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Abstract: A recent alternative method based on ultrafiltration membrane stacked in an electrodialysis cell was recently used for the separation of bio-active high added value charged molecules, such as peptides and polyphenols. However, the ultrafiltration membranes which are uncharged membranes present lower electrical conductivity, in comparison with conventional ion-exchange membranes. The purpose of this study was to evaluate the effect of conditioning ultrafiltration membranes of different molecular weight cut-off (MWCO) (10, 20, 50, and 100 kDa) in solution with different ionic strength (distilled water and 0.1 M $NaCl_{(aq)}$) on their electrodialytic properties. It appeared that the conditioning solution could have a major impact on the electrical conductivity value of an ultrafiltration membrane and that the final conductivity value after soaking increased with an increase in molecular weight cut-off. However, the soaking period and solution had no effect on membrane thickness. Furthermore, the electrical conductivity of the membrane was increased after an electrodialysis with ultrafiltration membranes process of a salt solution.

Keywords: Electrodialysis (ED), ultrafiltration membrane, limiting current density, conditioning, molecular weight cut-off (MWCO), ionic strength

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INTRODUCTION

Membranes are selective barriers that can be used to separate mixture of liquids into a concentrated and a diluted stream (1). A first distinction between membranes is usually established by separating porous membranes from non-porous ones. Ultrafiltration membranes are porous membranes, consisting of a porous network through which transport occurs, and are usually used for liquid separation in pressure-driven membranes processes (1). A second distinction between membranes is based on their capacity to exchange charges such as in anion exchange and cation exchange membranes used in ion-exchange and electrodialysis.

Recently, ultrafiltration membranes were used by Galier et al. (2) to investigate their use to replace ion-exchange membrane, a non-porous membrane, used in an electrodialysis module, where the driving force is an electric field. They used one derived cellulose membrane with a 100 kDa molecular cut-off, placed in an electrophoretic membrane contactor, to separate poly(L-glutamic) acid (1000 Da), α-lactalbumin (14 000 Da) and bovine hemoglobin, in a single passage. They reached separation yield of 86% for α-lactalbumin with a purity of 60%. More recently, Poulin et al. (3) introduced two ultrafiltration membranes in an electrodialysis cell for the simultaneous separation of acid and basic bioactive peptides contained in a β-lg hydrolysate. This arrangement called electrodialysis with ultrafiltration membranes (EDUF), demonstrated very high selectivity for the separation of the peptides. EDUF separates molecules according first to their charge, the electric field being the driving force, and also according to the molecular weight following membrane pore size or cut-off. However, due to their thickness and composition, the ultrafiltration membranes which are weakly charged membranes presented lower electrical conductivity, in comparison with conventional ion-exchange membranes, leading to higher energy consumption (4). Membrane conductivity is determined by the mobility, nature, and concentrations of counter-ions in the membrane (5, 6). Therefore, the electrical conductivity of an ion-exchange membrane is a dynamic characteristic, allowing to know the facility of an ion to cross the membrane (7). Furthermore, the lower electrical conductivity of UF membrane could lead to water dissociation. This phenomenon is linked to the flux of counter-ion migration between the solution and the membrane. Water molecule dissociation at the membrane interface appeared when the upper limit of the current intensity (or limiting current density) is overpassed. Beyond this limit it is no longer possible to increase ion transfer across the surface unit of the membrane (8, 9). And the main part of this additional current is used for the dissociation of water molecules which generates H^+ and OH^- ions immediately taken up by the ion transport (8, 10, 11). This results in a drastic pH increase at the CEM-diluate and AEM-concentrate interfaces, and a proportional decrease at the AEM-diluate and CEM-concentrate interfaces (8, 9, 12).

In order to maximize the efficiency of UF membrane in EDUF, the purpose of this study was to evaluate the impact of conditioning ultrafiltration membranes of different molecular weight cut-off (MWCO) (10, 20, 50, and 100 kDa) in solution with different ionic strength (distilled water and 0.1 M $NaCl_{(aq)}$) on their electrodialytic properties. This study had 3 objectives:

1. to evaluate the impact of the conditioning solution on UF membrane electrical conductivity and swelling as a function of soaking time,
2. to compare the electrodialytic performances of UF membrane conditioned in both aqueous solutions during EDUF treatment, and
3. to determine if ultrafiltration membranes conditioned in both aqueous solutions presented a limiting current density.

MATERIALS AND METHODS

Material

Chemicals

NaCl and KCl were purchased from Laboratoire MAT (Québec, QC, Canada).

Ultrafiltration Membranes

Cellulose ester ultrafiltration membranes with four different molecular weight cut-off (MWCO of 10, 20, 50, and 100 kDa) from Spectrum Laboratories Inc. (Rancho Dominguez, CA, USA) were tested.

