



# Removal of divalent ions from viscous polymer-flooding produced water and seawater via electro dialysis



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## ABSTRACT

The presence of multivalent ions in polymer-flooding produced water (PPFW) hampers its recycling mainly because i) they increase the risk of scaling and reservoir souring (sulfate), ii) they interfere with the viscosifying effect of the fresh polyelectrolyte. It is desirable to achieve the removal of most multivalent ions without completely desalting the stream. With the adequate process conditions, electro dialysis could help to achieve this goal, so this work focused on evaluating the removal of divalent ions from synthetic PPFW through varying operational conditions. The experimental work consisted on batch experiments run in an electro dialysis-stack composed of strong Neosepta ion-exchange membranes. Synthetic PPFW solutions containing a mixture of monovalent and divalent ions were desalted at four different current densities, and three different temperatures. Additionally, the effect of the dissolved polymer on the removal was assessed by performing half of the experiments on polymer-containing solutions and half of them on solutions without it. Our results demonstrate that it is possible to achieve preferential removal of divalent cations (calcium and magnesium) through electro dialysis, especially when employing low current densities ( $24 \text{ A/m}^2$ ) and high temperature ( $40^\circ \text{C}$ ). The removal of sulfate, a divalent anion, is also accelerated in these conditions. The presence of polyelectrolyte did not significantly affect the removal rate of divalent ions. Thus, it is concluded that meticulous application of ED to minimize concentrations of divalent ions in PPFW is a potential effective way for water and polymer recycling in enhanced oil recovery situations, as an alternative to the use of other non-selective desalination technologies.

## 1. Introduction

Electro dialysis was first applied at industrial scale to desalinate brackish water, more than 50 years ago [1]. Driven by the need of producing sodium chloride from concentrated sea water, Japanese scientists developed a few years later ion exchange membranes with permselectivity for monovalent ions [2], which eventually enabled electro dialysis to be applied in various new fields [3,4]. However, a similar selective process only allowing passage of multivalent ions seems more difficult to achieve: yet no membranes with permselectivity for multivalent ions are reported. Alternatively, some investigations have suggested that at adequate process conditions, electro dialysis can be used to preferentially remove multivalent ionic species from a stream [5–7]. This is especially of practical and economic importance for treating and reusing waters produced by enhanced oil recovery and in particular from polymer flooding, as later detailed. Therefore, this article is focused on achieving preferential multivalent ion removal

from saline water containing significant polymer concentrations.

Polymer flooding is a chemical enhanced oil recovery (cEOR) method that consists on the injection of large amounts of aqueous viscous solutions to increase the oil recovery from existing oilfields [8]. Given the increasing energy and oil demand together with the difficulty to find new oil fields, the technology has re-emerged and it is currently applied in numerous projects around the world [9,10]. However, two constraints still limit the use of polymer flooding and cEOR in general: little water accessibility and/or restrictions for the disposal of the produced water (water recovered together with the oil). Both restraints could be overcome when the water can be reused in a closed loop [11], for which it must be treated. A process for reusing produced water usually consist on primary and secondary treatments that strip it of the excess of dissolved oil, and subsequent tertiary (or polishing) steps [12], often designed to reduce the salinity and hardness of the produced water [13]. For the specific case of reusing produced water to prepare polymer flooding solution, the desalination step appears to be desirable

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for technical, economic, and environmental reasons. This is because polymer flooding solution is usually brought to adequate viscosity by adding high molecular weight polyelectrolytes, like partially hydrolyzed polyacrylamide (HPAM) and its derivatives. Its viscosity enhancing effect is extremely sensitive to the salinity of the water in which they are dissolved. Thus, when low salinity water is employed, less polymer is required to reach the design viscosity [14], and thus both the operational costs and the environmental impact of the produced streams are reduced.

Nevertheless, not all salt ions are equally disadvantageous for the preparation of a viscous polyelectrolyte solution (see Fig. A1 in the supplementary material). The viscid properties of HPAM solutions are significantly affected by the presence of multivalent cations [15–19], being calcium and magnesium (hardness), the most common ones. Solutions intended for cEOR applications must contain as less sulfate as possible to minimize the risk of reservoir souring problems and the deposition of scaling [14,20,21]. Since polymer flooding solution should not be prepared with wholly desalted water [14], partial desalination of the produced water stream with preferential removal of divalent ions would make the water fit for reuse in the make-up of viscous flooding solution to be injected into the subsurface.

Compared to other options available to desalinate produced water (like thermal and pressure-based membrane treatments) [12,22–24], electro dialysis offers two main advantages: 1) the desalination target can be easily adjusted; and 2) since only ions are removed, the remnant polymer in the desalted solution contributes to attain the viscosity needed, i.e. savings on fresh polymer additions [25]. Moreover, it has been reported that through varying operation parameters, like current density and flowrate, preferential removal of a number of ionic species can be achieved [5,26]. Thus, electro dialysis could be employed to desalinate water generated from polymer flooding applications – better referred as polymer-flooding produced water (PFPW) –, to enable its reuse. The first step would be to select the adequate type of membranes and process parameters.

### 1.1. Factors affecting permselectivity for specific ions: affinity, differences in migration speed, and process conditions

The core of an electro dialysis assembly are the ion-exchange membranes (IEMs), which selectively allow the passage of oppositely charged ions (counter-ions), while obstructing similarly charged ions (co-ions). However, for PFPW desalination and other applications, it is also desirable to have permselectivity between counter-ions of different valence [4], like  $\text{Na}^+$  and  $\text{Ca}^{2+}$ . The topic has been investigated by Sata [2], who found that the permselectivity for specific ions in ion exchange membranes is only governed by the affinity of the ions to the membrane (ion exchange equilibrium constant) and the differences in the migration speed of the ions in the membrane phase. However, this affirmation is conditioned to the elimination of the effect of the diffusion boundary layer, which is usually not realistic. Hence, the transport of counter-ions also depends on the operational conditions, explicitly, on the current density and fluid dynamics. These parameters directly influence the concentration polarization phenomena, controlling the formation of diffusion boundary layers close to the membrane, and thus affect its selectivity [4,27,28]. This and most findings regarding the selectivity of monopolar membranes can be found in a recent review by Luo et al. [4], so we limited our literature overview to the most relevant cases for the application.

Most studies related to competitive ion transport have been focused on the cation exchange membranes (CEMs). According to Kim et al., the competitive transport is governed mainly by two factors: the CEM selectivity and the boundary layer thickness [29]. While studying the separation of  $\text{K}^+$  and  $\text{Ca}^{2+}$ , they observed an increase in the transport number of  $\text{K}^+$  ions with an increase in current density (or cell pair potential drop). They concluded that despite the CEM has a higher affinity towards  $\text{Ca}^{2+}$  due to the greater ionic charge, the boundary layer

facilitates a higher  $\text{K}^+$  transport number due to its higher diffusivity. Zabolotsky et al. also had calculated that as a consequence of boundary layer development, the transport number of  $\text{Ca}^{2+}$  ions decreased if the current density was increased [30]. Thus, both studies coincide that divalent transport number is increased with lower current densities, when the boundary layers are less pronounced. Later, Galama et al. desalinated synthetic seawater and found that indeed the application of low current densities enhanced the transport numbers of both, divalent cations and divalent anions [5]. Other authors have also reported enhanced transport numbers of divalent cations by applying lower current densities [7] and temperature gradients [6].

However, most of the publications on competitive transport utilized aqueous solutions with diverse salts, in absence of other components. In case charged polymers are added, i.e. residual polymers in produced EOR waters, it is unclear how these would affect the processes in the boundary layers and thereby the permselectivities of salt ions.

### 1.2. Potential effects of polymer presence in selectivity

The presence of polymer may affect the transport of ions due to three main reasons. Firstly, it may alter the removal of all ions in general because it affects the macroscopic viscosity of the solution, which directly influences the attained turbulence of the fluid, concentration polarization, and thickness of the diffusion boundary layers [6,31].

