L of an electrolyte solution at 1 eq L^{-1} containing glucose at 1 mol L^{-1}, while the concentrate one was fed with 2 L of a solution at the same ionic composition but without glucose. The electrode rinse solution vessel was fed with 3 L of Na_2SO_4 solution at a concentration of 10 g L^{-1} for the demineralization of NaCl and Na_2SO_4 solutions, or NaCl at 10 g L^{-1} for the demineralization of $CaCl_2$ solutions.

The feed flow rates were set at constant values of 180 L h^{-1} for the diluate and concentrate, and 360 L h^{-1} for the electrode rinse solution. A heat exchanger was used to keep the temperature of the fluids at 25 °C.

Experiments were carried out at a constant current density, in the range 0–300 A m^{-2} (0–6 A).

In the ED experiments, solution conductivities, temperature, electric current and voltage were measured in real time. The solutes (anion and glucose) concentration and the volume were determined in the two compartments as function of time. The experiment duration was determined according to the conductivity of the diluate. They were stopped as soon as this conductivity reached 5 mS cm^{-1} in order to have an electric current lower than the limiting current for any set of experiments. Consequently, different experiment duration resulted according to the operating conditions.

Experimental Procedure and Data Treatment

Two phenomena can be considered to explain the influence of the electrolyte on the organic solute transfer. On one hand, the electrolyte can affect the organic solute/polymer interactions and thus the solute solubility inside the membrane. On the other hand, the electrolyte can change the polymer-polymer interactions and then the organic solute transfer following the modifications of the properties of the hydrated polymer network. Therefore, for each electrolyte, the membranes were first soaked in 4 L of the electrolytic solution at 1 eq L^{-1} for 4 h at a flow rate of 180 L h^{-1} and then at least 10 h without circulation. The quantity of ions in solution (4 eq) being about 50 times higher than the total ion-exchange capacity of AMX and CMX membranes in the ED stack, one can consider that this procedure ensures a complete exchange of the membrane counter ion.

Then, experiments were carried out without current ($I = 0$), and under normal ED conditions ($I \neq 0$). This procedure was repeated for each electrolyte studied in this work.

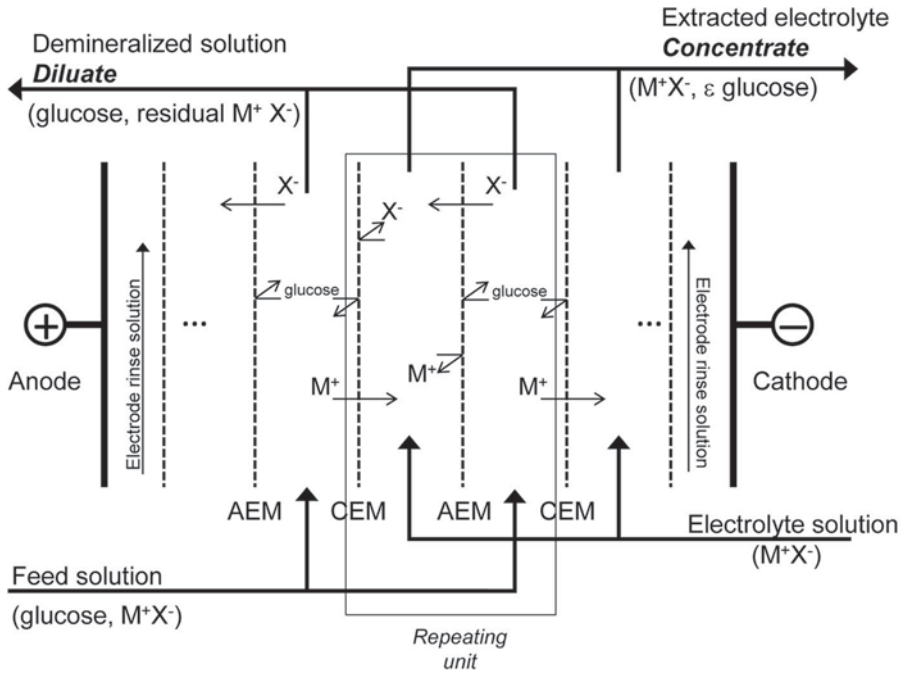

Figure 1. Schematic representation of the demineralization of an electrolyte solution containing glucose by ED (CEM: cation exchange membrane – AEM: Anion-exchange membrane).