Electrodialytic Configurations

Electrodialysis Configuration with Ultrafiltration Membrane (EDUF)

The electrodialysis cell was a MicroFlow type cell (effective area of 10 cm^2) (ElectroCell AB, Täby, Sweden) with one Neosepta CMX-S cationic membrane (Tokuyama Soda Ltd., Tokyo, Japan), one Neosepta AMX-SB anionic membrane (Tokuyama Soda Ltd., Tokyo, Japan) and one cellulose ester ultrafiltration membrane (Spectrum Laboratories Inc., Rancho Dominguez, CA, USA). The configuration of the cell, presented in Fig. 1, defines three closed loops. Each closed loop was connected to a separate external reservoir to allow continual recirculation of the solutions. The solutions were circulated using three centrifugal pumps and the flow rates were controlled using flowmeters. The anode was a dimensionally-stable electrode (DSA) and the cathode was a 316 stainless steel electrode. The anode/cathode voltage difference was supplied by a variable 0–30 V power source (model HPD 30-10SX, Xantrex, Burnaby,

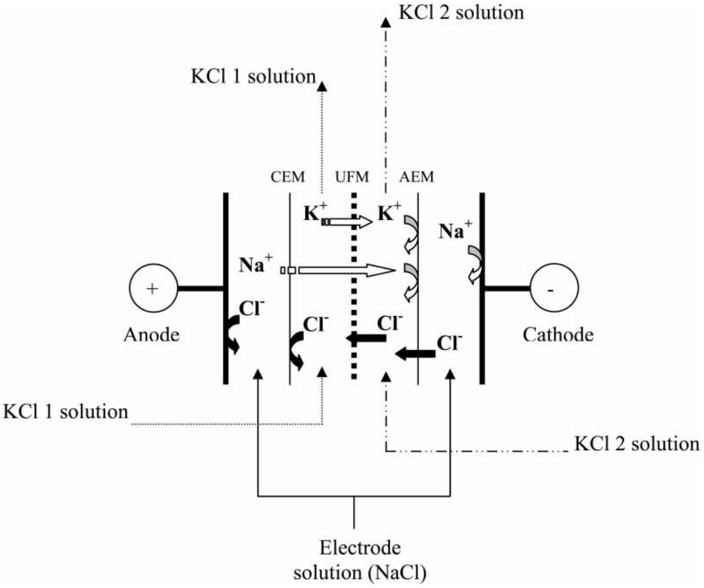

Figure 1. Electrodialysis with ultrafiltration membrane configuration. AEM: anion-exchange membrane, UFM: ultrafiltration membrane and CEM: cation-exchange membrane.

BC, Canada). The system was not equipped to maintain the temperature of the solutions constant.

Electrolysis Configuration with Ultrafiltration Membrane (EUF)

The same electrodialysis cell was used with only one cellulose ester ultrafiltration membrane (Spectrum Laboratories Inc., Rancho Dominguez, CA, USA). The configuration of the cell, presented in Fig. 2, defines two closed loops. Each closed loop was connected to a separate external reservoir to allow continual recirculation of the solutions. The solutions were circulated using two centrifugal pumps and the flow rates were controlled using flowmeters. The anode and cathode were the same as EDUF configuration, and the anode/cathode voltage difference was supplied by the same power supply as previously. The system was not equipped to maintain the temperature of the solutions constant.

Methods

Protocols

The first experiment was conducted to evaluate the impact of the conditioning solutions on UF membrane electrical conductivity and swelling as a function of soaking time. UF membrane coupons (4.1 cm × 8.0 cm) were immerged

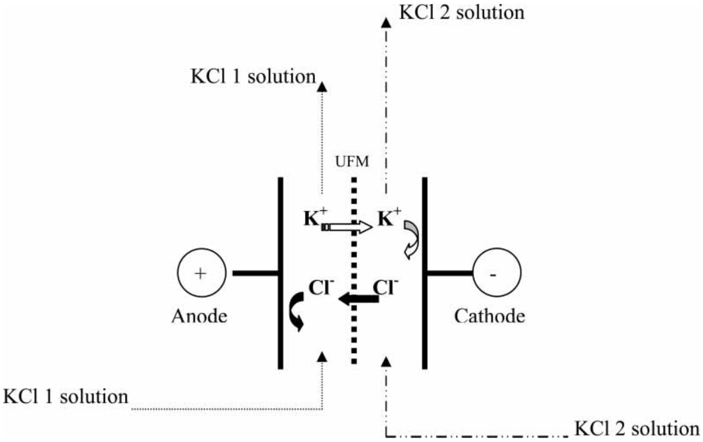

Figure 2. Electrolysis with ultrafiltration membrane configuration used for limiting current density determination. UFM: ultrafiltration membrane.

whether in distilled water or in a $NaCl_{(aq)}$ 0.1M solution for 120 hours. Distilled water is the solution generally used for ultrafiltration membrane soaking before use. The electrical conductivity and membrane thickness were measured at times 0, 8, 24, 32, 48, 56, 72, 80, 96, 104, and 120 hours. Two replicates of each condition were performed.

The goal of the second experiment was to evaluate differences between the membrane conditioned in distilled water or in a 0.1 M $NaCl_{(aq)}$ solution during electrodialysis with ultrafiltration membrane (EDUF) treatment. EDUF was performed in batch process using a constant voltage difference of 5.0 V. The duration of the treatment was 30 minutes. The electrode, KCl 1, and KCl 2 compartments contained a 20 g/L NaCl aqueous solution (250 mL), a 2 g/L KCl aqueous solution (250 mL) and a 2 g/L KCl aqueous solution (250 mL) respectively (Fig. 1). The KCl solution flow rates were 200 mL/min while the flow rate of the electrode solution was 300 mL/min. The current was noted every 5 minutes to determine the system resistance. One ED run was done with each membrane conditioned in the first part of the experiments; consequently, two replicates of each condition were performed.