Then, considering that the most common viscosifying polymer is HPAM, its presence in solution could affect the effective diffusion coefficient of ions, particularly of cations. The charged segments of the anionic polyelectrolyte may interact with the diffusing ions and give rise to some retardation of the diffusivity. Furthermore, there is a known affinity between the divalent cations and HPAM [32,33], and it has been described how  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  can interact with the acrylic anion in a polyacrylamide derivative [34]. If these cations remain bound to the polymer instead of being free in solution, they may stay longer in the diluate.

The presence of HPAM could also trigger some differences in the removal rate of anions, in this case due to the adsorption and concentration polarization of negatively charged HPAM on the surface of the AEM [35,36], as represented in Fig. 1. It has been reported that the adsorption of an anionic polyelectrolyte on the surface of strongly basic AEMs can decrease the transport number of  $\text{SO}_4^{2-}$  relative to that of  $\text{Cl}^-$  due to stronger electrostatic repulsion between the anionic surface layer and the  $\text{SO}_4^{2-}$  ions [37]. Concentration polarization is enhanced because the HPAM molecules tend to move towards the anode under the influence of the electric field [36], creating a gel layer that might hinder the transport of (certain) ions.

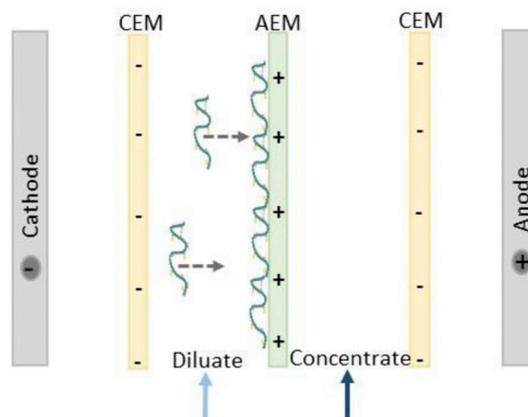


Fig. 1. Representation of the adsorption of HPAM to the AEM during the desalination process.

### 1.3. Objectives

The objective of this work was to achieve and evaluate the preferential removal of divalent ions from synthetic PFPW through varying operational conditions, namely current density and temperature. It must be emphasized that the selection of this last variable followed two main reasons: 1) the temperature of PFPW is highly dependent on the location where the EOR process is carried out [38], and 2) its variation can influence the results of an electro dialysis run in several ways, because many relevant parameters (including the diffusion coefficients of ions, the viscosity of the fluids, and the membrane properties) are temperature dependent [6,39,40].

Additionally, the effect of the dissolved polymer on the removal was assessed by performing half of the experiments on polymer-containing solutions and half of them on solutions without polymer. The effect of achieving preferential removal of divalent ions over the monovalent ones was assessed by measuring the viscosity attained when a fixed amount of fresh polymer is added to prepare viscous polymer solution from the desalinated water.

## 2. Materials and methods

### 2.1. Materials

#### 2.1.1. Electrodialysis setup

Experiments were performed in an ED stack and setup like the one previously described [25]. The stack contained five repeating cells, each consisting of a cation exchange membrane (Neosepta CMX) and an anion exchange membrane (Neosepta AMX), both from Tokuyama Co. (Japan). This membrane pair has been characterized elsewhere [41]. The working area of the membranes was 104 cm<sup>2</sup>. An additional CEM was placed at the beginning of the stack to close the first cell. The intermembrane distance was fixed by using woven ETFE fabric spacers (Fluortex 09-590/47, Sefar, Switzerland), with reported thickness of 485 μm. Gaskets made of silicone rubber with a thickness similar to the spacer thickness were used to seal all the compartments and to form the alternated flow channels for the diluate and the concentrate. On both sides of the stack, squared titanium electrodes (mesh 1.7, area 96.04 cm<sup>2</sup>) with a mixed metal oxide coating of Ru/Ir (Magnetospecial Anodes BV, The Netherlands) were employed as cathode and anode. The stack was closed with plates made of PMMA (poly(methyl methacrylate)) and 8 bolts.

A potentiostat/galvanostat (Ivium Technologies, The Netherlands) was employed to control electrical current and to measure the potential difference. The potential difference over the membrane stack was measured using two reference Ag/AgCl gel electrodes (QM711X, QIS, The Netherlands) placed at the inlet of each electrode compartment. Conductivities of the diluate and concentrate were measured inline with two conductivity probes (Orion DuraProbe 4-electrode conductivity cell 013005MD) directly before the ED stack. The probes were connected to a dedicated transmitter box (Orion Versastar Pro), which corrected the measured values to the reference value at 25 °C, and this last to a computer, where conductivity data was recorded. pH of the diluate and concentrate were also measured inline with two pH probes (MemoSENS Endress + Hauser, pH range 1–12), connected through a transmitter box (P862, QIS) with a data logger (Memograph M RSG30, Endress + Hauser).

The solutions were pumped through the stack by using peristaltic pumps (Cole-Parmer, Masterflex L/S Digital drive, USA). Temperature control during the experiments was achieved by employing 1.0 L glass jacketed vessels to store the diluate and concentrate solutions. On the external part of the vessels, water coming from a temperature-controlling recirculation bath was circulated. The electrolyte was also kept at the working temperature by means of a second temperature control bath.

**Table 1**

Measured mineral composition of diluate solutions. Prepared according to values reported in Refs. [25,42].

Cations	C (mM)	Anions	C (mM)
Na <sup>+</sup>	425.08	Cl <sup>-</sup>	482.95
K <sup>+</sup>	8.54	HCO <sub>3</sub> <sup>-</sup>	6.36
Ca <sup>2+</sup>	8.74	SO <sub>4</sub> <sup>2-</sup>	32.57
Mg <sup>2+</sup>	38.82		

#### 2.1.2. Solutions

The diluate consisted of salt solutions with an initial composition specified in Table 1 (TDS~32,000 mg/L), plus 1.0g/L of commercial HPAM. To prepare the synthetic PFPW, 500 mL of previously prepared salt solution were poured in a glass bottle containing a magnetic stirrer. Next, 500 mg of commercial HPAM (MW = 5–8 million Da, 30% hydrolyzed) were slowly poured in the vortex formed in the salt solution stirred at 600 rpm. Once all the polymer was added, the stirring rate was reduced to 200 rpm and the bottle was closed. Each polymer solution was mixed overnight to assure complete hydration and employed within 72 h of its preparation.

For comparative purposes, ED runs without any added polymer (using as diluate the salt solution described in Table 1) were also performed. In all experiments, the initial concentrate consisted on solutions containing 5.0 g/L of sodium chloride. For the electrolyte compartments, solutions of 20 g/L sodium sulfate were circulated.

Additional solutions were prepared with each of the salts and 1.0 g/L of high molecular weight HPAM (MW = 20 million Da, 30% hydrolyzed) to characterize their influence on the viscosity of the flooding solution.

Analytical grade salts (NaCl, CaCl<sub>2</sub>·2H<sub>2</sub>O, MgCl<sub>2</sub>·6H<sub>2</sub>O, NaHCO<sub>3</sub>, KCl, and Na<sub>2</sub>SO<sub>4</sub>) were purchased from VWR and employed without further purification. The HPAM employed were Flopaam 3230S (MW = 5–8 million Da, 30% hydrolyzed) and Flopaam 3630S (MW = 20 million Da, 30% hydrolyzed), both kindly provided by SNF (France). All the solutions were prepared with demi water.

