

# SYNTHESIS OF A MONOVALENT SELECTIVE CATION EXCHANGE MEMBRANE TO CONCENTRATE REVERSE OSMOSIS BRINES BY ELECTRODIALYSIS

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## Abstract

In this work, novel monovalent selective cation exchange membranes (CEMs) with different mixtures of polyvinylidene fluoride (PVDF) and sulfonated PVDF (S-PVDF) were synthesized. The selected composite membranes were modified by surface polymerization of polyaniline (PANi) to improve their monovalent cation selectivity. PANi was doped with p-toluene sulfonic acid (pTSA) or L-valine (2-amino-3-methylbutanoic acid) and the selectivity of each CEM was determined. Membrane properties, such as chemical composition, water uptake, ion exchange capacity, permselectivity, contact angle and crystallinity were measured. The influence of the applied voltage was also studied. The newly developed membranes were used for electro-dialytic concentration of NaCl from synthetic reverse osmosis (RO) brine. Doped membranes with pTSA ( $S_{Na}^{Mg} = 0.13$ ,  $S_{Na}^{Ca} = 3.59$ ) and valine ( $S_{Na}^{Mg} = 0.09$ ,  $S_{Na}^{Ca} = 0.8$ ) have a higher selectivity for sodium than the composite ones ( $S_{Na}^{Mg} = 0.63$ ,  $S_{Na}^{Ca} = 6.82$ ). Moreover, the increase of applied voltage results in an increase of the selectivity for monovalent ions.

**Keywords:** Monovalent cation selectivity, Membrane synthesis, Surface modification, Electrodialysis, Reverse osmosis brines

**Highlights:** Novel monovalent selective CEMs with mixtures of PVDF and S-PVDF were synthesized

Surface polymerization of PANi doped with pTSA or valine to improve the selectivity

Analysis of membrane properties and influence of the applied voltage with ED

Doped membranes (pTSA or valine) have a higher selectivity for Na<sup>+</sup> than the composite

The increase of applied voltage results in an increase of monovalent ions selectivity

## 1. Introduction

Electrodialysis (ED) is a separation process used for concentration of reverse osmosis (RO) desalination brines and as salt valorization option [1–4], such as sodium chloride concentration for the chlor-alkali industry [5]. The chlor-alkali process is one of the largest electrochemical processes in which chlorine and sodium hydroxide are produced simultaneously by the electrolysis of a sodium chloride solution [6]. The requirements of the raw solution for this industry are very strict in order to avoid membrane fouling and to generate a pure product. The brine needs to be pure and have a high concentration of NaCl; impurity concentrations must be very low. This often requires costly purification steps prior to electrolysis [4]. For this reason, a promising industrial approach for the chlor-alkali industry is to operate the salt manufacturing with ED using discharged brines from a seawater reverse osmosis (SWRO) desalination plant and using the ED concentrated brine for chlor-alkali application. In this method, ED mainly concentrates monovalent ions and removes polyvalent ions from concentrate through monovalent selective ion exchange membranes [7]. Despite the fact that other minor monovalent ions are present in the feed brine, NaCl is the major element and the one that has the highest final concentration, allowing its use in the chlor-alkali industry. This method also avoids the disposal problem of SWRO brine and the discharge of concentrated brines into the sea, while providing an important circular economy and industrial symbiosis between the sea water desalination waterworks and the chemical industry. The main waste generated in the sea water desalination process, brines, could be converted onto a raw material of the chlor-alkali industry.

Selective permeation of cations through cation exchange membranes (CEMs) is a very important feature that needs to be considered in the design and synthesis of these membranes. Many attempts have been made to prepare CEMs with permselectivity for specific cations and to develop ED based methods to separate these cations. Sata [8] reported the development of monovalent cation selective membranes for the production of table salt from seawater. One utilized method is to suppress the transport of bivalent ions by introducing cation exchange groups (such as sulfonic or carboxylic groups) with a strong affinity for these cations into the membranes. However, the current efficiency of the resulting membranes decreases due to the strong binding of the cation exchange groups to the bivalent cations, which causes inactivation of cation exchange groups. Attempts were also made to decrease the charge density on the membrane surface, but results according to this method were ineffective [9,10].

Farrokhzad et al. [11] recently developed a novel CEM based on sulfonated polyvinylidene fluoride (S-PVDF) blended with PVDF in order to improve the thermal and mechanical stability of the S-PVDF membranes. Also, to provide a good distribution and homogenous mixing of the two polymers, solution blending with the same solvent (N-methyl-2-pyrrolidone) was performed. It was found that for different percentages of S-PVDF, the resulting membranes can be monovalent selective [12].

1 Three influencing parameters have been classified to describe the selective permeation  
2 of ions through membranes. The first is the sieving of ions with change in the  
3 crosslinking degree of a membrane; the second is the charge and electrostatic repulsion;  
4 and the third is the interaction between the cation exchange groups, the membrane  
5 matrix, and the cations [13].  
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7 Sieving can be done effectively by introducing a dense polyelectrolyte layer on the  
8 membrane surface, like polymerization of pyrrole on the surface of CEMs to change the  
9 permselectivity of the larger cation because of the rigidity of the polymer. Sata et al.  
10 [14] observed that the permeation of calcium ions was markedly decreased by the  
11 formation of a polypyrrole layer on the cation exchange membranes in both cases where  
12 the layer faced the anode and the cathode compartments.  
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16 A novel method for surface modification was proposed recently by Deng et al. [15],  
17 who deposited polyethylenimine (PEI) onto a commercial CEM through an electric field  
18 enhanced procedure. The resulting membrane was subsequently modified with an ion  
19 imprinting technique as Cu-IIM. By this method a selective surface to remove Cu(II)  
20 cationic species from Zn(II) cationic species was synthesized. Non-imprinted  
21 membranes were prepared in a similar way but without template ion adsorption before  
22 crosslinking. The flux of cations in Cu-IIM was higher than for non-imprinted  
23 membranes, because of the penetrating path in the modified surface, but the properties  
24 of the modified membrane and the base membrane were not compared.  
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31 A useful method to provide the intended selectivity of CEMs for monovalent cations is  
32 to modify the membrane surface by surface polymerization and to provide a more  
33 compact structure. Furthermore, the possibility to change the surface hydrophobicity by  
34 the functionalization of the membrane surface is helpful to provide the selective  
35 permeation of monovalent cations.  
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39 According to previous works [16] it was resulted that by surface polymerization of  
40 PANi with hydrophobic doping agents, the monovalent selectivity increases in cation  
41 exchange membranes; especially when the membrane structure becomes more compact  
42 and water uptake decreases. For this reason, surface modification was done in the  
43 synthesized membranes by polyaniline (PANi) surface polymerization. PANi has been  
44 used for surface modification of CEMs and also anion exchange membranes previously  
45 [17,18]. PANi is an electrically conducting polymer, which is easy to synthesize and has  
46 high chemical stability [19]. It is reported that is easy to dope/dedope PANi with  
47 acid/base which allows keeping the ion exchange capacity (IEC) of the membranes as  
48 high as possible, and to enhance the solubility of PANi in NMP [20]. It is well known  
49 that the PANi crystallinity plays a crucial role in the electrical conductivity, because it  
50 contributes to delocalization of charges within three-dimensional regions [21]. Two  
51 different doping agents were selected to increase the hydrophobicity of coated PANi:  
52 pTSA and valine. In previous work [16] pTSA was selected as doping agent and the  
53 results demonstrated that PANi-pTSA has a very high selectivity for monovalent  
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1 cations. In the present study, valine was the second doping agent selected to increase the  
2 hydrophobicity.