The third experiment was conducted to evaluate the limiting current density of ultrafiltration membrane conditioned in distilled water or in a 0.1 M $NaCl_{(aq)}$ solution. To evaluate only the potential of the ultrafiltration membrane, an electrolysis configuration with ultrafiltration membrane (EUF) was used and performed in batch process (Fig. 2). The voltage (U, in Volt) was quickly increased by 0.5 V from 1.0 to 25.0 V, while noting the current value (I, in Ampere) corresponding to each voltage value. The electrolytes were 2 g/L KCl aqueous solutions (250 mL) (KCl 1 and KCl 2) (Fig. 2). The KCl solutions flow rates were 200 mL/min. Two replicates of each condition were performed.

Analyses

pH. A pH-meter model SP20 (Thermo Orion, West Chester, PA, USA) was used with a VWR Symphony epoxy gel combination pH electrode (Montreal, Canada).

Conductivity. A YSI conductivity meter, Model 3100, was used with a YSI immersion probe model 3252, cell constant $K = 1\ \mathrm{cm}^{-1}$ (Yellow Springs Instrument Co., Yellowsprings, OH, USA).

Apparent system resistance. The apparent system resistance was calculated, using Ohm's Law, from the voltage and the current read directly from the indicators on the power supply.

Limiting current density determination. Limiting current density was determined, according to Cowan and Brown (13). The apparent system resistance ($R = U/I$) was plotted against the reciprocal of the intensity. The inflection point on this graph was determined to be the limiting current density.

Membrane electrical conductivity. The membrane electrical conductivity was measured as previously described by Bazinet and Araya-Farias (14), using a specially designed clip from the Laboratoire des Matériaux Échangeurs d'Ions (Créteil, France). The electrical conductivity of the UF membrane was measured in a 0.1 M NaCl solution after being soaked in distilled water or 0.1 M $NaCl_{(aq)}$ solution. The membrane electrical conductivity κ ($\mathrm{mS \cdot cm^{-1}}$) was calculated as follows (6, 15):

$$\kappa = \frac{l}{R_m A}$$

where l is the membrane thickness (cm), R_m the transversal electric resistance of the membrane (Ω) and A the electrode area ($1\ \mathrm{cm}^2$).

Membrane thickness. Thickness of the membrane was measured using a Mitutoyo Corp. digimatic indicator (Model ID-110 ME, Japan) and digimatic mini-processor (Model DP-1HS, Japan), specially devised for plastic film thickness measurement. The resolution was of 1 μm and the range of 10 mm. Thickness was measured at four different points on the membrane and the values were averaged. This averaged value was also used for the calculation of the membrane electrical conductivity.

RESULTS AND DISCUSSION

Impact of the Conditioning Solution on Membrane Thickness and Electrical Conductivity

Membrane Thickness

Whatever the conditoning solution, the membrane thickness was constant during the whole soaking period at 0.294 ± 0.003, 0.295 ± 0.002, 0.300 ± 0.003, and 0.298 ± 0.004 mm respectively for 10, 20, 50, and 100 kDa MCO membranes (Fig. 3); the membranes, whatever their MWCO presented similar averaged thickness values of 0.297 ± 0.003 mm. Also, the thickness of the UF membranes did not vary as a function of soaking time according to the solution and the salt present. However, the thickness values of ion-exchange membranes were previously shown to vary from 0.090 to 0.200 mm for the anion exchange membranes (4, 16, 17, 18) and up to 0.500 mm (18) and from 0.149 to 0.372 mm for cation-exchange membranes (6, 7, 14) and up to 0.516 mm (6). Furthermore, Lteif et al. (6) showed for cation-exchange membranes that the thickness of the membranes, and consequently their swelling, varied as a function of the hydrated radius of the counter-ion and that this can be explained by the structural characteristics of the membrane.

Membrane Electrical Conductivity

Whatever the molecular weight cut-off (MWCO) of the membrane, the conductivity value (Fig. 4) increased as a function of time to reach a plateau.

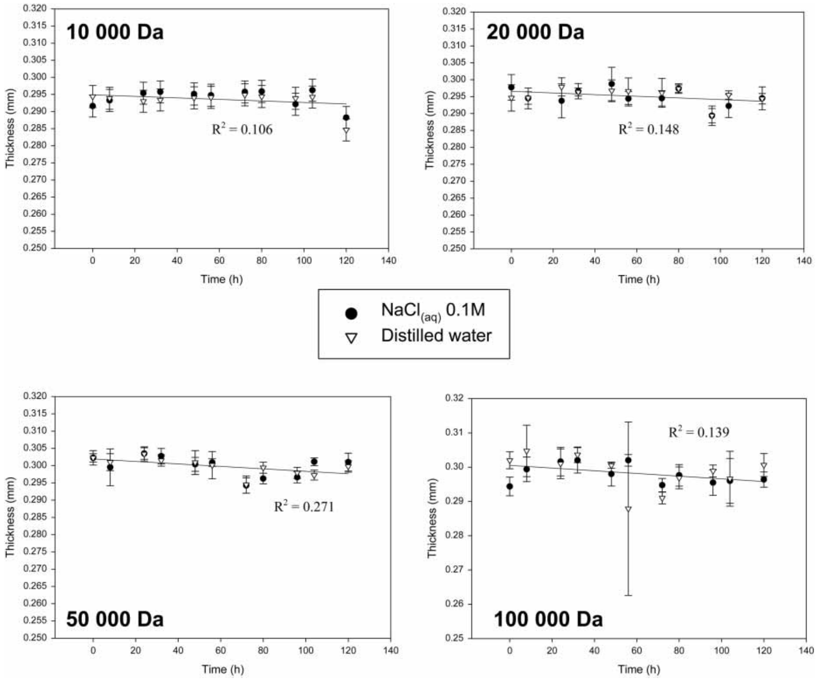

Figure 3. Evolution of the thickness value of four molecular weight cut-off ultrafiltration membranes (10,000, 20,000, 50,000, and 100,000 Da) as a function of time during soaking in distilled water and 0.1 M NaCl aqueous solution.