### 2.2. Methods

#### 2.2.1. Electrodialysis runs

ED experiments were carried out in a batch operation mode at fixed working temperatures (10, 20, and 40 °C). The diluate and concentrate containing vessels were pre-conditioned to the desired temperature by circulating through their heating jacket water from the temperature-controlling bath. Later, 500 mL of the diluate and concentrate solutions were poured in their corresponding vessels. The electrode rinse solution (2.0 L of sodium sulfate 20 g/L) was also conditioned to the experiment working temperature by immersing the container in a second temperature-controlling bath. The concentrate and the diluate were recirculated through the corresponding compartments of the ED stack at a flow rate of 120 mL/min (linear velocity of 1.03 cm/s), while the electrode solution was recirculated at a flow rate of 100 mL/min. The solutions were circulated in their correspondent circuits during 10 min before starting the experiment, allowing them to stabilize at the desired working temperature.

The experiments were run in constant current mode, with current densities values ranging 24–96 A/m<sup>2</sup>, and switched to constant voltage mode when the limit value of the potentiostat of 8.8 V was reached. All experiments were stopped when the diluate's conductivity dropped to 1.0 mS/cm. During the experiments, stack voltage, electric current, pH, conductivity and the mass of the diluate were monitored. Samples of 1.0 mL were taken periodically from the diluate and concentrate reservoirs.

After each experiment with HPAM involved, the membrane stack was cleaned in-place. The procedure consisted in pumping a series of

solutions in both the diluate and the concentrate compartments, each solution for a period of 10 min. The sequence of solutions was: sodium chloride solution (5 g/L), sodium hydroxide solution (0.1 M), fresh sodium chloride solution (5 g/L), hydrochloric acid solution (0.1 M), and finally fresh sodium chloride solution (5 g/L). This last solution would remain in the stack until a new experiment was performed.

All the experiments were performed at least in duplicate, and the results shown are the average of the values obtained for each case.

### 2.2.2. Viscosity measurements

The dynamic viscosities of the polymer solutions were measured with an Anton Paar MCR 102 rheometer, with the standard measuring system CC27/T200/SS (bob and cup configuration). The measurements were performed at constant shear rate, from 1.0 to 100 s<sup>-1</sup>, at a controlled temperature of 40 °C.

### 2.2.3. Charge density

The charge density of Flopaam 3230S was determined by colloid titration using a Mutek Particle Charge Detector (PCD03), as described elsewhere [43]. In brief, a 0.1 g/L polymer solution was prepared in MiliQ water (section 2.1.2) and later diluted to obtain a concentration of 1 mg/L. Then, a 10 mL sample with unadjusted pH (~6.5) was titrated against a complexing agent of opposite charge (0.01 M polydiallyldimethylammonium chloride, pDADMAC), using an automatic titrator (Metrohm titrando 888). To perform the titration, the titrant was added in steps of 0.02 mL to the PCD measuring cell, while simultaneously recording the streaming potentials (mV). The specific charge quantity was then determined based on the titrant consumption in mL.

### 2.2.4. Analytical methods

Samples taken during the ED runs were analyzed to determine their cation and anion content. Cations (Na<sup>+</sup>, K<sup>+</sup>, Ca<sup>2+</sup>, Mg<sup>2+</sup>) were measured by inductive-coupled plasma optical emission spectroscopy (ICP-OES, Optima 5300DV, PerkinElmer) and anions (Cl<sup>-</sup> and SO<sub>4</sub><sup>-</sup>) by ion chromatography (IC, 761 CompactC, Metrohm). For the runs with HPAM involved, both diluate and concentrate samples were analyzed for total carbon (TC) and total organic carbon (TOC) using a TOC analyzer (Shimadzu TOC-VCPH). The total dissolved solids (TDS) content of each sample was calculated by adding the obtained concentrations of cations and anions.

### 2.2.5. Evaluation of permselectivity

The ion selectivity between divalent and monovalent ions of the same sign was quantified in terms of the ratio  $P_{monov}^{div}$ , which is defined as [4,44]:

$$P_{monov}^{div} = \frac{t_{div}/t_{monov}}{C_{div}/C_{monov}} \quad 1$$

where  $t$  represents the transport number of either divalent (*div*) or monovalent (*monov*) ions (-), and  $C$  their concentrations in the diluted compartment (eq/m<sup>3</sup>). The transport number  $t$  is defined as [44]:

$$t_k = J_k / \sum [J_s] \quad 2$$

where  $J_k$  denotes the ion flux (eq/m<sup>2</sup>h) of ion or group or ions  $k$  and  $\sum [J_s]$  is the total ion flux. In order to focus on the monovalent vs divalent effect, a single transport number  $t$  and concentration  $C$  were calculated for monovalent cations (comprising Na<sup>+</sup> + K<sup>+</sup>) and another for divalent cations (Ca<sup>2+</sup> + Mg<sup>2+</sup>). Ion fluxes were obtained from the ion concentration time courses in the diluted compartment during each experiment.

## 3. Results and discussion

### 3.1. General electro dialysis performance

ED experiments were carried out at three different temperatures: 10, 20 and 40 °C, and four different current densities: 24, 48, 72, and 96 A/m<sup>2</sup>. The initial conductivity of the solutions circulating in the diluate circuit was, on average, 49.7 mS/cm when only salts were present, and 49.1 mS/cm when 1.0 g/L of HPAM was dissolved in the solution. The corrected conductivities (section 2.1.1) did not show any significant variation for experiments running at different temperatures. Experiments running at a lower temperature had longer durations than the ones running at higher temperatures due to an earlier reaching of the limiting potential of 8.8 V and the consequent switching to the constant voltage mode. Detailed information is provided in Table A1.

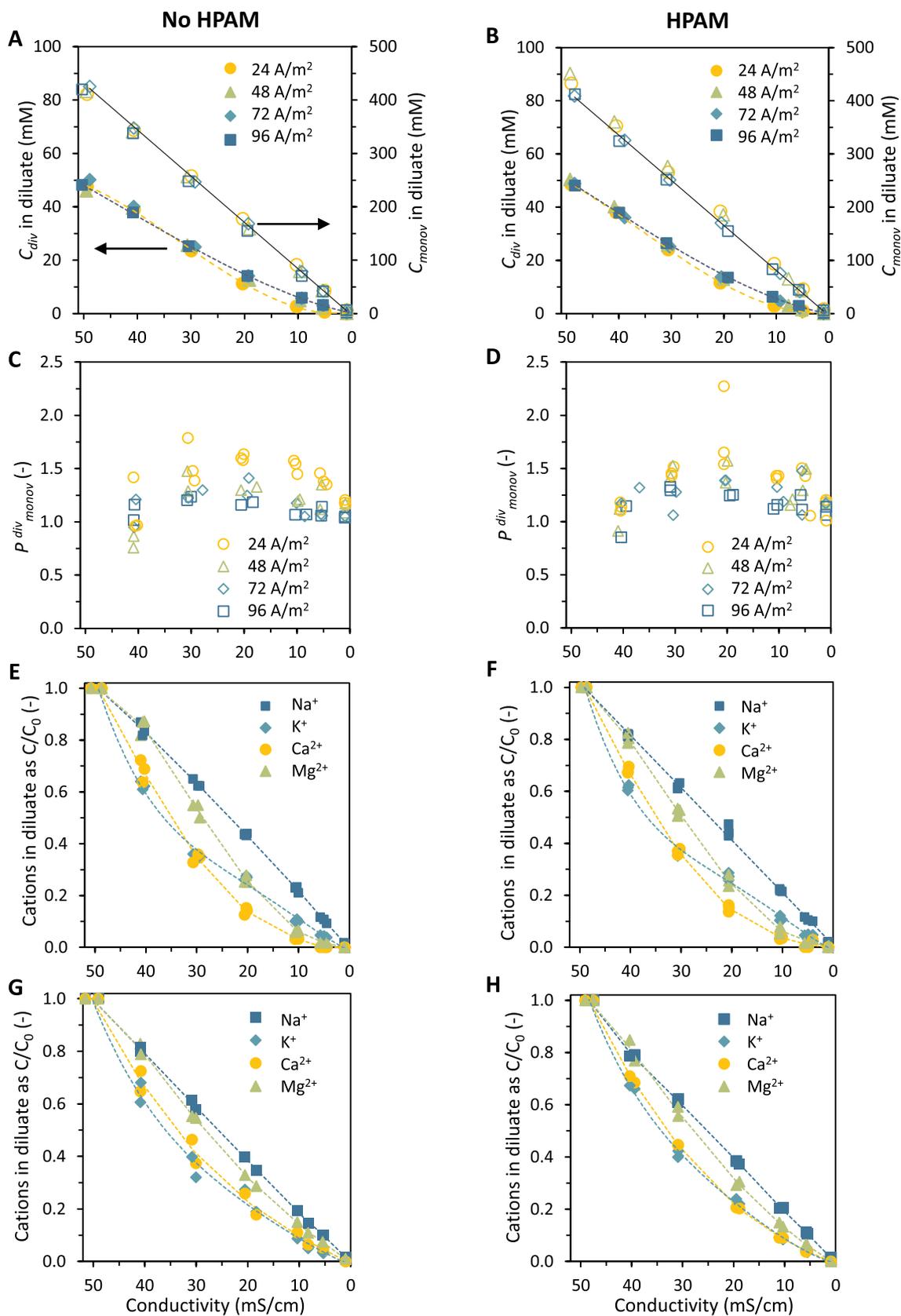
The amount of TDS at different moments of the process was calculated by adding the measured concentrations of cations and anions from the samples taken (section 2.2.4). By plotting the TDS values against the diluate's conductivity, a constant linear relationship between these two parameters was confirmed, regardless of the different experimental conditions e.g. temperature and polymer presence (Figure A2 in the supplementary material). This is emphasized because later in the document comparisons are made for samples taken at analogous moments based on the conductivity in the diluate. Thus, these comparisons will not only refer to samples taken at same conductivity, but also at similar TDS content.