The solvent and solute (glucose and ions) fluxes were respectively deduced from the variation of the volume and solute mass transferred between the compartments versus time. For all the experiments, these variations were found to be linear (deviation less than 10 %) (Figure 2). As a result, the solvent, ions and glucose flux densities, j_v ($m^3\,m^{-2}\,s^{-1}$), j_i ($eq\,m^{-2}\,s^{-1}$) and j_{Glu} ($mol\,m^{-2}\,s^{-1}$), were obtained as the slope of the corresponding straights. The total active membrane areas considered were 0.2 m^2 for ion transfer, and 0.4 m^2 for the solvent and glucose transfer.

RESULTS AND DISCUSSION

Firstly, experiments were carried out in order to evaluate the influence of the ionic composition on the solvent and solutes transfer (glucose and ions) through the membrane under different conditions (ionic compositions: NaCl, Na_2SO_4 and $CaCl_2$; with or without current).

Then, the solvent, ions and glucose fluxes were used to calculate the glucose loss factor versus the demineralization factor to evaluate the influence of the electrolyte nature on the demineralization process performances.

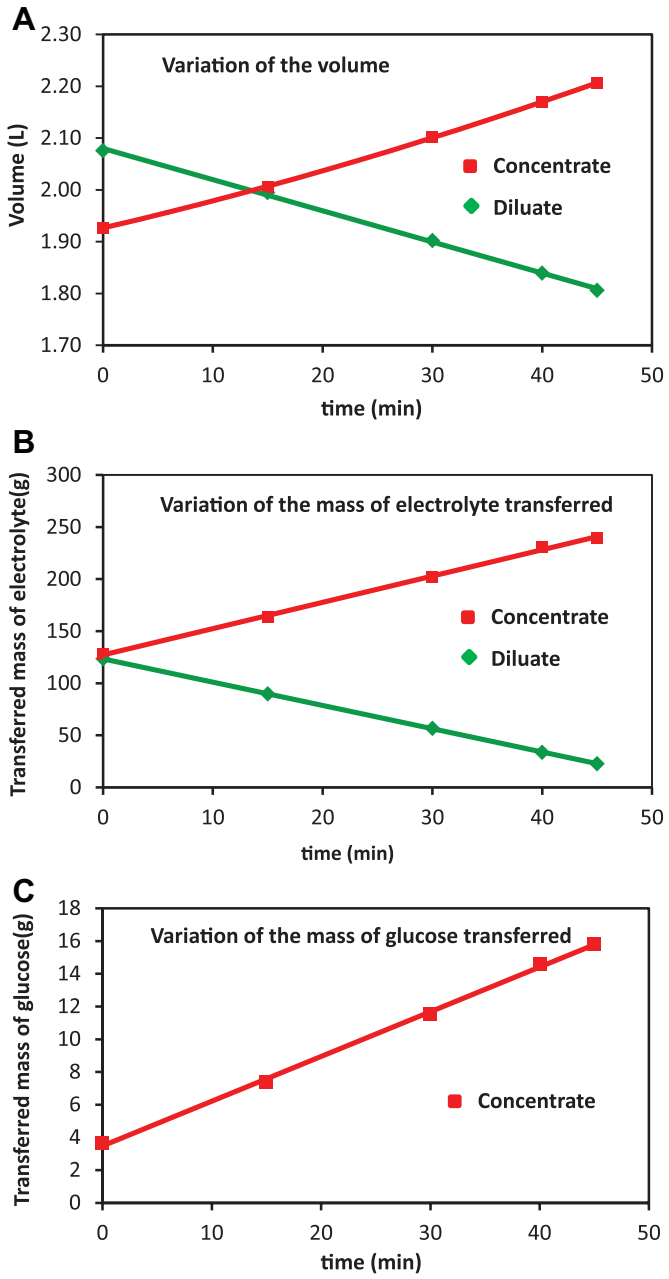

Figure 2. Variation of volume (A), mass of electrolyte (B) and glucose (C) transferred in the concentrate and diluate compartments versus time for glucose/electrolyte solutions at 25°C; [Glucose] = 1 mol L^{-1}; [Na_2SO_4] = 1 eq L^{-1}; I = 6 A.