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4 Sun et al. [22] synthesized a PANi doped with valine; by controlling the synthesis parameters  
5 such as the reaction time, they could fabricate a super-hydrophobic flower like PANi. To have a  
6 more hydrophobic doped PANi and because of small structure of valine (comparing to  
7 bigger organic doping agents as DBSA), this doping agent was selected to improve the  
8 monovalent selectivity.  
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11 The aim of this work was to synthesize a novel cation exchange membrane with  
12 monovalent selectivity in order to be able to concentrate SWRO brines for the chlor-  
13 alkali industry by means of ED.  
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## 19 **2. Materials and methods**

### 20 **2.1 Reagents and solutions**

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22 PVDF (grade Solef<sup>®</sup> 6020) from Solvay, N-methyl-2-pyrrolidone (NMP) from Acros  
23 and chlorosulfonic acid ( $\geq 95\%$ ) from Fluka were used as base solution for the  
24 membrane synthesis.  
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29 Different reagents were used for the surface polymerization of the membranes, such as  
30 aniline (99.8%) from Acros, ammonium peroxodisulfate (APS) from Chem-Lab, para-  
31 toluene sulfonic acid (pTSA) (ACS reagent,  $\geq 98.5\%$ ) and sulfuric acid (95-97%) from  
32 Sigma-Aldrich, ammonium hydroxide (NH<sub>4</sub>OH 32%) from VWR chemicals and L-  
33 valine (98.5-100.5%) from Fischer Scientific.  
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### 39 **2.2 Synthesis of S-PVDF**

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41 Sulfonation of PVDF has been explained elsewhere [11]. 50 mL of chlorosulfonic acid  
42 were mixed with 10 g of PVDF during 45 minutes of stirring at 80 °C. After the  
43 reaction, the obtained mixture was filtered with deionized water twice. Finally the S-  
44 PVDF powder obtained was dried at the vacuum oven at 55°C during the night. A 10  
45 wt% solution of S-PVDF in NMP was then prepared by stirring during a couple of days.  
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### 51 **2.3 Synthesis of s-PVDF/PVDF composite membranes**

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53 Different mixtures of 10% PVDF/NMP and 10% S-PVDF/NMP were used to prepare  
54 the base polymer solutions of the new membranes.  
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57 The S-PVDF solution was then added to the PVDF solution under stirring in an  
58 appropriate amount to form S-PVDF/PVDF blend with a share of 30% S-PVDF. This  
59 composition was selected because the related CEM was found to have the lowest  
60 bivalent selectivity [23] and can be used to provide the highest monovalent cation  
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selectivity after surface modification (especially for NaCl saturation for chlor-alkali application). These solutions were stirred and mixed throughout 4 hours.

The solution of S-PVDF/PVDF was then casted on a glass plate (with a 250  $\mu\text{m}$  thickness of casting knife) and immediately, introduced into the vacuum oven to dry at 55°C overnight. After that, the synthesized membrane was peeled off by immersion of the glass plate in deionized water during 10 minutes. The membrane was cut and immersed in 1 M NaCl solution at least for 2 days before testing it in order to reach equilibrium conditions (maximum exchange of  $\text{Na}^+$  and membrane protons). These CEMs are denoted as S-30 in the text.

## 2.4 Membrane surface polymerization

A very simple procedure was performed to carry out the surface polymerization by modifying described procedures [18,24]. The membranes were immersed in 5 % aniline and 0.1 M  $\text{H}_2\text{SO}_4$  for 1 h while the solution was stirring with a low rate shaking. After that time, membranes were rinsed with deionized water and immersed in 0.5 M ammonium peroxydi-sulfate (APS) for 1 h by a low rate shaking. Membranes were then rinsed again with deionized water. Subsequently, membranes were immersed in 0.1 M  $\text{NH}_3$  solution for 12 h and rinsed once more with deionized water. Finally, membranes were immersed in acid pTSA solution, as the doping agent, for 12 h. Another organic doping agent that was selected to increase the hydrophobicity of coated PANi was valine [22]. Figure 1 shows the chemical structure of pTSA and L-valine, respectively.

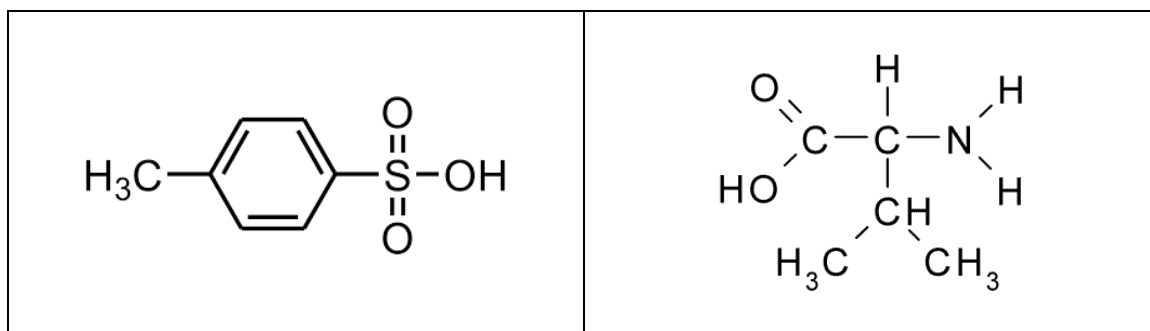


Figure 1. Chemical structure of pTSA and L-valine, respectively

Once the surface polymerization was done, membranes were immersed in NaCl 1 M for at least 48 h in order to reach the equilibrium conditions before starting the ED tests.

The membranes are denoted as S30-pTSA and S30-valine, referring to S-30 composite membrane coated by PANi-pTSA and PANi-valine, respectively.

## 2.5 Membrane characterization techniques

Different techniques and methods were used to characterize the electrochemical properties of the prepared membranes: water uptake (WU), ion exchange capacity (IEC), transport number and permselectivity, contact angle, Fourier transform infrared spectroscopy (FTIR) and X-Ray diffraction (XRD).

### Water uptake (WU)

First, membranes were dried at 55 °C in the vacuum oven for 4-5 h and weighted (dry weight). Then, they were immersed in deionized water during 24 h. Membrane samples were removed from water and water covering their surface was removed with a cellulose tissue and then weighted again (wet weight). WU can be calculated as:

$$WU (\%) = \frac{\text{wet weight} - \text{dry weight}}{\text{dry weight}} \cdot 100 \quad \text{Equation 1}$$

### Ion exchange capacity (IEC)

First, membrane samples were soaked in 1M HCl for 24 hours in order to exchange H<sup>+</sup> ions. After that, deionized water was used to remove the excess of H<sup>+</sup> ions until membranes had a neutral pH. Then, membranes were dried in the vacuum oven at 55 °C for 4-5 h and weighted (dry weight). Then, they were immersed in a 2 M NaCl solution for 24 h more to exchange the H<sup>+</sup> with Na<sup>+</sup>. Finally, the resultant solution was titrated with 0.01M NaOH. IEC was calculated as:

$$IEC (meq/g) = \frac{C_{NaOH} \cdot Volume_{NaOH}}{\text{dry weight}} \quad \text{Equation 2}$$

### Electrical resistance and ion conductivity (IC)

First, membrane samples were soaked in 1 M NaCl in order to equilibrate them. Impedance spectroscopy measurements were done at room temperature in 0.5 M NaCl solution following the procedure described earlier [25]. The electrical resistance of equilibrated membrane was measured with a digital LCR meter (HP 4262A) at a frequency of 1500 kHz and a clip cell composed of two graphite electrodes fixed in a plexiglass tank (Figure 2).

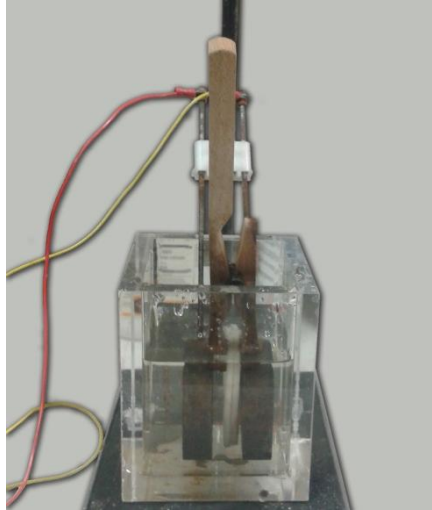


Figure 2. Ion conductivity measurement set-up

The membrane resistance ( $R_{mem}$ ) was calculated by the resistance difference of the cell ( $R_{cell}$ ) and the electrolyte solution ( $R_{sol}$ ).