The final conductivity value seemed to increase with an increase in MWCO. However, the evolution of the membrane conductivity was different according to the conditioning solution and the molecular weight cut-off (MWCO) of the membrane.

For 10 and 50 kDa MWCO membranes, although the initial values of the conductivity were higher in distilled water than $NaCl_{(aq)}$ solution with respective values of 0.129 ± 0.009 vs 0.046 ± 0.011 mS/cm and 0.146 ± 0.001 vs 0.057 ± 0.004 mS/cm, thereafter the values for $NaCl_{(aq)}$ solution were slightly higher or similar to the ones obtained for distilled water (Fig. 4). However, for 50 kDa MWCO membrane, a plateau was reached at a maximum value of 0.494 ± 0.031 mS/cm after only 8 hours of soaking while for 10 kDa MWCO membrane, the plateau at 0.422 ± 0.023 mS/cm was reached after 24 hours of soaking. For 20 kDa MWCO membrane, the initial value for $NaCl_{(aq)}$ solution was slightly higher than the one measured for distilled water, with respective values of 0.109 ± 0.004 and 0.063 ± 0.024 mS/cm (Fig. 4). Thereafter, for distilled water, the conductivity increased linearly during the first 48 hours of soaking to reach a plateau

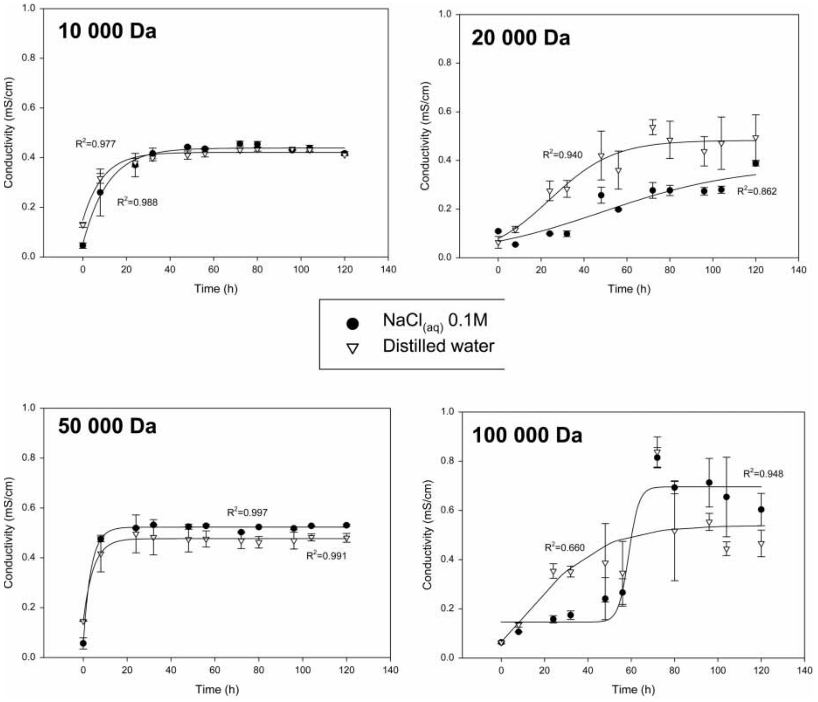

Figure 4. Evolution of the electrical conductivity value of four molecular weight cut-off ultrafiltration membranes (10,000, 20,000, 50,000, and 100,000 Da) as a function of time during soaking in distilled water and 0.1 M NaCl aqueous solution.

value, while for $NaCl_{(aq)}$ solution the conductivity increased slowly and linearly to reach its maximum value after 72 hours. Furthermore, the plateau value was higher for distilled water than for $NaCl_{(aq)}$ solution with respective values of 0.485 ± 0.036 and 0.299 ± 0.049 mS/cm. This result was quite surprising since the addition of salt should increase the conductivity of the membrane or give similar value as distilled water as observed for the 10 and 50 kDa membranes. No explanation could be given for such a phenomena except the composition of the membrane which is confidential. The 100 kDa MWCO membrane presented the most special evolution (Fig. 4). At the beginning, the conductivities were similar for both conditioning solutions at an averaged value of 0.064 ± 0.006 mS/cm. The conductivity of the membrane soaked in distilled water increased to reach a plateau value of 0.507 ± 0.162 mS/cm after 48 hours, while for $NaCl_{(aq)}$ solution, the conductivity of the membrane increased very slowly to 0.266 ± 0.056 mS/cm during the first 56 hours, then presented a rapid increase in conductivity to reach the value of 0.815 ± 0.042 mS/cm at 72 hours and then remained quite constant. The final conductivity value for 100 kDa in $NaCl_{(aq)}$ solution of 0.604 ± 0.065 mS/cm was the highest value obtained for all the membrane.