Mass Transfer Investigation

Solvent and ion transfer

From experiments carried out without current (I = 0) with an electrolyte concentration difference across the membranes equal to 1 eq L^{-1}, it has been shown that, the contribution of osmosis to the solvent flux as well as that of diffusion to the ions flux were negligible compared to that coming from electro-osmosis and migration, obtained under normal ED conditions ($I \neq 0$) (results not shown). For instance, the osmotic and the $CaCl_2$ diffusion fluxes were 10 and 60 times lower than the electro-osmotic and migration ones measured at 6 A, respectively.

As previously mentioned, the solvent and ions flux densities were obtained from the linear variations of the volume and amount of ions transferred between the compartments versus time. The corresponding values of the flux densities, j_v and j_i, obtained at various electric currents, are reported in Table 1. As expected, one can observe that the solvent and ion flux densities increase with the electric current.

Moreover, Figures 3 and 4 show that under normal ED conditions, i.e., when an electric current is applied, the solvent and ions flux densities increase linearly with the electric current. Then, according to Equations (1) and (2) one can deduce the values of the coefficient, β, and the electro-osmotic coefficient, α, which are also reported in Table 1. As expected, the variation of the coefficient β obtained with the different electrolytes is small (lesser than 6 %) since the experiments were carried out at a constant current density, which controls the ion migration flux.

However, one can observe that the electro-osmotic coefficient, α, depends on the ionic composition. Indeed, the electro-osmotic flux, which is due to the shell of water molecules accompanying the migration of charged species under the influence of the electric current, is fixed by the ions hydration.

Glucose transfer

The transfer of glucose in the ED stack (AMX/CMX) has been also considered as function of the ionic composition without current (I = 0) as well as under ED conditions ($I \neq 0$).

The values of the glucose flux density obtained from the diffusion experiments (I = 0) in presence of various electrolytes are reported in Table 2.

One can observe that the glucose diffusion flux density, $j_{diff\ Glu}$, depends on the ionic composition. More precisely, the flux changes according to the following sequence:

$$j_{diff\ Glu}(\mathrm{NaCl}) > j_{diff\ Glu}(\mathrm{CaCl_2}) > j_{diff\ Glu}(\mathrm{Na_2SO_4}).$$

These results can be correlated to the hydration scale of the ions: $Cl^- < SO_4^{2-}$ and $Na^+ < Ca^{2+}$. One can observe that the glucose diffusion flux density decreases with the hydration of the ion.[25,26] Indeed, for a fixed cation (or anion), decreasing glucose flux densities, are obtained for increasing anion (or cation) hydration.

These solute transfer variations can reflect changes in the membrane properties associated with the hydration of the counter-

Table 1. Flux densities of the solvent and electrolyte – Electro-osmotic coefficient (α) and coefficient (β): influence of the ionic composition

	(A) Solvent transfer			(B) Electrolyte transfer		
Electrolyte	j_v (3 A) ($\times 10^8$ $m^3.m^{-2}.s^{-1}$)	j_v (6 A) ($\times 10^8$ $m^3.m^{-2}.s^{-1}$)	α ($\times 10^8$ $m^3.m^{-2}.s^{-1}A^{-1}$)	J_i (3 A) ($\times 10^4$ $eq.m^{-2}.s^{-1}$)	j_i (6 A) ($\times 10^4$ $eq.m^{-2}.s^{-1}$)	β ($\times 10^4$ $eq.m^{-2}.s^{-1}A^{-1}$)
NaCl	26.9	53.0	4.43	13.1	26.2	4.36
Na_2SO_4	25.9	51.0	4.26	13.7	28.0	4.64
$CaCl_2$	28.2	55.5	4.64	13.0	26.0	4.33