Moreover, the IC of the membranes was calculated based on the electrical resistance measurement, following equation 3:

$$IC (S/cm) = \frac{L}{R_{mem} \cdot A} \quad \text{Equation 3}$$

where L is the thickness of the membrane (0.025 cm) and A is the effective membrane area (22 cm<sup>2</sup>).

### Transport number and permselectivity

Membrane samples were preconditioned by soaking them into 1M NaCl for at least 12 h before the test to reach equilibrium conditions. The transport number was determined by the membrane potential measured in a two compartment cell. Each compartment contains a fresh 0.1 M and 0.01 M NaCl solution, respectively. Both solutions were stirred and separated by a 22 cm<sup>2</sup> membrane. With two calomel reference electrodes in each solution and a voltmeter, the diffusion potential across the membrane was measured. Then, the membrane transport number ( $t_+^m$ ) was calculated as:

$$2t_+^m = \frac{\Delta E}{\frac{RT}{nF} \ln \left( \frac{\alpha_1}{\alpha_2} \right)} + 1 \quad \text{Equation 4}$$

where  $\Delta E$  is the membrane potential (V), R is the universal gas constant (8.314 J K<sup>-1</sup> mol<sup>-1</sup>), T is the temperature (K), n is the valence of the counter-ion, F is the Faraday constant (96485.3 C mol<sup>-1</sup>) and  $\alpha_1$  and  $\alpha_2$  are the mean activities of electrolytic solutions.

The permselectivity ( $P_s$ ) was calculated by equation 5:

$$P_s = \frac{t_+^m - t_+^{sol}}{1 - t_+^{sol}}$$

Equation 5

where  $t_+^{sol}$  is the solution transport number of the counter-ion in the membrane (without concentration profiles in the solution), e.g., 0.39 is the  $\text{Na}^+$  transport number for NaCl in water at 25°C.

### Contact angle

A Kruss device DSA 10-MK” (Germany) was used to measure the contact angle of each membrane. The plate method was utilized at room temperature. The reported angle for every sample was the average from at least five measurements.

### Fourier transform infrared spectroscopy (FTIR)

Dried membrane samples were analyzed by a Perkin-Elmer FTIR spectrometer (Spectrum 100) in the range from 4000 to 650  $\text{cm}^{-1}$ .

### X-Ray diffraction (XRD)

The ordering and crystallinity of dried membrane samples were evaluated with a Philips X-ray diffractometer (PW1830 model) using a  $\text{CuK}\alpha$  radiation source ( $\lambda=1.542 \text{ \AA}$ ) and a scan range ( $2\theta$ ) of 5-50° at a scan rate of 2° $\text{min}^{-1}$ . The crystalline and amorphous peaks were both integrated ( $I_c$ ,  $I_a$ ) in  $2\theta$  space using diffrac plus evaluation (EVA) software. From these integrated peak areas, the ratio  $X_c/X_a$  can be calculated by equation 6:

$$\frac{X_c}{X_a} = 1.8 \cdot \left( \frac{I_c}{I_a} \right)$$

Equation 6

A Ryland’s factor of 1.8 is commonly used for semi-crystalline polymers. The percentage of crystallinity is obtained from equation 7 [26]:

$$X_c(\%) = 100 - \frac{100}{\left(1 + \frac{X_c}{X_a}\right)}$$

Equation 7

## 2.6 Concentration assays by a electrodialysis cell

An ED lab-scale system (Berghof BEL-500) with an effective membrane area of 58  $\text{cm}^2$  was used to perform the experiments. It consisted of four synthesized cation exchange membranes (CEMs) and three commercial anion exchange membranes (AEMs) between the electrodes. A CEM was located in contact with the anode in order to prevent  $\text{Cl}_2$  production, and another one next to the cathode [27]. The synthesized membranes were cut in 11 × 11 cm pieces and perforated to fit in the ED system. The CEMs were soaked in 1 M NaCl solution, while commercial AEMs were placed in a 1 % wt NaCl solution for at least 48 h before running the experiment.



1 Three separated and recirculated circuits of 1 L volume were used: diluate, concentrate  
2 and electrode rinse solutions. The membrane stack was connected to a DC electrical  
3 potential through TiO<sub>2</sub>-coated titanium electrodes. Experiments were run during 2 h at  
4 room temperature and constant voltage. Samples were taken from the concentrate  
5 stream every 30 minutes and conductivity measurement was performed by CDM 83  
6 conductivity meter for each sample.  
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## 10 11 **2.7 Experiment design**

12 Synthetic solutions, as the feed of ED experiment, were prepared by simulating reverse  
13 osmosis brine from the desalination plant of El Prat del Llobregat in Barcelona.  
14 Concentrate and diluate solution consisted, each one, of 1.1 M NaCl, 0.02 M CaSO<sub>4</sub> and  
15 0.11 M MgSO<sub>4</sub>, while the electrode rinse solution was 0.015 M CaSO<sub>4</sub>.  
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19 All the experiments were carried out under potentiostatic conditions (PC). Firstly, S-30  
20 CEMs were tested at a constant voltage of 7 V. After that, more membranes were  
21 prepared with the same polymer blend base, but with pTSA surface polymerization.  
22 Two different voltages of 5 and 7 V were applied under PC on the ED stack to  
23 investigate the influence of voltage on the concentration, selectivity and flux of different  
24 cations through the synthesized S30-pTSA hybrid membranes. Finally, S-30 was used  
25 as base solution for the last set of experiments, but surface polymerization was carried  
26 out using valine instead of pTSA and also they were tested under PC applying constant  
27 voltage of 7 V.  
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## 35 **2.8 Cation concentration measurement**

36 Online monitoring of the solutions composition changes in ED experiments was carried  
37 out by measuring their electrical conductivity. Samples were also collected and the  
38 concentration of individual cations was determined. The sodium concentration was  
39 measured by means of an ion selective electrode (S220 Seven compact Ion/pH).  
40 Magnesium and calcium concentration were measured using an ICP-MS (Inductively  
41 coupled plasma mass spectrometry) (X Series ICP-MS, Thermo Elemental).  
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## 49 **2.9 Evaluation of the concentrate data: cation flux ( $J_{\text{cation}}$ ) and cationic selectivity** 50 **( $S_{\text{Na}}^{\text{div}}$ ).**

51 Cation flux ( $J_{\text{cation}}$ ) through the membranes was calculated from the concentration  
52 change with time ( $dC_{\text{cation}}/t$ ) in the concentrate compartment according to equation 8:  
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$$55 J_{\text{cation}} \left( \frac{\text{mol}}{\text{cm}^2 \cdot \text{s}} \right) = \frac{V}{A} \left( \frac{dC_{\text{cation}}}{t} \right) \quad \text{Equation 8}$$

1 where V is the volume (cm<sup>3</sup>) of the concentrate solution, A is the effective membrane  
2 area (cm<sup>2</sup>), C<sub>cation</sub> is the cation concentration (mol/cm<sup>3</sup>) and t is experimental time (s).  
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4 The cation selectivity ( $S_{Na}^{div}$ ) was calculated by a reference equation [17]:  
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$$6 \quad S_{Na}^{div} = \frac{t_{div}/t_{Na^+}}{C_{div}/C_{Na^+}} \quad \text{Equation 9}$$

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11 where  $t_{div}$  and  $t_{Na^+}$  are the transport numbers of bivalent cation (Mg<sup>2+</sup> or Ca<sup>2+</sup>) and  
12 sodium ions in the membrane, respectively.  $C_{div}$  and  $C_{Na^+}$  are the average  
13 concentrations (e.g., arithmetic average between the initial and final concentrations) of  
14 bivalent cations (Mg<sup>2+</sup> or Ca<sup>2+</sup>) and sodium ions during the ED, respectively. Transport  
15 numbers were estimated by the change in the concentration of Mg<sup>2+</sup> or Ca<sup>2+</sup> cations in  
16 the concentrate solution.  
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21 A low  $S_{Na}^{div}$  corresponds to a high selectivity for monovalent cations, while a high  $S_{Na}^{div}$   
22 represents a high divalent cation selectivity.  
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### 28 **3. Results and discussion**