### 3.2. Removal of cations

The CEM used in this study, Neosepta CMX, is a strong membrane with fixed sulfonic groups. For this type of membranes, a general transport order has been recently described as: Ca<sup>2+</sup> > Mg<sup>2+</sup> > K<sup>+</sup> > Na<sup>+</sup> regarding the cations presently involved [4]. Additionally, the reported permeability of sodium over calcium ( $P_{Ca^{2+}}^{Na^{+}}$ ) for the mentioned membrane is 0.64 (measured at 150 A/m<sup>2</sup> for a equimolar solution of both ions) [45]. At these conditions, the membrane is intrinsically more selective towards calcium, or in other words, it will permit the preferential removal of the divalent cations, presuming operational conditions allow the minimization of the effects of the boundary layers.

#### 3.2.1. Effect of current density on the removal of cations

The results concerning ion removal at 20 °C in absence of polymer are first discussed to facilitate the linking to the literature. Plot A on Fig. 2 shows the measured decrease of divalent cations ( $C_{div}$ , mM) and monovalent cations ( $C_{monov}$ , mM) versus the extent of desalination (presented as decreasing conductivity of the diluate), for the experiments performed on seawater at different current densities. Firstly, it must be noticed that the cation concentration decrease is linear for monovalent and slightly curved for divalent ions. Additionally, the curvature is more pronounced for experiments ran at lower current densities. The curves indicate a faster decrease in ion diluate concentration for the divalent cations compared to that of the monovalent ones. This can be better visualized in plot C of the same figure, which shows the permeability of divalent over monovalent cations, calculated as described in section 2.2.5. Most of the obtained values are above 1, indicating preferential removal of divalent over monovalent cations. Indeed, the average value is 1.3, which is close to the value reported by Ref. [45]. In addition, it is possible to distinguish some differences in transport behavior depending on the applied current densities. While the experiments performed at 96 A/m<sup>2</sup> maintain an almost constant permeability during their entire duration, the values calculated for the runs carried on at 24 A/m<sup>2</sup> change during the desalination, peaking between 30 and 20 mS/cm. This variation in permeability suggests that the transport of ions is governed by different processes during the



**Fig. 2.** Experiments performed at 20 °C. **A, B)** Concentration of  $\text{Ca}^{2+} + \text{Mg}^{2+}$  ( $C_{div}$ , mM) (filled symbols) and  $\text{Na}^+ + \text{K}^+$  ( $C_{monov}$ , mM) (open symbols) vs conductivity in the diluate during the electrodesialysis at different current densities and 20 °C. Continuous lines are presented to guide the eye. **C, D)** Permeability of divalent over monovalent cations (Eq. (1)) vs conductivity in the diluate. **E, F)** Normalized concentrations of cations remaining in the diluate for experiments performed at 24 A/m<sup>2</sup>, and **G, H)** 96 A/m<sup>2</sup>. For **E, F, G,** and **H)** the results of individual experiments are shown with the markers, while the trend lines indicate the median values of the measurements. **A, C, E,** and **G)** refer to experiments without HPAM, while **B, D, F,** and **H)** to experiments with HPAM.

desalination, as will be further analyzed.

A further analysis of the transport of each cation for the two extreme current density cases is presented in plots E and G of Fig. 2. The different profiles obtained in plots E and G, show the effect of the applied current density on the transport of cations, which is noteworthy for  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$ , and in less obvious for  $\text{Na}^+$ . This can be explained considering that at low current densities the competitive transport is governed by the CEM selectivity, which prefers  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  over the monovalent ions [5,6,45,46]. On contrary, for higher current densities, the diffusion boundary layer becomes thicker [47] becoming the rate-limiting region [29], favoring the transport of monovalent cations due to their smaller hydrated size and faster diffusion rates. The exception is the  $\text{K}^+$  profile, independent of the applied current density, which is in line with its high mobility/diffusivity, i.e. the boundary layer was not a limiting factor to the transport of this ion. The observed divalent ion transport order [ $\text{Ca}^{2+} > \text{Mg}^{2+} > \text{Na}^+$ ] is in agreement with the ion-exchange and selectivity hierarchies reported in the literature [4]. Actually, a previous study [40] already reported a selectivity reversal for the [ $\text{K}^+/\text{Ca}^{2+}$ ] system, finding in ion-exchange equilibrium experiments that the CMX membrane is more selective for potassium than for calcium, which seems to be the case for the initial part of the runs at  $24 \text{ A/m}^2$  in plot 2E.

Overall, the observed preferential removal of divalent cations is in agreement with other studies [13,29,48–50], and especially with the one of Galama et al. [5], who also focused on the desalination of seawater at  $20^\circ\text{C}$  when applying similar current densities ( $30$  and  $100 \text{ A/m}^2$ ) in a stack containing Neosepta CMX membranes. It must be noticed that similar composition profiles were obtained for the mentioned current densities despite having differences in the experimental conditions (like initial composition of the concentrate and linear fluid velocity), and slightly different feed composition (they had 10% higher TDS). Thus, the influence of the applied current density over other process variables results noteworthy. These results show that the transport of divalent cations is favored over the transport of the monovalent ones, for conditions with less pronounced diffusive boundary layers, such as at low current densities.

### 3.2.2. Effect of polymer presence on the removal of cations

The addition of HPAM increased the viscosity of the solution. For the experiments at  $20^\circ\text{C}$ , the seawater solution with  $1.0 \text{ g/L}$  of polyelectrolyte had an average viscosity of  $4.8 \text{ mPa s}$ , calculated from the initial ( $3.33 \text{ mPa s}$ ) and final ( $6.03 \text{ mPa s}$ ) viscosities measured with the rheometer, as reported in our previous study [25]. This value is approximately 4.6 times the viscosity of the seawater solution without polymer [25]. However, it must be remarked that a rheometer reports the macroscopic viscosity, which may deviate significantly from the microscopic viscosity felt by the ions in the solution due to their friction with the solvent [51]. The microscopic viscosity is not affected much because the solvent is still water plus a very low concentration of dissolved polymer segments at  $20^\circ\text{C}$ . This means that the diffusion coefficients of the ions should remain the same despite the changes in macroscopic viscosity. This was validated by the conductivity readings, which were practically the same for solutions with and without HPAM (section 3.1), and is also reported in the literature for other solutions viscosified with polymers [31,52]. Thus, the presence of HPAM could only influence the selectivity by changing the fluid dynamics in the electrolyzer, and by interacting with the ions in solution.