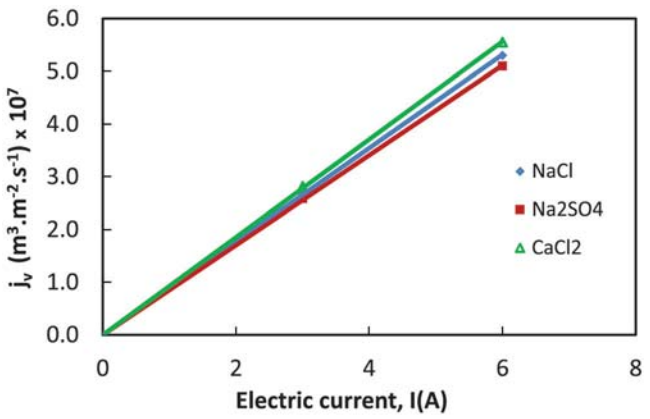

Figure 3. Variation of the solvent flux density versus electric current for glucose/electrolyte solutions at 25 °C; [Glucose] = 1 mol L^{-1}; [Electrolyte] = 1 eq L^{-1}.

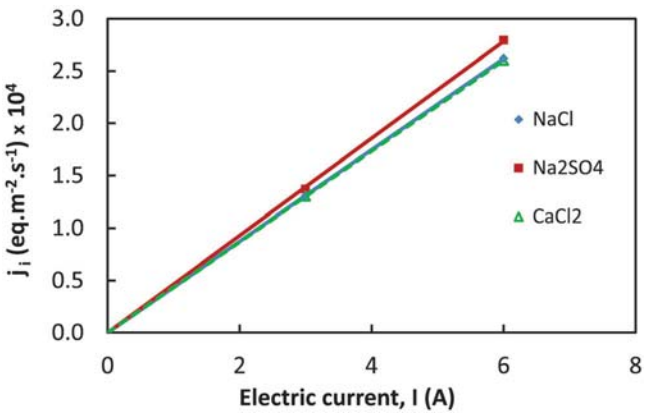

Figure 4. Variation of the electrolyte flux density versus electric current for glucose/electrolyte solutions at 25 °C; [Glucose] = 1 mol L^{-1}; [Electrolyte] = 1 eq L^{-1}.

ion coming from swelling mechanisms at a microscopic scale. These effects were particularly studied in the case of ion-exchange resins[27,28] and Nafion membranes.[29] In presence of solvent, the ion exchanger usually expands or swells due to the combination of different phenomena such as the solvation of the fixed and mobile ions, the osmotic pressure difference between the solutions inside and outside the ion-exchanger and the electrostatic repulsion between the fixed ionic groups.[27]

The results obtained in this study are in agreement with those obtained in a previous work showing a relation between the transfer modification, which is likely linked to swelling mechanisms, and the hydration number of the counter-ion.[21] Indeed, the presence of more hydrated counter-ion in the membrane leads to a decrease of the free-water content or the free volume and therefore to a decrease of the solute transfer.[21,27,28]

The values of the glucose flux density obtained in normal ED conditions ($I \neq 0$) in presence of various electrolytes are also reported in Table 2. One can observe that the glucose flux density varies increases with the current. The variation of the glucose flux density, in presence of various electrolytes, versus the electrical current is represented in Figure 5. The diffusion fluxes (values at $I = 0$) are also reported. One can observe that the glucose flux density varies linearly with the current. Then, whilst glucose is an uncharged solute, its transfer under ED conditions is the sum of two contributions: diffusion and convection, due to the electro-osmotic flux which, as previously discussed, is proportional to the electrical current (Equation (2)). This kind of results is rather scarce in literature and to our knowledge the coupled transfer of a neutral solute, diffusion/convection, during ED demineralization has been only observed in the case of aqueous solutions of phenol in presence of sodium chloride.[12]

Then, the total glucose flux density can be expressed from the following equation:

$$j_{Glu} = j_{diff\ Glu} + j_{conv\ Glu} = j_{diff\ Glu} + \gamma\ I. \quad (4)$$

In this expression, the coefficient γ relates the amount of glucose transferred by convection, which is proportional to the electro-osmotic flux (Equation (3)), and the electric current.