#### 29 **3.1 Membrane chemical characterization**

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31 Figure 3 shows the spectra of S-30 composite CEM and both hybrid membranes (S30-  
32 pTSA and S30-valine).  
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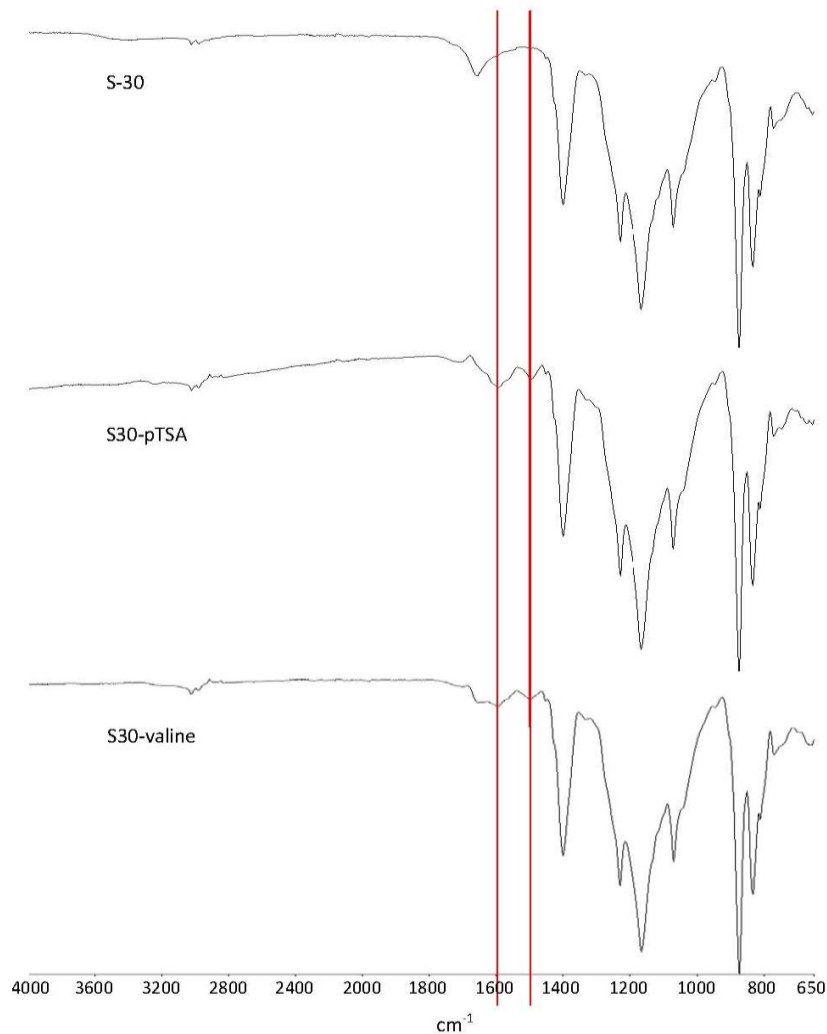


Figure 3. FTIR spectra of composite membrane (S-30) and hybrid membranes with different dopants (S30-pTSA and S30-Valine)

Most of the peaks are the same for the three membranes studied. These correspond to the base polymer solution S-PVDF/PVDF, such as the peak at  $\sim 1040 \text{ cm}^{-1}$  with indicates the S=O stretching vibration of  $\text{SO}_3^-$  group or the peak at  $\sim 1650 \text{ cm}^{-1}$  that is attributed to the stretching vibration of the C=O group of S-PVDF [16].

Otherwise, in comparison with S30 both hybrid membranes coated with PANi have two characteristics peaks. One at  $\sim 1593 \text{ cm}^{-1}$ , assigned to the C=N stretching vibration and one at  $\sim 1501 \text{ cm}^{-1}$  is assigned to the C=C stretching vibration. Both peaks prove the emeraldine structure of PANi.

### 3.2 Membrane crystallinity

X-Ray diffraction has been used to investigate crystallinity/ordering in different composite and hybrid membranes [16,28]. The XRD patterns for S-30 and both hybrid CEMs synthesized in this work are given in Figure 4.

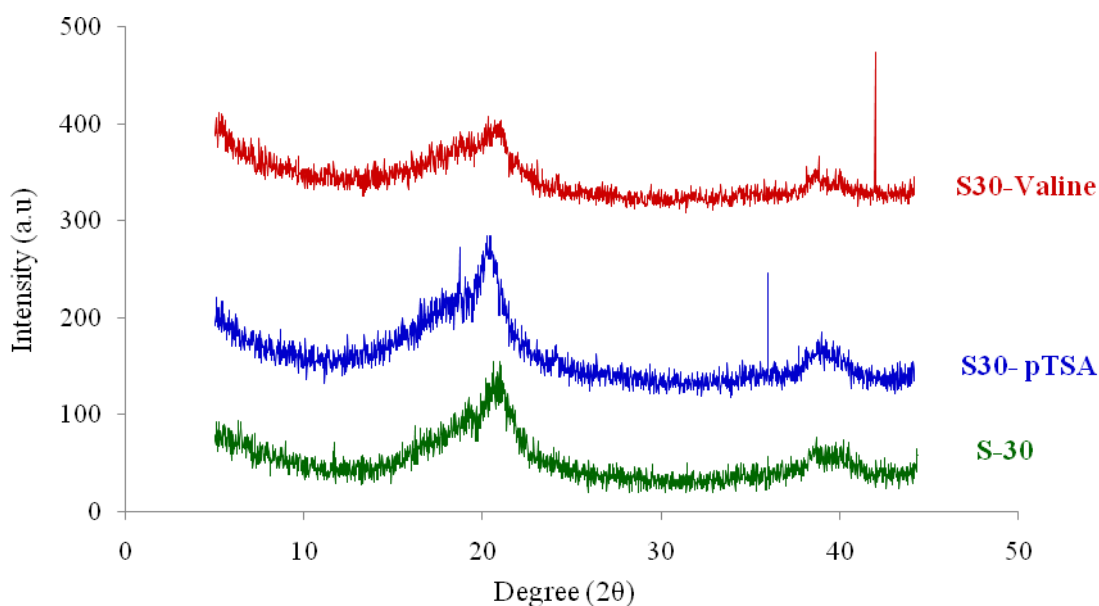


Figure 4. X-ray diffraction patterns of composite membrane (S-30) and hybrid membranes with different dopants (S30-pTSA and S30-Valine)

Different doping agents can change the XRD pattern of PANi [29,30]. As shown in Figure 4, for both of the hybrid CEMs crystalline peaks appear. This indicates that the membranes coated with PANi and doped with pTSA and valine have a more compact structure on their surface. However, S30-pTSA ( $X_c=3.8$ ) has a more crystalline and compact structure than S30-valine ( $X_c=2.4$ ). By means of the XRD patterns, it can be seen that S-30 coated with pTSA has changed its structure to a microcrystalline and more compact form, while S-30 coated with valine has also increased its ordering.