Although, the membranes were all composed of ester cellulose, the effect of the conditioning solution on their electrical conductivity values was different and that independently of their MWCO. These results suggested that the real composition of the membrane, kept confidential by the manufacturer, has a more important effect on the final conductivity than the conditioning solution. However, the fact that some membrane soaked in a $NaCl_{(aq)}$ solution could have their conductivity increased (Ex. increase of 22.8% for 100 kDa MWCO membrane), could be very interesting for use of these membranes in an electrodialysis (ED) configuration. Indeed the conductivity of the membrane affect the global resistance of the ED system and consequently its energy consumption (4). It has been demonstrated also for conventional electrodialysis that the membrane conductivity varies with the limiting ionic conductivity of counter-ions (6, 15). Consequently, the nature of the salt present in the membrane as counter-ion in conventional ED membrane, and probably also in filtration membranes, could affect their conductivity. In previous works where membrane conductivity was measured after soaking in 0.1 N NaCl solution as the one used in the present work, the electrical conductivity of ion-exchange membranes varied from 0.56 to 12.0 mS/cm for the cation-exchange membrane (6, 7, 14) and from 1.0 to 10.3 mS/cm for the anion-exchange membrane (17–19). Some of these lowest values are similar to the ones obtained for UF membranes. Furthermore, the final conductivity of the UF membrane that increased with an increase in MWCO would probably be due to the water content of the membrane. For the ion-exchange membrane, many authors (5, 20, 21) demonstrated that the conductive properties of membranes are greatly influenced by the water content of the membrane. Stenina et al. (5) observed that the water content decreases with cation radius growth and increases in electrolyte concentration as well. This is determined by the well-known effect of salting-out. Consequently in the case of the ultrafiltration membrane, the water content, at equal porosity percentage, may increase with the MWCO since less polymer concentration was present per square meter of membrane.

Impact of the Conditioning Solution on Electrodialysis with Ultrafiltration Membrane (EDUF) Performances

Conductivity Variations in KCl 1, KCl 2 and NaCl Solutions

During EDUF treatment, the respective conductivity variations in the three compartments were different according to the MWCO and the conditioning solutions (Table 1).

For the KCl 1 solution (Starting averaged conductivity value of 3647 μS/cm), whatever the conditioning solution, conductivity increases of 168 ± 18 μS/cm were observed for 10, 20, and 50 kDa MWCO, while for 100 kDa MWCO a larger increase of 226 ± 35 μS/cm was calculated (Table 1). Furthermore, for 100 kDa MWCO, the increase in conductivity seemed to be higher for a membrane soaked in distilled water solution than in $NaCl_{(aq)}$ solution; respectively, 250 ± 20 versus 201 ± 5 μS/cm. For the KCl 2 solution (Starting averaged conductivity value of 3667 μS/cm), the conductivity increases were higher than those observed for KCl 1 solution with respective averaged increase values of 231 ± 28 μS/cm and 182 ± 32 μS/cm (Table 1). Furthermore, whatever the conditioning solution, the conductivity increases seemed to be higher for 20 and 100 kDa MWCO membranes, 264 ± 10 and 241 ± 25 μS/cm respectively, in comparison with 10 and 50 kDa MWCO membranes, 195 ± 11 and 224 ± 25 μS/cm respectively. For the NaCl solution, in the electrolyte compartment, the conductivity decreased during the treatment; all condition averaged, the conductivity decreased was 399 ± 77 μS/cm (Table 1). As for KCl 2, whatever the conditioning solution, the variations in the conductivity for 20 and 100 kDa seemed to be higher than the ones of 10 and 50 kDa; with respective decrease values of 447 ± 25 and 487 ± 67 compared to 317 ± 17 and 345 ± 49, μS/cm. Furthermore, it appeared that the decreases in conductivity calculated for the NaCl solution (Starting averaged conductivity value of 32.3 mS/cm) compartment was mostly equal to the sum of increases observed for the KCl 1 and KCl 2 compartments.

The conductivity variations are in accordance with the EDUF configuration and the results obtained by Labbé et al. (22) for a similar configuration on green tea brewing. The conductivity in the NaCl compartment decreased due to the migration of Na^+ and Cl^- across the cationic and anionic exchange membranes respectively (Fig. 1). The Na^+ migrated first in the KCl 1 compartment to increase its conductivity and then migrated to the

Table 1. Variations in conductivity and pH of the KCl 1, KCl 2 and NaCl solutions during EDUF treatment

		Conductivity variation (μS/cm)			pH variation (ΔpH)		
	Soak solution	KCl 1	KCl 2	NaCl	KCl 1	KCl 2	NaCl
10 kDa	0.1 N $NaCl_{(aq)}$	+168.5 ± 17.5	+189.0 ± 10.0	−320.0 ± 20.0	−0.28 ± 0.02	+3.08 ± 0.07	+3.78 ± 0.01
	Distilled Water	+147.5 ± 18.5	+200.5 ± 11.5	−315.0 ± 15.0	−0.30 ± 0.12	+2.93 ± 0.10	+3.72 ± 0.03
20 kDa	0.1 N $NaCl_{(aq)}$	+186.5 ± 1.5	+259.0 ± 12.0	−465.0 ± 45.0	−0.27 ± 0.05	+3.06 ± 0.07	+3.80 ± 0.02
	Distilled Water	+176.5 ± 20.5	+269.0 ± 4.0	−430.0 ± 20.0	−0.24 ± 0.08	+3.13 ± 0.03	+3.97 ± 0.03
50 kDa	0.1 N $NaCl_{(aq)}$	+184.0 ± 21.0	+242.0 ± 2.0	−380.0 ± 10.0	−0.34 ± 0.13	+3.11 ± 0.01	+3.79 ± 0.02
	Distilled Water	+143.5 ± 45.0	+207.0 ± 19.0	−310.0 ± 140.0	−0.31 ± 0.02	+3.16 ± 0.07	+3.77 ± 0.02
100 kDa	0.1 N $NaCl_{(aq)}$	+201.0 ± 5.0	+223.5 ± 19.0	−440.0 ± 160.0	−1.20 ± 0.04	+3.07 ± 0.10	+3.67 ± 0.15
	Distilled Water	+250.5 ± 20.5	+258.5 ± 1.5	−535.0 ± 55.0	−0.78 ± 0.18	+3.29 ± 0.10	+3.78 ± 0.02