Moreover, concerning the influence of the electrolyte nature, one can observed that the coefficient γ (given in Table 2), which

Table 2. Flux densities of glucose (with and without current) – Mass transfer parameters characterizing the glucose convection transfer, γ and σ_{Glu}: influence of the ionic composition

Electrolyte	$j_{diff\ Glu}$ (0 A) ($\times 10^6$ $mol.m^{-2}.s^{-1}$)	j_{Glu} (3 A) ($\times 10^6$ $mol.m^{-2}.s^{-1}$)	j_{Glu} (6 A) ($\times 10^6$ $mol.m^{-2}.s^{-1}$)	γ ($\times 10^6$ $mol.m^{-2}.s^{-1}A^{-1}$)	σ_{Glu}
NaCl	12.2	26.7	47.8	8.2	0.81
Na_2SO_4	9.2	36.1	63.3	10.9	0.74
$CaCl_2$	11.0	36.1	62.5	10.7	0.77

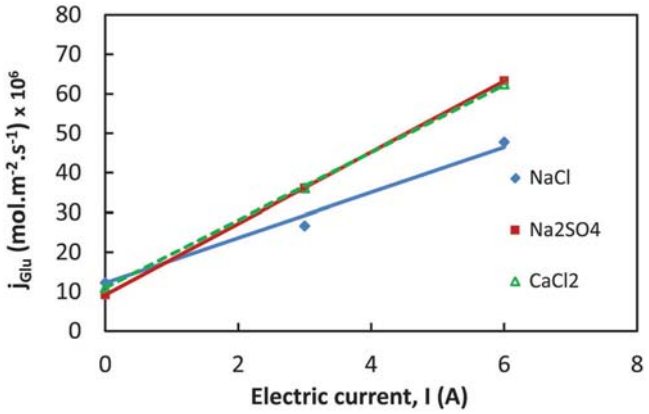

Figure 5. Variation of the glucose flux density versus electric current for glucose/electrolyte solutions at 25 °C; [Glucose] = 1 mol L^{-1}; [Electrolyte] = 1 eq L^{-1}.

characterizes the convective contribution to the glucose flux, varies according to the following sequence: γ (NaCl) < γ ($CaCl_2$) ~ γ (Na_2SO_4).

From Equations (2)-(4), one can determine the reflection coefficient of glucose, σ_{Glu}, which represents the relative restriction of the membrane the solute flux ($0 \leq \sigma_{Glu} \leq 1$) from the following expression:

$$\sigma_{Glu} = 1 - \frac{\gamma}{\alpha\, C_{Glu}^{d,0}} \tag{5}$$

where we assume that the mean glucose concentration on either side of the membrane, $\overline{C_{Glu}}$, is equal to the initial glucose concentration in the diluate compartment, $C_{Glu}^{d,0}$, since the amount of glucose transferred is negligible compared to the initial amount of glucose ($\Delta C = C_{Glu}^{d} - C_{Glu}^{c}$ variation less than 10 %).

The values of the reflection coefficient of glucose, σ_{Glu}, in presence of NaCl, $CaCl_2$ and Na_2SO_4 are 0.81, 0.77 and 0.74, respectively (Table 2).

The value of the reflection coefficient of glucose is closed to 1, which means that the glucose is strongly retained by the ion-exchange membranes AMX and CMX. Borges et al.[12] obtained a value of 0.24 for the phenol restriction coefficient using the same ED stack (AMX/CMX) from the ED demineralization of aqueous solutions of phenol (94.11 g mol^{-1}) in presence of sodium chloride. This result is in agreement with the value of the glucose restriction coefficient obtained in this study ($\sigma_{Glu} = 0.81$), since increasing values are expected for increasing solute size.