### 3.3 Electrochemical and physical properties

The electrochemical and physical properties of S-30 and hybrid CEMs such as permselectivity (Ps), IEC, IC, contact angle and water uptake are listed in Table 1.

| CEM        | Ps   | IEC (meq/g)     | IC (S/cm)        | Contact angle (°) | Water uptake (%) |
|------------|------|-----------------|------------------|-------------------|------------------|
| S-30       | 0.89 | $0.38 \pm 0.10$ | $11.36 \pm 1.05$ | $78.4 \pm 4.0$    | 4.1              |
| S30-pTSA   | 0.84 | $0.24 \pm 0.01$ | $2.27 \pm 0.51$  | $69.9 \pm 1.7$    | 5.9              |
| S30-Valine | 0.83 | $0.35 \pm 0.02$ | $1.62 \pm 0.24$  | $73.9 \pm 5.4$    | 6.3              |

Table 1. Electrochemical and physical properties of S-30, S30-pTSA and S30-valine CEMs

The permselectivity for both hybrid membranes decreased with respect to S-30. The main reason for this is the formation of a dense layer on top of the membranes, which decreases the surface charge and reduces the Donnan exclusion. For S30-valine, IEC was not substantially decreased and therefore the permselectivity was only slightly

1 reduced. For S30-pTSA, although the IEC declined more, the more compact structure  
2 increases the diffusion potential and results in a similar permselectivity as S30-valine.  
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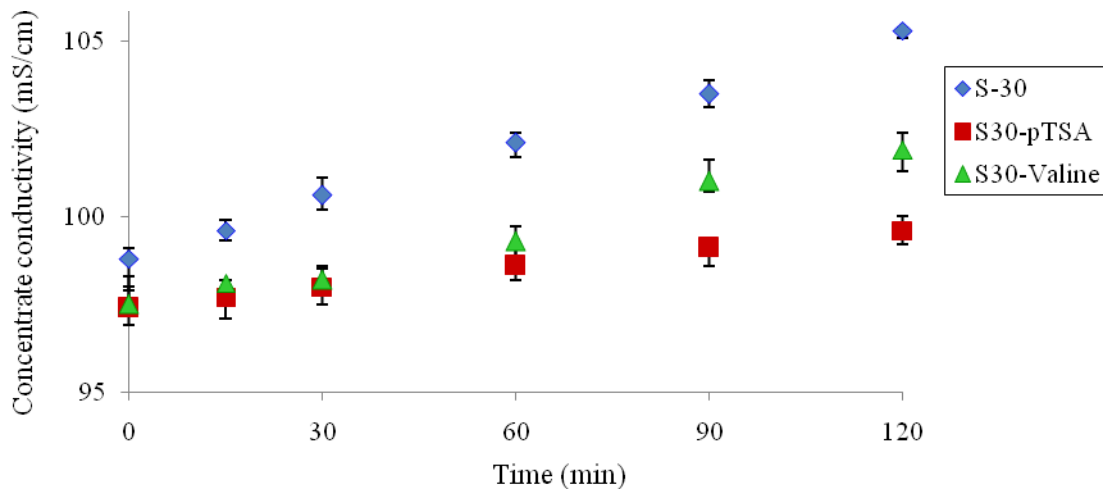
4 Moreover, the IC for the hybrid membranes declined due to the formation of a dense  
5 layer on the membrane surface with lower charge density than the matrix, which  
6 prevents the facile migration of cations through the membrane.  
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9 For the hybrid membranes made by S-30, here also after coating of S-30 CEMs with  
10 PANi, the contact angle decreased. This is due to the hydrophilic nature of PANi and  
11 the presence of amine groups in its structure. However, this decrease is very low for  
12 S30-valine. This shows that valine (as expected) keeps the hydrophobicity of the surface  
13 high. As shown in Figure 1, two terminal methyl groups in the structure of valine  
14 provide more hydrophobicity in the doped sites of PANi than pTSA.  
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18 The water uptake was slightly increased for both hybrid CEMs compared to S-30, but  
19 the total water uptake for all CEMs is low. The water uptake increase should be  
20 associated to the inclusion on the structure of the hydrophilic groups.  
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### 26 3.4 Brines concentration performance: cations flux and enrichment factors

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28 The increase in conductivity of the concentrate solution for S-30 composite CEM and  
29 hybrid CEMs (S30-pTSA and S30-valine) is presented in Figure 5.  
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50 Figure 5. Evolution of the electrical conductivity of the concentrated compartment for S-30, S30-pTSA  
51 and S30-valine CEMs by electrodialysis for a concentrated brine (1.1 M NaCl, 0.02 M CaSO<sub>4</sub> and 0.11 M  
52 MgSO<sub>4</sub>)  
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54 The enhancement in conductivity for hybrid membranes is lower than for the related  
55 composite membrane S-30. These results confirm the trend observed in the literature  
56 [16]. Farrokhzad et al. worked with S-70 CEM and after the surface polymerization by  
57 PANi-pTSA, the conductivity reduction in the diluate decreases.  
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This phenomenon may be due to the formation of a dense and compact layer of PANi-pTSA on the surface of composite membrane, which decreases the permeation of different cations through the membranes.

The concentration changes of Na<sup>+</sup> cations in the concentrate stream are presented in Figure 6, while Figure 7 shows the flux of sodium through the membranes.

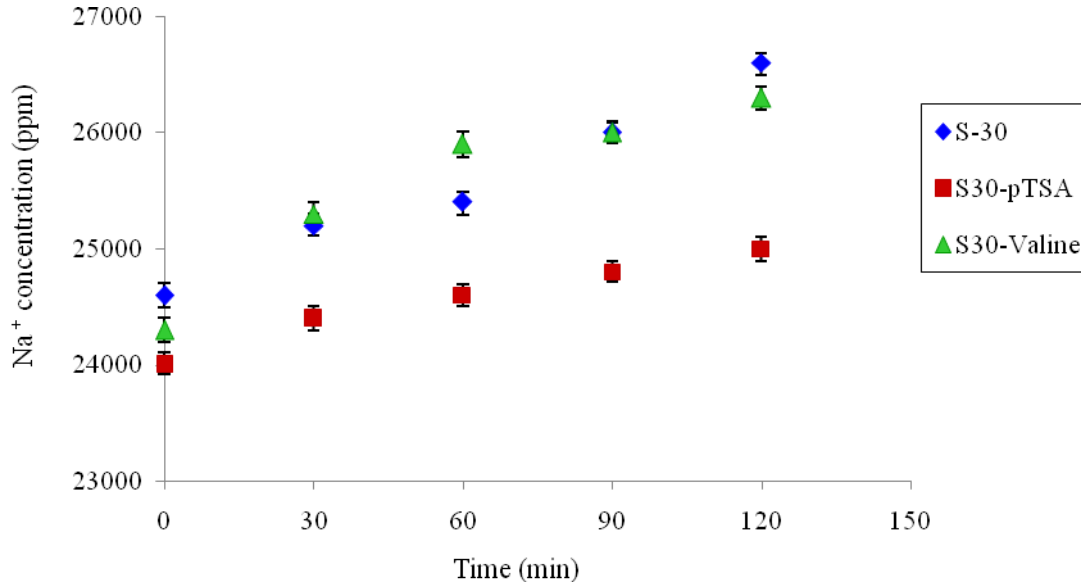


Figure 6. Time evolution of Na<sup>+</sup> in the concentrated stream for S-30, S30-pTSA and S30-valine CEMs during electro dialysis

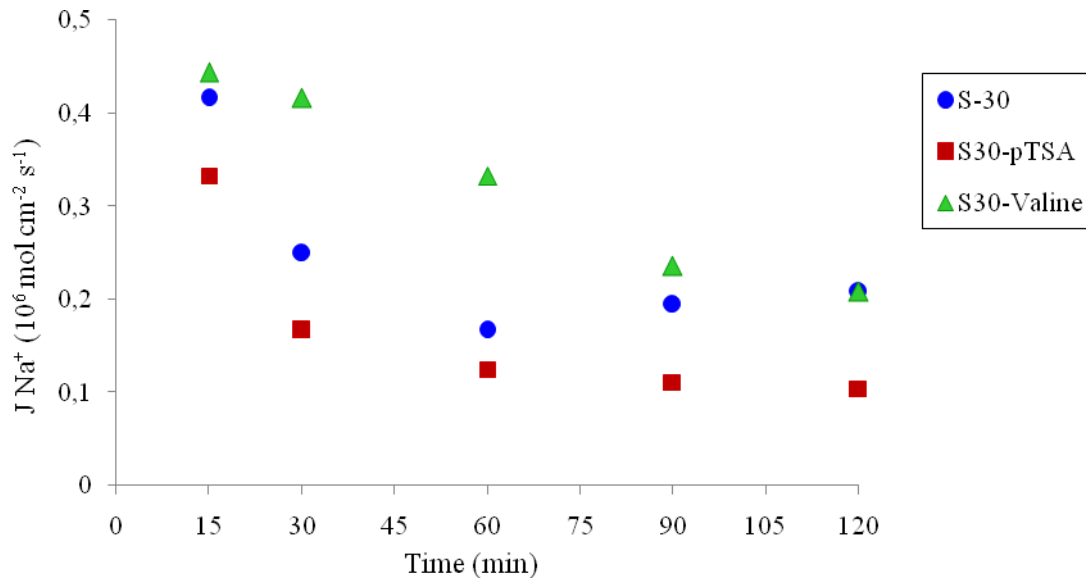


Figure 7. Time evolution of Na<sup>+</sup> flux through S-30, S30-pTSA and S30-valine CEMs (10<sup>-6</sup> mol cm<sup>-2</sup> s<sup>-1</sup>) at different times during electro dialysis

The Na<sup>+</sup> concentration values are lower for S30-pTSA compared to S-30, but it is remarkable that the sodium concentrations for S30-valine as well as for S-30 are higher. Figure 7 supports this trend, because the average flux of Na<sup>+</sup> for both S30-valine and S-

30 is higher than for S30-pTSA. The high values of  $\text{Na}^+$  concentration and flux using S30-valine membranes can be explained because of the formation of a selective barrier for sodium by doping the PANi in the surface layer with valine. These results imply that S30-valine membranes will have a very good selectivity for sodium compared to magnesium and calcium ions.