Regarding the change of fluid dynamics on the electro dialyzer, we drew on the potential requirement during the experiments to find out if there was an impact on concentration polarization. The data is included in Fig. 3, from which two main facts can be noticed. The first is that, no matter the experimental conditions, the voltage kept increasing since the start of the experiments, indicating continuous increase of resistance in the stack (according to Ohm's law). However, during the first half of our desalination experiments, the ohmic resistance was supposed to decrease, given that the resistivity of the initial concentrate

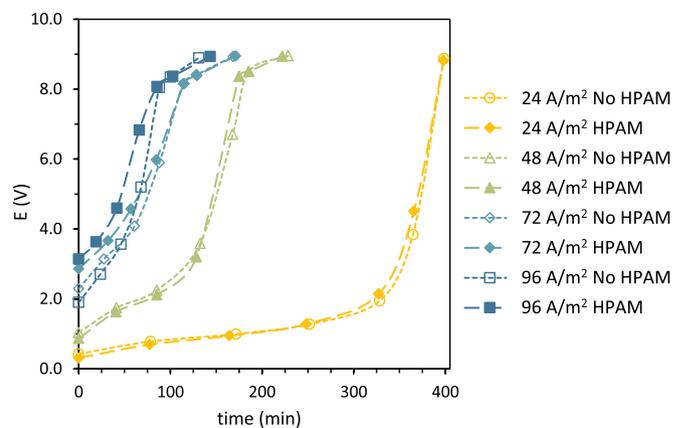


Fig. 3. Voltage applied to the stack as a function of time for experiments at  $20^\circ\text{C}$ .

solution was five times higher than the one of the diluate ( $95$  vs  $20 \Omega \text{ cm}$ , respectively). The continuous increase thus suggests that the dominating resistance was in the diluate compartment, possibly due to the progressive development of concentration polarization in the diffusion boundary layer [6,47].

The second remark for Fig. 3 is the similarity of the curves obtained for the experiments with and without polymer. For the experiments run at lower current densities ( $24$  and  $48 \text{ A/m}^2$ ) the presence of polymer was not a determining factor in the potential needed to sustain the fixed current densities. However, for the experiments performed at  $72$  and  $96 \text{ A/m}^2$ , the presence of HPAM resulted in a higher voltage in the cell, a sooner reaching of the limiting voltage in the potentiostat, and slightly longer experiments (Table A1). This could be caused by the lower turbulence in the cell when the diluate is viscosified, which affects the mass transfer from the bulk of the fluid to the surface of the membrane [31]. However, it appears that the changes in fluid viscosity, and presumably in concentration polarization, were not severe enough to affect the “ordinary” selectivity for cationic species. Fig. 2 shows that there was practically no difference between the concentration profiles for experiments performed at the same current density, disregarding the presence of polymer.

Concerning the interaction of HPAM with the cations, again Fig. 2 shows that the composition profiles and permeabilities of divalent over monovalent cations are alike the ones obtained for the solutions without polymer (left vs right side in the figure). The main difference is the presence of small amounts of divalent cations ( $0.1 \text{ mM}$  of  $\text{Mg}^{2+}$ ) in the last samples taken from the experiments run with HPAM at  $24 \text{ A/m}^2$ , while for the analogues without HPAM no divalents were detected. These results were somewhat surprising because, as mentioned in section 1.2, HPAM has a special affinity to divalent cations [32,33], and its acrylic group bonds particularly well with calcium [34]. However, the plots show that the transport rate of both divalent and monovalent ions is only affected by the applied current density and not by the presence of polymer. The charge density of HPAM in solution was experimentally determined (section 2.2.3) to a value of  $5.62 \text{ meq/g}$ . Thus, considering the polymer concentration in the diluate bulk ( $1.0 \text{ g/L}$ ), approximately  $5.62 \text{ meq/L}$  of the cations could remain bound to the polymer instead of being free in solution, being retained in the diluate. The initial solution contained approximately  $95 \text{ meq/L}$  of divalent cations ( $17 \text{ meq/L}$  of  $\text{Ca}^{2+}$  and  $78 \text{ meq/L}$  of  $\text{Mg}^{2+}$ ) and  $433 \text{ meq/L}$  of monovalent cations, so they were present in excess. However, the remaining part of divalent ions was much less than  $5.62 \text{ meq/g}$  (a maximum of  $0.74 \text{ meq/g}$   $\text{Mg}^{2+}$ , and  $0 \text{ meq/g}$   $\text{Ca}^{2+}$ ), hence the forces of the imposed electric field on the cations appear to overrule the electrostatic attractive forces in solution between divalent cations and polymers.

### 3.2.3. Effect of temperature on removal of cations

Let us next consider the removal of divalent cations at different temperatures, 10 and 40 °C, in the presence of HPAM. Again, the effect of having a viscous diluate in the formation of a boundary layer can be extracted from the information in Table A1. At 40 °C, we observed that for runs at the same current density, the switching points and total durations were practically indifferent to the presence of HPAM. On the contrary, for 10 °C, the presence of HPAM significantly affected the behavior of runs at current densities above 24 A/m<sup>2</sup>. In the most extreme case (96 A/m<sup>2</sup>), the limiting potential was reached when only  $1.68 \times 10^3$  C had been transported, half the amount that theoretically passed in the absence of polymer.

To explain these observations, as well as the removal of divalent cations, it must be considered that the difference in temperature can influence the boundary layers by two mechanisms: by affecting the diffusion coefficient of the ions [53,54], and by changing the macroscopic viscosity of the fluid [25]. Both factors contribute to make ion mobility less susceptible to diffusion limitation due to thinner boundary layers. Therefore, the differences in experimental results in presence and absence of HPAM (evaluated at the same current density and temperature) are attributed to the changes in flow conditions and its effect in concentration polarization. Then, as shown in Fig. 4, most of the normalized concentrations for experiments at same temperature and current density fall within the same trend lines, indicating that the transport of divalent cations was practically unaltered by the different flow conditions attained within the cell. Indeed, even the results obtained at different temperatures were very similar. Fig. 4 highlights by means of tendency lines the two most extreme cases regarding experimental conditions: the experiments performed at 40 °C without HPAM

(low viscosity and high diffusion coefficients) and the ones at 10 °C with HPAM (high viscosity and low diffusion coefficients). Yet, even between these two extremes the differences in transport of divalent cations are only perceptible for the runs performed at 24 and 48 A/m<sup>2</sup>. This can be explained by considering that at high current densities the boundary layer is already so significant that the selective transport is governed by the diffusion of the ions through it [29]. At this point, the changes in temperature and hydrodynamic conditions are not enough to make a difference in the observed selectivity. In contrast, when lower current densities are applied, the differences in diffusivity can still impact the thickness of the boundary layer, so the membrane properties can still exert influence on the removal. However, it is also noted that the early reaching of the maximum voltage for the experiments at 72 and 96 A/m<sup>2</sup> and 10 °C limits the data points available for comparison, and therefore extensive mechanistic interpretations.