Moreover, it was shown that the glucose reflection coefficient, σ_{Glu}, depends on the ionic composition according to the following sequence: σ_{Glu} (NaCl) > σ_{Glu} ($CaCl_2$) > σ_{Glu} (Na_2SO_4) (Table 2). Then, as previously discussed for diffusion experiments, these variations can be correlated to the hydration scale of ions. However, in this case, the influence of the ion hydration on the convection flux is different.

These results can be explained from a previous study which has investigated the influence of the ionic composition on the mass transfer of saccharides through a Nanofiltration membrane.[20] In this work, it was shown that the saccharides are less hydrated in presence of any electrolyte compared to water. More precisely, more hydrated ions and increasing electrolyte concentrations were found to increase this dehydration, which has been quantified through the variation of the apparent molar volume, since it is expected to reflect the release of water from the solute hydration shell.[30,31] Then it was concluded that the increase of the saccharide transfer in presence of electrolyte was due to the lower apparent size resulting from its partial dehydration.

Consequently, the influence of the electrolyte nature on the reflection coefficient observed in this work is in agreement with the dehydration phenomenon. Indeed, for a fixed cation (or anion), decreasing reflection coefficient, expected from decreasing solute size, are obtained for increasing anion (or cation) hydration.

The contributions of the diffusive flux as well as that of the convective flux on the total glucose transfer are evaluated from the mass transfer parameters, $j_{diff\ Glu}$ and γ (Table 2). The results are plotted in Figure 6 for the various electrolytes and the 2 electric currents investigated. One can observe that the contribution of the diffusive flux, mainly fixed by the membrane properties, is lower than the convective one, which is mainly governed by the neutral solute dehydration in presence of electrolyte. Moreover, as expected, for a given electrolyte, the contribution of the convective flux increases with the electric current.

Impact on the Process Performances

As previously mentioned, the objective of the demineralization by ED of solutions containing organic solute (valuable organic matter or organic contaminants) is to keep the organic solute loss as low as possible, i.e., to reach quite high recovery values, while maximizing the removal of ions. The mass transfer parameters characterizing the solvent, ions and glucose flux densities are used to calculate the glucose loss factor and the demineralization factor to evaluate the influence of the electrolyte nature on the process performances. The glucose loss, $(1-Y_{Glu})$, as well as the demineralization factor, Γ, which are defined by the amount of solute transferred (glucose or ions) to the initial amount in the diluate ratio, were calculated from the following equations:

$$(1 - Y_{Glu}) = \frac{\left(j_{diff\ Glu} + \gamma I\right) 2\, S_m\, t}{C_{Glu}^{d,0}\, V^{d,0}} \tag{6}$$

$$\Gamma = \frac{\beta\, 2\, S_m\, I\, t}{C_{el}^{d,0}\, V^{d,0}} \tag{7}$$

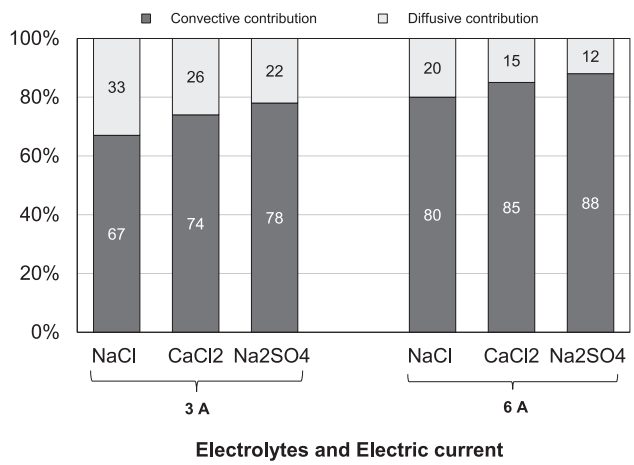

Figure 6. Diffusive and convective contributions to the glucose mass transfer: influence of the electrolyte nature and electric current; [Glucose] = 1 mol L^{-1}; [Electrolyte] = 1 eq L^{-1}.

where S_m is the total active membrane area of one type of membrane (AMX or CMX), t the time, $V^{d,0}$ the initial volume in the diluate, $C_{el}^{d,0}$ and $C_{Glu}^{d,0}$ the initial concentrations of ions and glucose in the diluate, respectively.