Figures 8 and 9 represent the magnesium concentration and ionic flux.

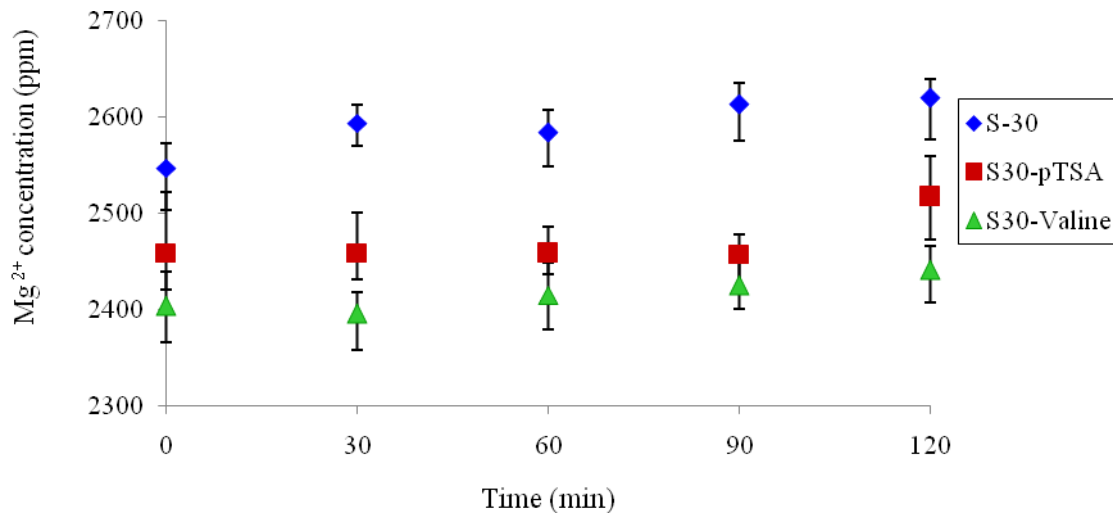


Figure 8. Concentration of  $\text{Mg}^{2+}$  cations in concentrate for S-30, S30-pTSA and S30-valine CEMs at different times of electro dialysis

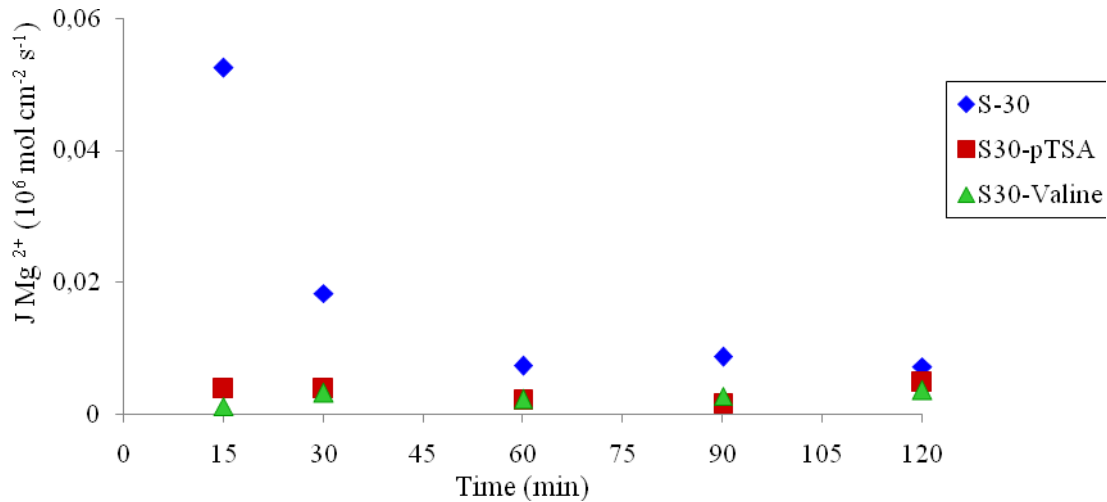


Figure 9. Partial flux of  $\text{Mg}^{2+}$  cations through S-30, S30-pTSA and S30-valine CEMs ( $10^{-6} \text{ mol cm}^{-2} \text{ s}^{-1}$ ) at different times of electro dialysis

As shown in Figure 8, the concentration of  $\text{Mg}^{2+}$  at the concentrated compartment for S-30 is slightly higher than for S30-pTSA and S30-valine. Comparing the hybrid membranes, there is no considerable change until 120 min of ED. This can be related to the flux of  $\text{Mg}^{2+}$  for the CEMs (Figure 9). Although the magnesium flux for S-30 is low, the hybrid membranes show a near to zero flux. This is a good indication for the

selective permeation of sodium compared to magnesium, which is due to the surface polymerization of PANi-pTSA and PANi-valine.

The concentration and flux of calcium for the composite and hybrid CEMs are presented in Figure 10 and Figure 11, respectively.

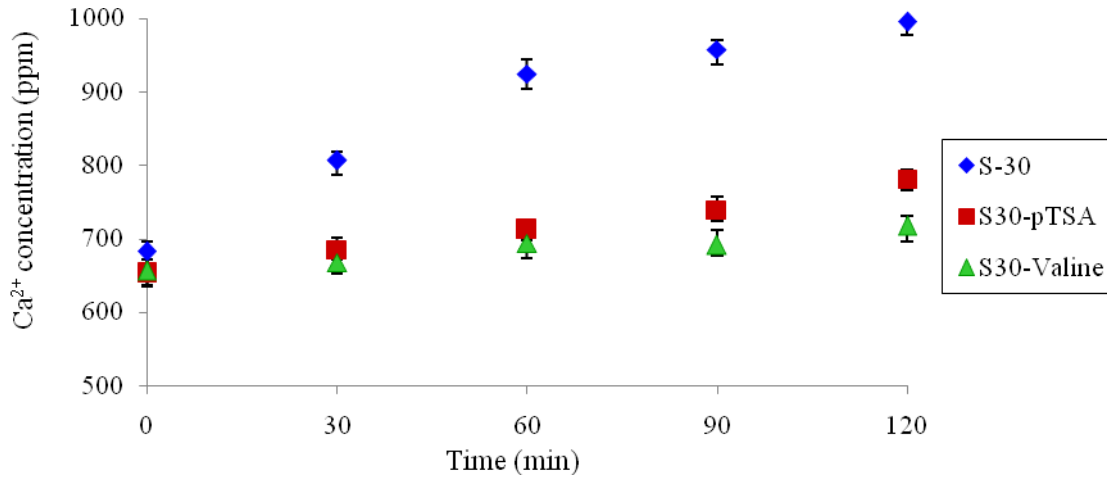


Figure 10. Concentration of Ca<sup>2+</sup> cations in concentrate for S-30, S30-pTSA and S30-valine CEMs at different times of electro dialysis