KCl 2 compartment by crossing the UF membrane (not permselective to ions) where it was stopped by the anion-exchange membrane. Oppositely, to keep the NaCl solution electrically neutral, Cl^- from NaCl compartment migrated to the KCl 2 compartment to increase its conductivity and then crossed the UF membrane to migrate to the KCl 1 compartment where it was stopped by the cation-exchange membrane. Furthermore, Cl^- from the KCl 2 solution migrated into the KCl 1 solution while K+ from the KCl 1 solution migrated into the KCl 2 solution (Fig. 1). In addition, the transport of H^+ ions, generated at the anode, across the cation-exchange membrane to the KCl 1 and eventually to the KCl 2 compartment as well as OH^- ions, generated at the cathode, across the anion-exchange membrane to the KCl 2 and KCl 1 compartments would also contributes to the change in conductivity. Therefore, the difference of conductivity observed between KCl 1 and KCl 2 compartments would be due to the difference in ionic electrical mobility of the respective conductive species: $325\,cm^2/s.V$ for H^+, $176\,cm^2/s.V$ for OH^-, $67.10^5\ cm^2/s.V$ for K^+, $68\,cm^2/s.V$ for Cl^- and $45\,cm^2/s.V$ for Na^+ (23).

pH Variations in KCl 1, KCl 2 and NaCl Solutions

For KCl 1 solution, small decreases of 0.29 ± 0.03 pH unit were observed for 10, 20 and 50 kDa MWCO, while for 100 kDa MWCO a larger decrease of 0.99 ± 0.3 pH unit was measured (Table 1). Furthermore, for 100 kDa MWCO, the decrease in pH seemed to be higher for the membrane soaked in $NaCl_{(aq)}$ solution than in distilled water respectively, 1.20 ± 0.04 versus 0.78 ± 0.18 pH unit (Table 1). On the opposite side, whatever the MWCO and the conditioning solution, for KCl 2 and NaCl solutions, similar increases in pH were observed; respective increases of 3.10 ± 0.10 and 3.79 ± 0.08 pH units.

The variations in pH, would be a consequence of the transport of H^+ ions, the most mobile specie, generated at the anode and OH^- ions, the most mobile after the proton, generated at the cathode. These two species can easily cross the CEM and the AEM respectively. However, due to a great variation in pH, and great differences between values in the three compartments, a second phenomenon could also have been appeared, the water dissociation. In fact, the difference in electrical mobility of the mobile species implicated in the mass transport, would have led to water molecule dissociation at the interface of the ion-exchange membrane. This water dissociation at the interfaces of the anionic membrane, coupled with water dissociation at the cation-exchange membrane interface, thus provided the species necessary to carry the current and to compensate for lower mobility of sodium. In addition, since water dissociation is usually larger for anion-exchange membranes than for cation-exchange membranes (24, 25), this would explain that KCl 2 compartment was more basified by OH^- from AEM than KCl 1 solution was acidified by H_3O^+ from CEM and H_3O^+ produced at the AEM interface in the NaCl solution and migrating therafter. This phenomenon was demonstrated by Labbé and Bazinet (26) during electromigration of catechin from green tea brewing with a similar EDUF configuration. For the NaCl solution, the increase in pH will result from three phenomena: the migration of OH^- from KCl 1 and 2 compartments by leakage through the CEM; the production of OH^- at the interface of the CEM by water dissociation; and the migration of H_3O^+ produced at the AEM interface in the NaCl solution. All these pH variations would also be accentuated by the fact that H_3O^+ is 2 time more mobile than OH^- and 5 times more mobile than K^+ and Cl^-(23).

Apparent System Global Resistances

Initially, resistance values were different according to the conditioning solution and the molecular weight cut-off (MWCO) of the membrane (Fig. 5). For 10 kDa MWCO membrane, the initial values were similar at $98.7 \pm 0.3\ \Omega$ for both conditioning solutions. For 50 kDa MWCO