However, also from Fig. 4 it can be noted that the concentration of divalent cations for experiments performed at 40 °C was always lower than for the other temperatures, no matter the current density nor the presence of HPAM. There is another factor to be considered when discussing the effect of temperature on the competitive transport: its influence on the membrane properties. It was already mentioned that at 25 °C, the CMX membrane has a larger permeability for calcium over sodium [45]. Furthermore, it has been reported that the selectivity coefficient of the CMX for Ca<sup>2+</sup> over Na<sup>+</sup> increases with temperature, doubling when measured at 40 °C instead of 10 °C [40]. Even if Mg<sup>2+</sup> was not included in the referred study, its similarity with Ca<sup>2+</sup> and our own observations indicate that the enhanced selectivity of the CMX membrane at higher temperatures is probably also applicable to the system [Mg<sup>2+</sup>/2Na<sup>+</sup>].

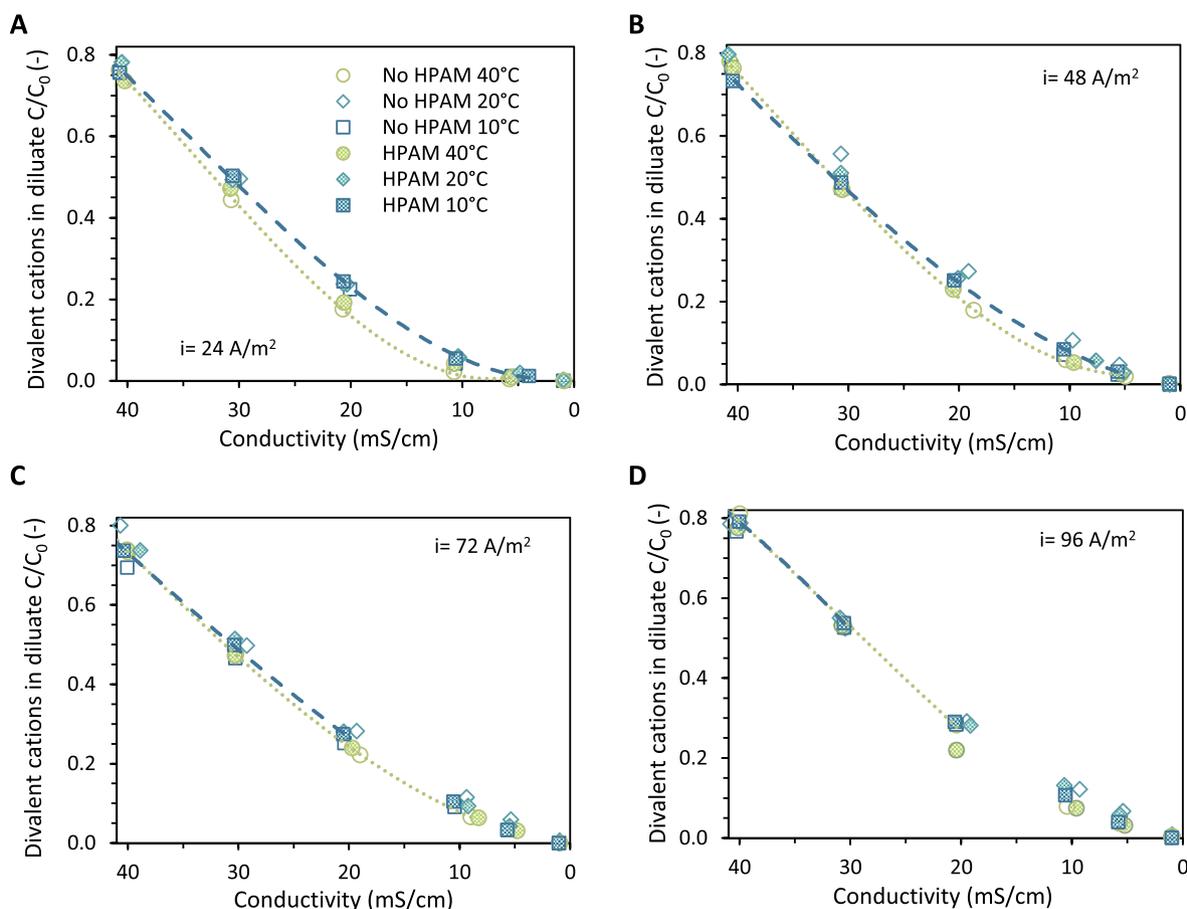


Fig. 4. Normalized concentrations of divalent cations remaining in the diluate for experiments performed at different temperatures, with and without HPAM, at fixed current densities A)  $i = 24$  A/m<sup>2</sup>, B)  $i = 48$  A/m<sup>2</sup>, C)  $i = 72$  A/m<sup>2</sup> and D)  $i = 96$  A/m<sup>2</sup>. Data from the initial part of the runs is not shown to give visibility to the final stage. Discontinuous lines for the most extreme cases are included for guiding the eye and to indicate when the system got voltage limited.

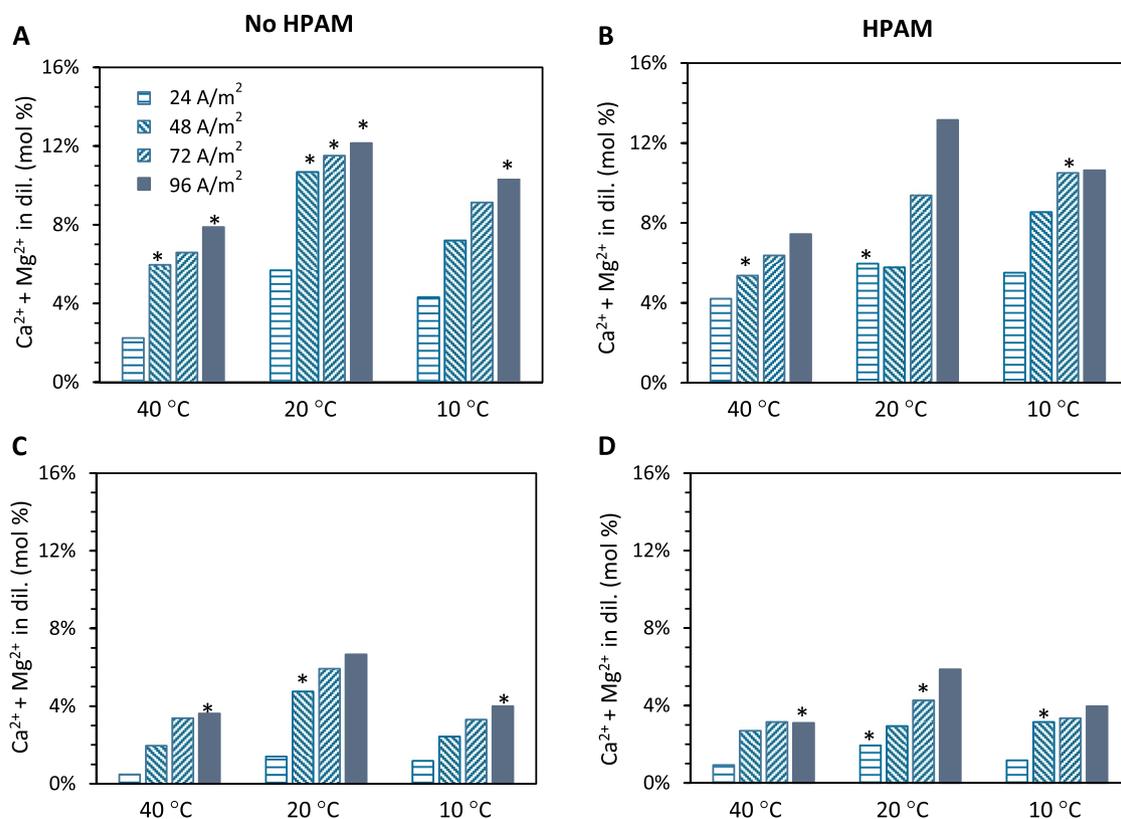


Fig. 5. Percentage of  $\text{Ca}^{2+} + \text{Mg}^{2+}$  remaining in the diluate. A) Samples taken at 10.5 mS/cm from experiments without HPAM; B) Samples at 10.5 mS/cm with HPAM; C) Samples taken at 5.5 mS/cm from experiments without HPAM; D) Samples at 10.5 mS/cm from experiments with HPAM. Each bar is the average calculated from 2 independent experiments, and the star (\*) indicates that the individual values differed above 10%.