Figure 7 shows the variation of the glucose loss factor versus demineralization factor for various electrolyte solutions. One can observe that the loss of glucose is low and does not exceed a few percent. It is also observed that, for a fixed demineralization factor, the glucose loss factor increases with the ion hydration. Indeed, for a fixed cation, Na^+, the less the anion hydration, the lower the glucose loss. In the same manner, for a fixed anion, Cl^-, the less the cation hydration, the lower the glucose loss.

As previously discussed, this is due to the higher contribution of the glucose convection flux, mainly governed by the glucose dehydration in presence of electrolyte, compared to the diffusion one, mainly fixed by the membrane properties modification.

Finally, this study shows that the performances of the process for demineralization of a solution containing neutral organic matter, which transfer is mainly governed by convection, increases as the hydration of ions contained in the solution decreases.

Usually, the organic solute loss decreases for increasing electric current since the duration of the operation is reduced. Indeed, as shown in Figure 8a, in which only the solute transfer due to the diffusion contribution is considered, the losses decrease is proportional to the increase in the electric current. On the other hand, the organic solute transfer can be the sum of two contributions, diffusion and convection. It has been demonstrated that the convection flux is proportional to the electric current. Consequently, in these conditions, the influence of the electric current on the neutral solute loss factor is significantly reduced (Figure 8b).

Finally, the knowledge of the mechanisms governing the neutral solutes transfer during ED demineralization can be used to improve the process performances. Two situations can arise. When the transfer of the neutral solute is purely diffusive, the use of electrolytes containing strongly hydrated ions upstream to the demineralization would minimize the loss of organic solute. On the contrary, the use of electrolytes containing weakly hydrated ions upstream to the demineralization would minimize the loss of organic solute when its transfer is mainly governed by convection. However, in this case, the impact of the electric current increase on the neutral solute losses decrease is reduced.

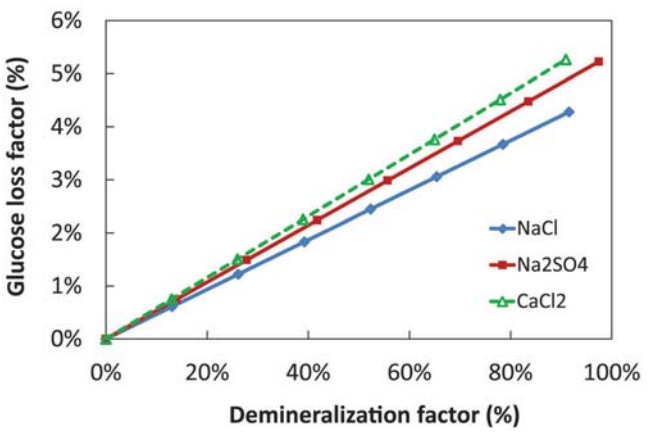

Figure 7. Variation of the glucose loss factor versus demineralization factor for glucose/electrolyte solutions at 25 °C; [Glucose] = 1 mol L^{-1}; [Electrolyte] = 1 eq L^{-1} : influence of the electrolyte nature.

CONCLUSION

The aim of the present work was to investigate the influence of the ionic composition on the demineralization of a saccharide solution containing glucose in order to evaluate the impact of the electrolyte nature on the process performances. More precisely, the modification of the glucose transfer has been evaluated under different conditions: nature of the electrolyte, with or without electric current.

It was shown that the transfer of glucose under ED conditions is the sum of two contributions: diffusion and convection.

Different correlations have been established between the hydration scale of the ions and the modifications of the diffusive and convective contributions to the glucose flux. Indeed, the convective transfer increased with hydration number of the ions while the diffusive transfer decreases.

The modifications of the glucose diffusion flux were related to the changes in the membrane properties associated with the hydration of the counter-ion which is likely linked to swelling mechanisms at a microscopic scale. Indeed, the presence of more hydrated counter-ion in the membrane is expected to lead to a decrease of the free-water content or the free volume and therefore to a decrease of the solute transfer.