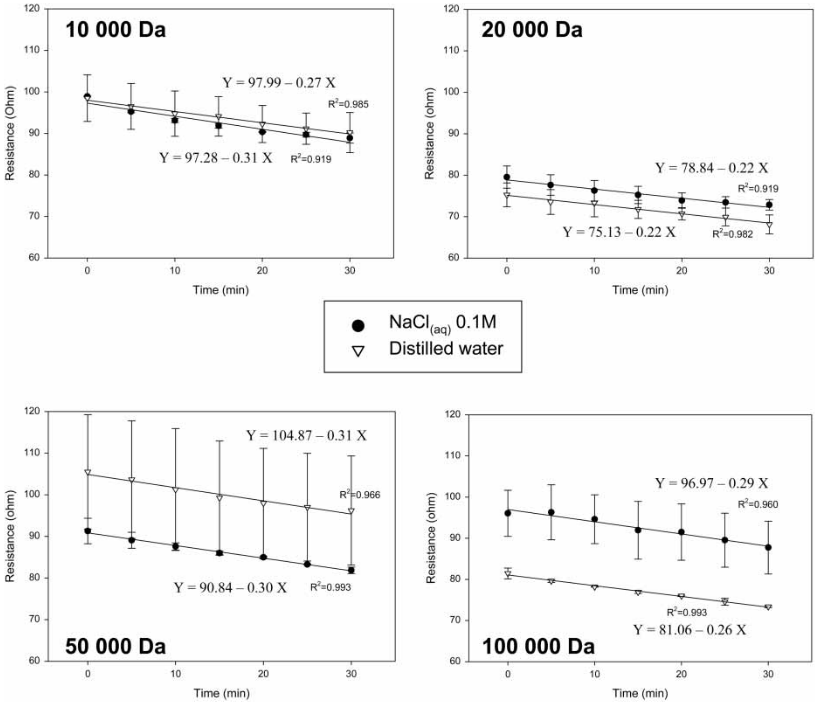

Figure 5. Evolution of the apparent system global resistance of four molecular weight cut-off ultrafiltration membranes (10,000, 20,000, 50,000, and 100,000 Da) soaked in distilled water and 0.1 M NaCl aqueous solution during electrodialysis with ultrafiltration membrane.

membrane, the initial resistance value was higher for the system in which UF membrane soaked in distilled water was stacked (105.5 ± 13.7 vs 91.3 ± 3.1 Ω). On the opposite, for 20 and 100 kDa MWCO membrane the initial resistance value was higher for the system in which UF membrane soaked in $NaCl_{(aq)}$ solution was stacked. However, the difference in initial resistance between $NaCl_{(aq)}$ solution and distilled water conditioning solutions was higher for the 100 kDa MWCO membrane (96.0 ± 5.6 vs 81.4 ± 1.3 Ω respectively) compared to the 20 kDa MWCO membrane (79.5 ± 2.7 vs 75.2 ± 2.9 Ω respectively). Whatever, the molecular weight cut-off (MWCO) of the membrane and the conditioning solution, the system global resistance decreased linearly during EDUF treatment. The variation of the system global resistance at the end of the EDUF treatment was the same for all the MWCO and conditioning solution; 9.26 ± 0.80%. This is confirmed by the slopes of the curves calculated for all conditions (Fig. 5).

Bazinet et al. (4) and Labbé et al. (22) reported a decrease in the system global resistance during electrodialysis with ultrafiltration membrane of tobacco extract and green tea brewing. In both cases, the membranes fixed the starting values of the system global resistance and the solution the evolution. Indeed, at the beginning of the EDUF process, the system global resistance was mainly linked to the conductivity or resistivity of the membranes stacked in the ED cell as observed by Bargeman et al. (27) during the electro-membrane filtration process of casein hydrolysate. Except for 100 k Da MWCO membrane, these results confirmed the previous results observed for membrane electrical conductivity. When the electrical conductivity was higher, in one conditioning solution, the system global resistance was logically decreased. The conditioning solution has a real effect on the system resistance and consequently on the total energy consumption.

In addition, it appeared from these results that after EDUF run of salt solution, the conductivity of the membrane conditioned with salt was higher than the one measured for distilled water; 0.439 ± 0.003 vs 0.421 ± 0.003 mS/cm, 0.989 ± 0.039 vs 0.715 ± 0.243 mS/cm, 0.538 ± 0.011 vs 0.501 ± 0.025 mS/cm and 0.936 ± 0.001 vs 0.861 ± 0.030 mS/cm respectively for 10, 20, 50, and 100 kDa MWCO. These values were higher than the ones measured after the soaking period of 120 hours, slightly higher for 10 and 50 kDa MWCO, and largely higher for 20 and 100 kDa MWCO. According to these observations, before use for electromigration of organic charged molecules by EDUF, salt solutions could be first circulated to enhance further filtration membrane electrical conductivity.

Impact of the Conditioning Solution on the Limiting Current Density of Ultrafiltration Membrane

During EDUF of salt solution, large variations in pH were observed in the three different compartments. The objectives of this third part was to evaluate if the ultrafiltration membranes as non-charged membranes could reach a limiting current density, consequently leading to water molecule dissociation and if the conditioning solution had an impact on this limiting current density value.

It appeared (Fig. 6) that the limiting current density was never reached in the range of voltage of 0 to 25 V for a system using only one membrane UF stacked. Furthermore, the conditioning solution had no effect on the evolution of the system resistance (U/I) as a function of 1/I.

The limiting current density was also determined in both EDUF cell systems used by Poulin et al. (3) with a 20kDa MWCO membrane with similar conditions of salt, hydrolysate, and concentration. For the microflow cell, the voltage range was between 0 and 30 V, while for the MP cell, the voltage range was between 0 and 80 V. It appeared that with the MicroFlow cell with one UF membrane, the limiting current density was reached at about 27–28 A^{-1}, which correspond, according to the membrane active surface of 10 cm^2, to a current density of 3.6–3.7 mA/cm^2 (Fig. 7a). In the case of the MP type cell with two UF membranes, the limiting current density was reached at about 3.3 A^{-1}, which corresponds, for a 100 cm^2