Thus, for the system studied, a combination of factors was shown to be beneficial to achieve higher removal of divalent cations: i) low current densities which allow the intrinsic selectivity of the membrane to dominate the process, and ii) higher temperatures which reduce the thickness of the boundary layer and increase the selectivity of the CMX membrane towards the divalent species. This can be better visualized in Fig. 5, which shows the percentage of divalent cations remaining in the diluate for the samples taken at conductivities 10.5 and 5.5 mS/cm (corresponding to approximately 83 and 91% of TDS removal). In all cases, the experiments at 24 A/m<sup>2</sup> and 40 °C retained a lower amount of  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  compared to experiments run at higher current densities and lower temperatures, as expected from the previous analysis. In addition, it is shown that the effect of the low current density is less pronounced when HPAM is present, which is thought to be related to the viscosity of the fluid increasing during the last part of the process.

### 3.3. Removal of anions

#### 3.3.1. Effect of current density on the removal of anions

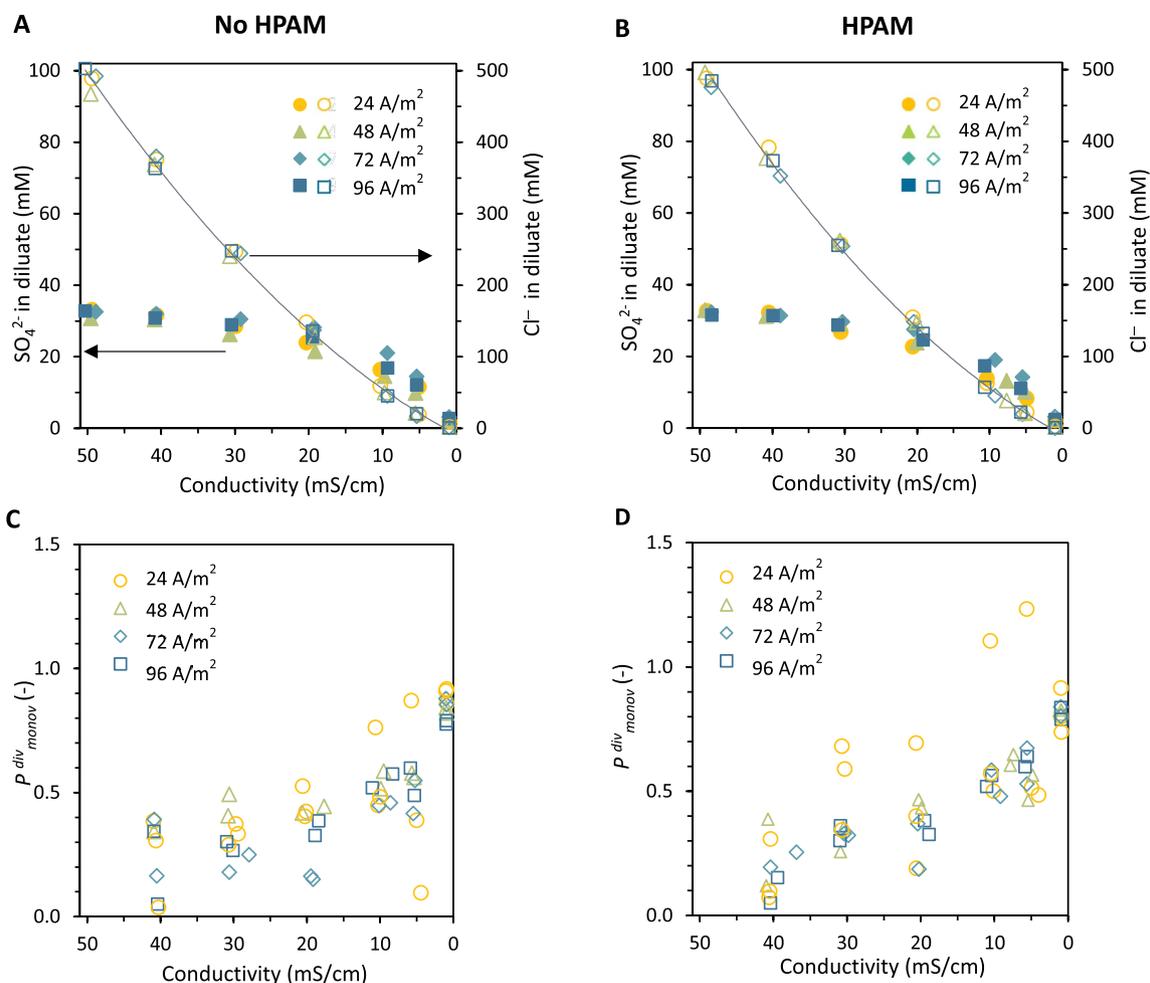
Following a similar scheme as for the transport of cations, Fig. 6 shows the concentration of anions in the diluate during the experiments run at 20 °C at different current densities. It must be added that although the feed water contained bicarbonate, its concentration was minimal (6.36 mM) compared to that of chloride (490 mM), so its removal was not monitored. Then, Fig. 6A shows that, for the experiments without HPAM, the concentration of chloride decreased in a fast and constant mode, while sulfate ions tended to stay longer in the diluate, without much apparent influence of the applied current density. Only when the concentration of chloride had dropped to around 150 mM, the sulfate decreases more meaningfully. This can be better observed in Fig. 6C, which shows how the permeability of sulfate over chloride started in low values (around 0.3) and kept increasing during the

experiment, finalizing around 0.9 for all current densities. This means that the removal of sulfate was always lower than that of chloride, so at the end of the desalination the molar concentration of both anions was nearly the same. Regarding the influence of the current density, only one of the experiments performed at 24 A/m<sup>2</sup> (out of 3) slightly deviated from the general behavior of the rest of the experiments, so a possible explanation for this observation is explored further in the text.

The transport tendencies for the anions agree with the results of Galama et al. [5], who reported a constant reduction of chloride while the removal of sulfate accelerated after approximately two thirds of the salts had been removed, although in their study they found differences in transport rate depending on the applied current density. Sirivedhin et al. [13] also reported different removal rates of anions depending on the initial salinity of the water to be desalted. For waters with high salinity (TDS above 62,000 mg/L), chloride was preferentially removed, most probably due to its higher feed concentration. Meanwhile, for low salinity waters (TDS ~5,000 mg/L) the removal of sulfate was faster than for the other anions, especially when a low voltage was applied [13]. Indeed, the expected removal order of anions passing through a strong AEM is  $\text{Cl}^- > \text{SO}_4^{2-}$  [4,37], although it has also been reported that the AMX membrane is more selective for sulfate than for chloride ( $P_{\text{Cl}^-}^{\text{SO}_4^{2-}} = 1.3$ ) when evaluated for an equimolar solution of chloride and sulfate at 30 °C and 20 A/m<sup>2</sup> [44]. Thus, our results together with the literature indicate that the competitive transport of chloride and sulfate ions through the AMX membrane is highly dependent on the concentration of the bulk solutions and the process operational conditions.