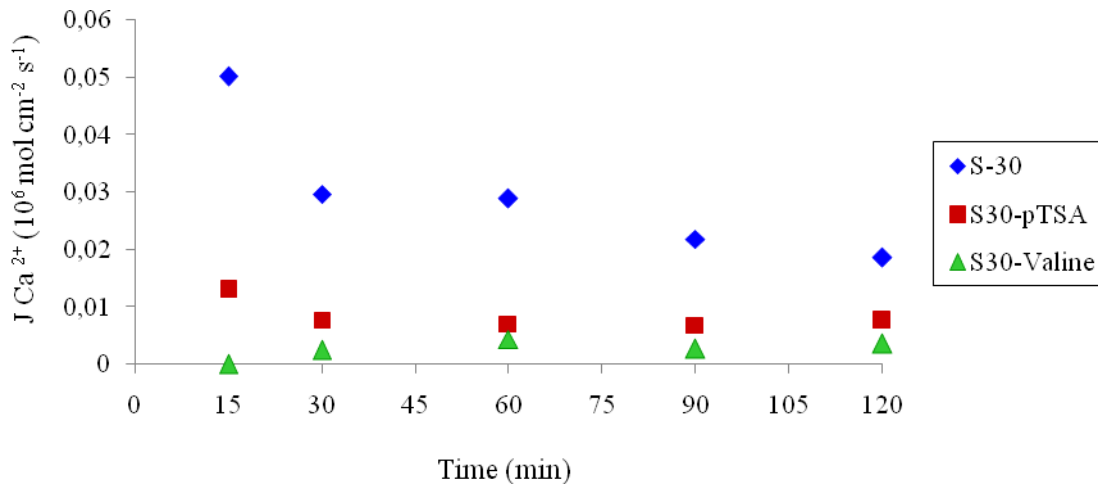


Figure 11. Partial flux of Ca<sup>2+</sup> cations through S-30, S30-pTSA and S30-valine CEMs (10<sup>-6</sup> mol cm<sup>-2</sup>s<sup>-1</sup>) at different times of electro dialysis

The Ca<sup>2+</sup> concentration increases for S-30 membranes but its increase is lower for S30-pTSA and only marginal for S30-valine. Ca<sup>2+</sup> flux was decreased for both hybrid membranes compared to S-30, and S30-valine has a lower Ca<sup>2+</sup> flux than S30-pTSA.

A general trend for three cations is that the flux decreases drastically after 30 min and does not change significantly until the end of the experiment. This phenomenon can be related to the concentration polarization near the feed side. This effect was not observed



for bivalent cations in S30-valine, since the flux of these cations was too low in these membranes.

### 3.5 Cation selectivity

The selectivities of  $Mg^{2+}$  to  $Na^+$  and  $Ca^{2+}$  to  $Na^+$  at different times of ED were evaluated. The average of the selectivities was calculated and given in Table 2.

| CEM           | S-30 | S30-pTSA | S30-valine |
|---------------|------|----------|------------|
| $S_{Na}^{Mg}$ | 0.63 | 0.13     | 0.09       |
| $S_{Na}^{Ca}$ | 6.82 | 3.59     | 0.8        |

Table 2. Average cation selectivities (S) of  $Mg^{2+}$  to  $Na^+$  and  $Ca^{2+}$  to  $Na^+$  for composite and hybrid CEMs

Both  $S_{Na}^{Mg}$  and  $S_{Na}^{Ca}$  decreased drastically after surface polymerization, thus the monovalent selectivity increased. This pattern agrees with Farrokhzad et al., who worked with the S-70 and S70-pTSA membrane, except that S-30 is sodium selective (while S-70 was magnesium selective [16]), which can be due to the more hydrophobic and compact structure of S-30 compared to S-70.

It is noticeable that S-30 gives a very high selectivity to calcium ( $S_{Na}^{Ca} = 6.82$ ). The ionic radius of  $Ca^{2+}$  is somewhat larger than that of  $Na^+$  (Table 3) and although its charge is twice as large, in an electrical field with higher voltage (i.e., 7 V), it seems to be more attracted toward the cathode than  $Na^+$  and therefore the selectivity is high.

A remarkable result in this test is that S30-valine CEM has a very good selectivity for monovalent cations compared to both bivalent cations. This membrane has a very high  $Na^+$  to  $Mg^{2+}$  selectivity and a good  $Na^+$  to  $Ca^{2+}$  selectivity as well. This is valuable because the concentration of  $Na^+$  in the concentrate and the  $Na^+$  flux will not decrease after the surface polymerization of S-30 by PANi-valine. This means that this surface layer acts as a selective barrier for sodium in a mixture of three cations.

| Cation    | Hydrated ionic radius (nm) [31] | Hydration enthalpy (kJ/mol) [32] |
|-----------|---------------------------------|----------------------------------|
| $Na^+$    | 0.36                            | 407                              |
| $Mg^{2+}$ | 0.43                            | 1921                             |
| $Ca^{2+}$ | 0.41                            | 1577                             |

Table 3. Hydrated ionic radius and hydration enthalpy of the cations studied

According to Table 3, the ionic radius of  $Na^+$  is smaller than that of  $Ca^{2+}$  and the hydrated ionic radius of  $Mg^{2+}$  is higher than that of  $Na^+$ . So, calcium and magnesium ions transport will be more sterically hindered than sodium passage [33]. The presence of a dense layer of doped PANi on top of the S-30 membrane causes that sodium diffusion is higher than bivalent cation diffusion through the membrane. For this reason, the monovalent selectivity for both hybrid membranes increased. Thus, the diffusion

theory of cations through a CEM can be applied to explain the selectivity of the membranes. Firdaous et al. [10] explains that the hydration shell is the responsible of the cations diffusion in a membrane, although the passing of solution/membrane interface requires overcoming the energy barrier caused by the necessity of partial dehydration of ions. In order to break this barrier, the hydration energy of cations is the effective parameter. Furthermore, the hydration energy of  $Mg^{2+}$  and  $Ca^{2+}$  is higher than that of  $Na^+$ . This means that by increasing the membrane hydrophobicity after surface polymerization, the diffusion of sodium increases, and therefore  $S_{Na}^{Mg}$  and  $S_{Na}^{Ca}$  decrease.

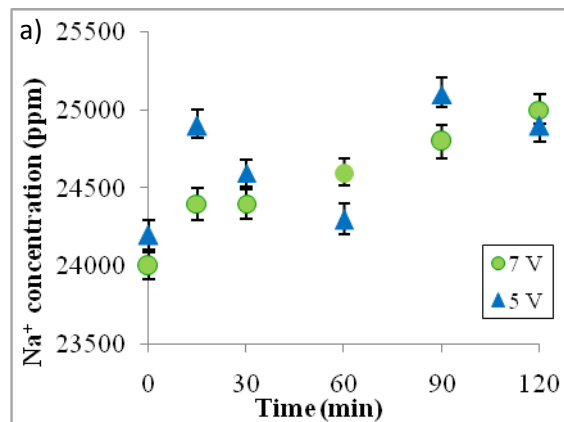
Another important parameter to explain the selectivity is the IEC. When IEC is higher, more bivalent cations will be hindered to pass through the membrane. The IEC value for S30-valine after surface modification remains high. This can be due to the good cation exchange capacity of valine. This effect can be another reason why S30-valine allows sodium to diffuse better than calcium. If the COO- group of valine acts as a cation exchange site, it can absorb bivalent cations and prevent their diffusion because of their higher positive charge.

Therefore, the surface polymerization of the S-30 membrane by PANi-valine gives a CEM with very high monovalent selectivity, which can be used for sodium concentration of SWRO brines and which can also be used in industrial applications such as the chlor-alkali industry.

### 3.6 Influence of applied voltage on ions transport behaviour

The conductivity variation using 5 and 7 V is shown in figure 12. The increase in the electrical conductivity along the experiment for both voltages was nearly the same, since the slope for both conductivity/time curves of 5 and 7 V was 0.014 and 0.0184, respectively. This shows that the change in voltage does not have a significant influence on the total salt removal.

For a more detailed evaluation of cation removal, the concentrations of different cations during the ED experiments are given in Figure 12.