The variation of the convective flux of glucose in presence of electrolyte was related to the interactions between the neutral solute and the ions in the solution. Indeed, it has been demonstrated that the saccharide transfer increase can be due to its dehydration in presence of electrolyte.

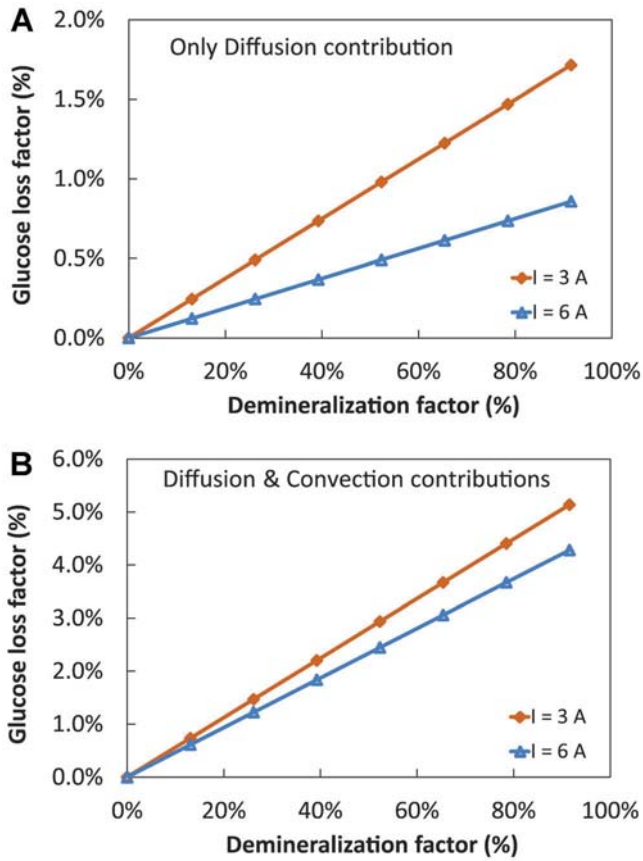

Figure 8. Variation of the glucose loss factor versus demineralization factor for glucose/NaCl solutions at 25 °C; [Glucose] = 1 mol L^{-1}; [NaCl] = 1 eq L^{-1}: influence of the electric current – (A) Only Diffusion contribution – (B) Diffusion & Convection contributions.

The solvent, ions and glucose mass transfer parameters have been also used to determine the glucose loss factor versus the demineralization factor to evaluate the influence of the electrolyte nature on the process performances. It was observed that, for a fixed demineralization factor, the neutral solute loss factor increased with the ion hydration. Consequently, it was concluded that this behaviour was due to the higher contribution of the glucose convection flux, mainly governed by the neutral solute dehydration in presence of electrolyte, compared to the diffusion one, mainly fixed by the membrane properties modification.

NOMENCLATURE

C	Concentration ($mol\,m^{-3}$)
$\overline{C_i}$	Mean solute concentration on either side of the membrane($mol\,m^{-3}$)
I	Electric current (A)
j_i	Ion density flux ($eq\,m^{-2}\,s^{-1}$)
j_v	Volumetric solvent flux density ($m^3\,m^{-2}\,s^{-1}$)
j_{Glu}	Glucose flux density ($mol\,m^{-2}\,s^{-1}$)
Y	Recovery factor
$(1-Y)$	Loss factor

Greek Letters

α	Electro-osmotic coefficient ($m^3\,m^{-2}\,s^{-1}\,A^{-1}$)
β	Current coefficient ($eq\,m^{-2}\,s^{-1}\,A^{-1}$)
γ	Mass transfer parameter characterizing the convection flux of glucose ($mol\,m^{-2}\,s^{-1}\,A^{-1}$)
Γ	Demineralization factor
σ	Reflection coefficient

Subscripts

conv	Convection
diff	Diffusion
d	Diluate
Glu	Glucose
i	Solute or ion
v	Solvent

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