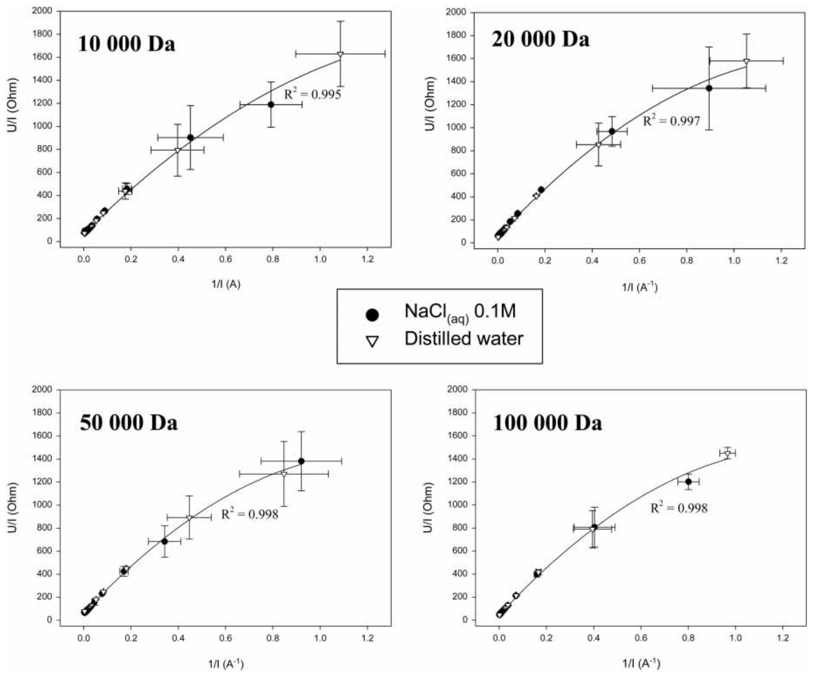

Figure 6. Determination of the limiting current density of four molecular weight cut-off ultrafiltration membranes (10,000, 20,000, 50,000, and 100,000 Da) soaked in distilled water and 0.1 M NaCl aqueous solution.

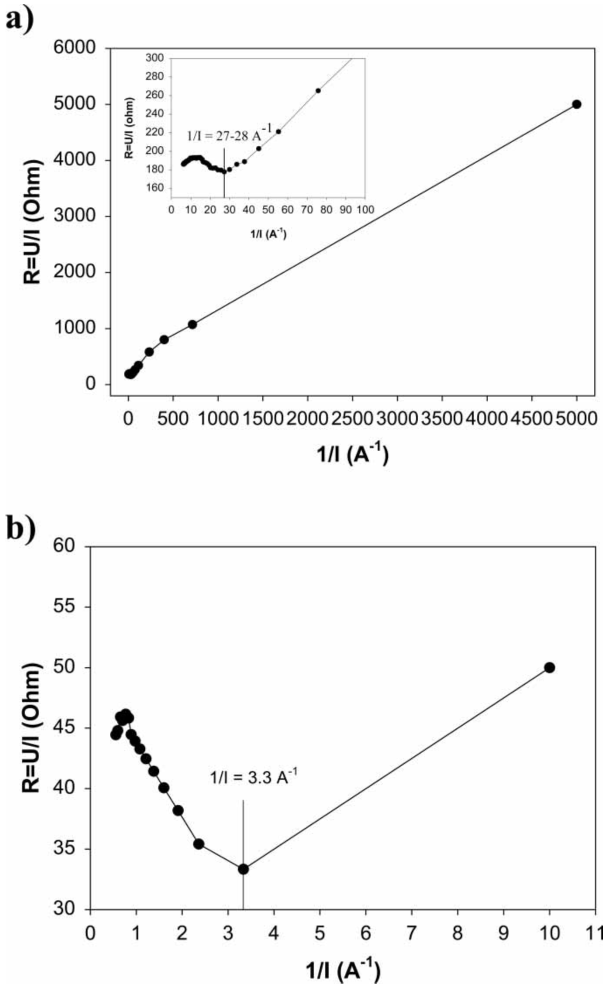

Figure 7. Determination of the limiting current density of 20,000 Da molecular weight cut-off ultrafiltration membranes during EDUF of a 1% beta-lactoglobulin hydrolysate in the conditions of Poulin et al. (2006) with a) one ultrafiltration membrane stacked in a MicroFlow type cell and b) two ultrafiltration membranes stacked in a MP type cell.

membrane active surface, to a 3 $\mathrm{mA/cm^2}$ current density quite similar to the one measured for the MicroFlow cell (Fig. 7b). As expected, the limiting current density seemed to be reached due to the presence of the ion exchange membrane and not to the UF membrane. No such data about limiting current density measured for UF membrane in electrodialytic configuration was found in the literature.

CONCLUSIONS

It appeared from these results that the conditioning solution could have a major impact on the electrical conductivity value of an ultrafiltration membrane and that the final conductivity value after soaking increased with an increase in the molecular weight cut-off. However, the soaking period and solution had no effect on membrane thickness. A simple soaking of membrane in salt solution could be used for conditioning ultrafiltration membrane prior to electrodialysis with ultrafiltration membrane to increase their electrical conductivity and then to decrease energy consumption. Furthermore, the electrical conductivity of the membrane increased after an EDUF process. In order to enhance filtration membrane conductivity before use for electromigration of organic charged molecules by EDUF, salt solutions could be first circulated and low current density used to make salt to migrate in the membrane. This procedure would simply accelerate the conditioning of the membranes.

Further works will be aimed at the effect of different salt nature and concentration on the electrical conductivity of ultrafiltration membranes before use in EDUF treatment.

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