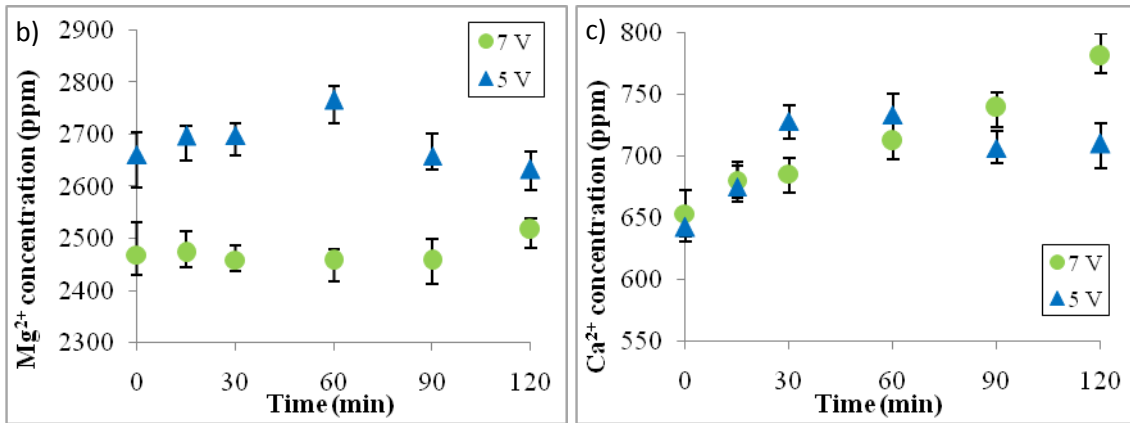


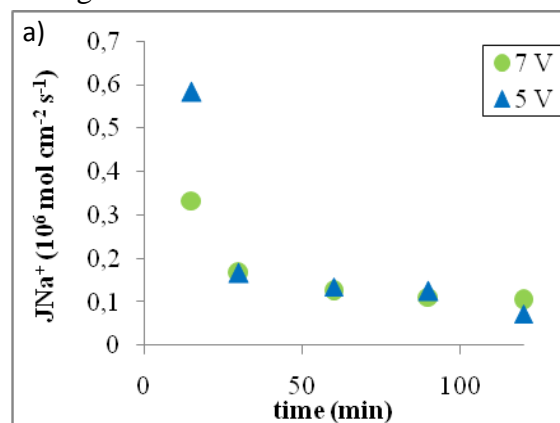
Figure 12. Concentration of a) Na<sup>+</sup>, b) Mg<sup>2+</sup>, c) Ca<sup>2+</sup> cations in concentrate for S30-pTSA CEMs in different times of electro dialysis at 5 and 7 V

Figure 12 shows that the Na<sup>+</sup> concentration increases for 7 V as well as for 5 V, but the concentration of Mg<sup>2+</sup> and the average concentration of Ca<sup>2+</sup> are lower at 7 V than at 5 V. This results in a higher monovalent selectivity for both cations in 7 V, as presented in Table 4.

|               | 5 V  | 7 V  |
|---------------|------|------|
| $S_{Na}^{Mg}$ | 0.46 | 0.13 |
| $S_{Na}^{Ca}$ | 4.01 | 3.59 |

Table 4. Average cation selectivities of Mg<sup>2+</sup> to Na<sup>+</sup> and Ca<sup>2+</sup> to Na<sup>+</sup> for S30-pTSA CEMs at 5 V and 7 V

The increase of the applied voltage leads to an increase of the monovalent selectivity. The selectivity results can be interpreted by the fluxes of different cations and their physicochemical properties. The fluxes of monovalent and bivalent cations in different voltages are presented in Figure 13.



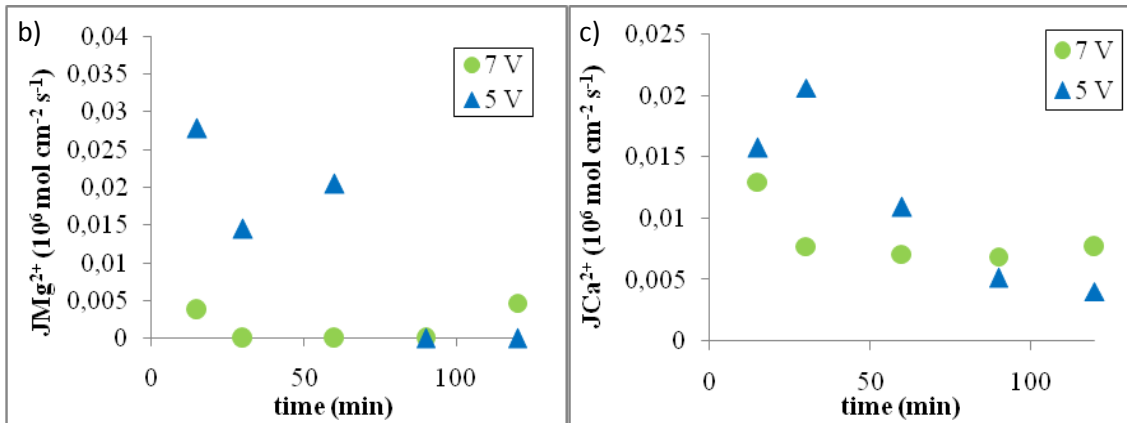


Figure 13. Partial flux of a)  $\text{Na}^+$  b)  $\text{Mg}^{2+}$  c)  $\text{Ca}^{2+}$  cations through S30-pTSA CEMs at different voltages

The fluxes of all cations are lower at higher voltage in the beginning. This can be explained by the concentration polarization phenomenon and the consequent repulsion between the cations at the interface of membrane and salt solution. By increasing the voltage, a very strong local electric field is created, which may promote the repulsion of cations near to membrane surface region and decrease their diffusion in the membrane [34]. This effect is less pronounced at lower voltage and therefore the initial fluxes are higher for 5 V.

Although the primary flux of bivalent cations at 5 V is higher than at 7 V, the fluxes drop down after 90 min, while the fluxes for 7 V remains constant after 30 min (or even increase). This can be due to the more powerful attraction of cations by the cathode at higher voltage. Therefore, the monovalent selectivity increases by increasing the applied voltage.

#### 4. Conclusions

Novel hybrid cation exchange membranes were synthesized by surface polymerization of polyaniline (PANi) on S-PVDF/PVDF composite membranes with different doping agents. FTIR proved the formation of a PANi layer on the membrane surface, leading to a change in functional groups. XRD showed that after surface polymerization, the hybrid membrane structure becomes more ordered than that of the composite membrane, especially for pTSA doping agent. The combination of structure information with other membrane properties such as water uptake, IEC and permselectivity helped to determine the relation between membrane properties and ED performance.

To synthesize a membrane with excellent sodium selectivity among the mixture of three cations in the solution ( $\text{Na}^+$ ,  $\text{Mg}^{2+}$  and  $\text{Ca}^{2+}$ ) for the concentration of SWRO brine as feed for the chlor-alkali process, S-30 was selected to be modified by PANi surface polymerization. These membranes were doped with pTSA and valine and the results showed that for both doping agents the selectivity of sodium will increase. A

1 remarkable result was achieved for S30-valine, which showed a very good selectivity  
2 for monovalent ions compared to both bivalent cations. This membrane had a very high  
3  $\text{Na}^+$  to  $\text{Mg}^{2+}$  selectivity and also good  $\text{Na}^+$  to  $\text{Ca}^{2+}$  selectivity. This is valuable because  
4 the surface polymerization of S-30 by PANi-valine did not decrease the concentration of  
5  $\text{Na}^+$  in the concentrate and kept the flux of  $\text{Na}^+$  as high as S-30. Valine is an amino acid  
6 that can keep the surface hydrophobicity as well as membrane IEC high and provide a  
7 selective barrier for  $\text{Na}^+$  because of its special chemical structure after doping on coated  
8 PANi.  
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12 The influence of the applied voltage was also evaluated on hybrid membranes; it was  
13 found that by increasing the voltage from 5 V to 7 V, the monovalent cations selectivity  
14 increases. This result can be explained by the lower flux of bivalent cations at 7 V  
15 which is due to more powerful attraction of cations by the cathode at higher voltage.  
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