#### 3.3.2. Effect of polymer presence on the removal of anions

Regarding the influence of HPAM in the removal of anions, Fig. 6 shows that there were no significant differences between the experiments performed with and without HPAM. In both cases, chloride was preferentially removed, the final diluates contained equimolar amounts



**Fig. 6.** A, B) Concentration of anions in the diluate during the electro dialysis at different current densities and 20 °C. The concentration of divalent anions (filled symbols) can be read in the left axis, while the concentration of the monovalent ones (non-filled symbols) can be read in the right axis. Continuous lines are presented to guide the eye. C, D) Ratio of monovalent over divalent anions. A and C refer to experiments without HPAM, while B and D to experiments with HPAM.

of both anions, and there was no distinction regarding the applied current density. This similarity can be explained by considering that the concentration polarization of HPAM on the membranes only occurs mainly in the final stage of the experiments, when the ionic strength of the solution has diminished considerably, as observed in our previous study [25]. Thus, during most part of the experiments the polyelectrolyte remains free in solution, not interfering with the normal electro dialysis performance.

Additionally, it was observed that again one of the triplicates of the experiment at 24 A/m<sup>2</sup> presented a slightly higher permeability of sulfate over chloride (Fig. 6D). Both observations are thought to be due to a higher pH of the diluate stream, particularly when the last sample was taken, which was the only anomaly in common for both experiments. While for the two referred cases the final pH of the diluate was around 5, for most of the experiments the pH reached a value of 4. This was most probably caused by an incomplete removal of the acidified solution during the washing procedure.

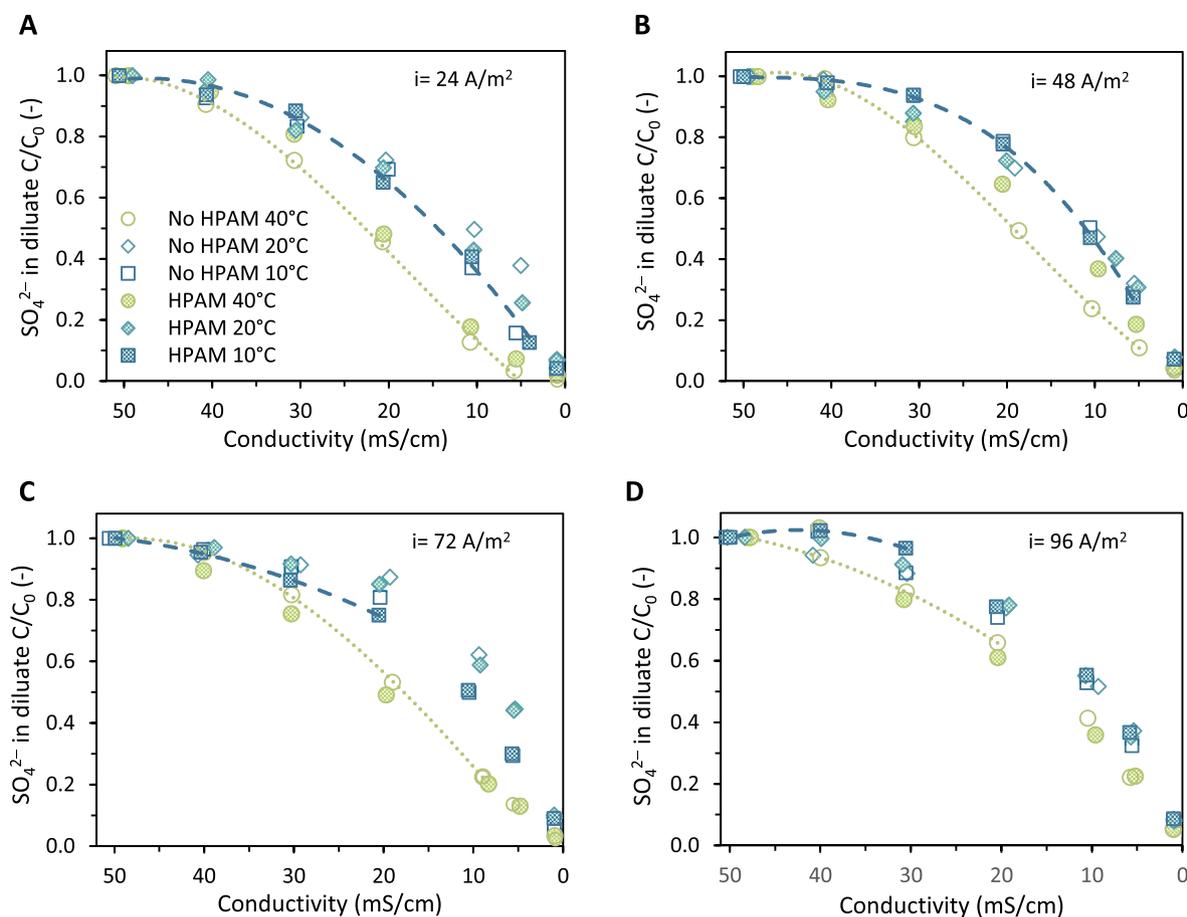
### 3.3.3. Effect of temperature on anions removal

The effect of temperature on the removal rate of sulfate was more substantial than the one measured for the divalent cations, as can be seen on Fig. 7. While for the experiments performed at 10 °C the sulfate removal was like the one obtained at 20 °C, experiments at 40 °C showed a faster transport of the referred anion. This faster removal at increasing temperature could be due to two factors: i) the faster diffusion coefficient of the sulfate anion, which would increase its

concentration near the membrane, and ii) the increased affinity of the AMX membrane towards sulfate with higher temperature [39]. In this regard, Guesmi et al. reported that the selectivity coefficient of the AMX membrane for SO<sub>4</sub><sup>2-</sup> over 2Cl<sup>-</sup> increases almost tenfold for experiments at 40 °C compared to the one measured at 10 °C, this as a consequence of an increase of the equilibrium extent of reaction mounting with temperature [39].

Fig. 7 also shows that the presence of polymer did not affect the transport tendencies of sulfate, as had been already observed for the experiments at 20 °C. However, contrary to those, the runs at 40 °C indicated an effect of the applied current densities on the removal of sulfate. The faster removal of sulfate at lower current densities is perceptible when comparing the removal at specific salinities. A feasible explanation is that at low temperatures, the transport through the AMX membrane is limiting the removal of sulfate, so varying current density does not have any effect on its removal. At higher temperatures, the transport of sulfate through the membrane is facilitated, so now the limiting process would be the transport from the bulk solution to the surface of the membrane, which is affected by concentration polarization and current density.

To close this section, we include Fig. 8, which shows the percentage of sulfate remaining in the partially desalted diluate (10.5 and 5.5 mS/cm) for the different experimental conditions. The percentages of sulfate are significantly higher than the ones presented in Fig. 4 for the divalent cations, so it becomes clear that this anion was transported with more difficulty. For instance, when the diluate solutions had a



**Fig. 7.** Normalized sulfate remaining in the diluate for experiments performed at different current densities and temperatures, with and without HPAM. **A)** 24 A/m<sup>2</sup>, **B)** 48 A/m<sup>2</sup>, **C)** 72 A/m<sup>2</sup>, **D)** 96 A/m<sup>2</sup>. Discontinuous lines for the most extreme cases are included for guiding the eye and to mark the period for which the constant current was maintained.

conductivity of 10.5 mS/cm, most of them still had 50% of the initial amount of sulfate, while roughly 80% of the other ions had already been removed. Thus, the only conditions that allowed the preferential removal of sulfate were 40 °C and 24 A/m<sup>2</sup>, coinciding with the best settings for the removal of divalent cations. Our results indicate that in the presence of HPAM the removal of sulfate was slightly decreased, although the differences are minimal.

### 3.4. Water reuse after desalination

As a final evaluation, we include a comparison of the properties of viscous solutions obtained when using electro dialysis versus a non-selective desalination. To represent the electro dialysis case, salt solutions were prepared with the compositions obtained in the best preferential removal case, this is, when the sea water was desalted at 40 °C and 24 A/m<sup>2</sup>. The no-preferential removal solution was prepared by adding demi water to the synthetic seawater until reaching the conductivity goal. Then, for both cases, high MW polymer was added and hydrated as described in section 2.1.2, and their viscosities measured at 40 °C.

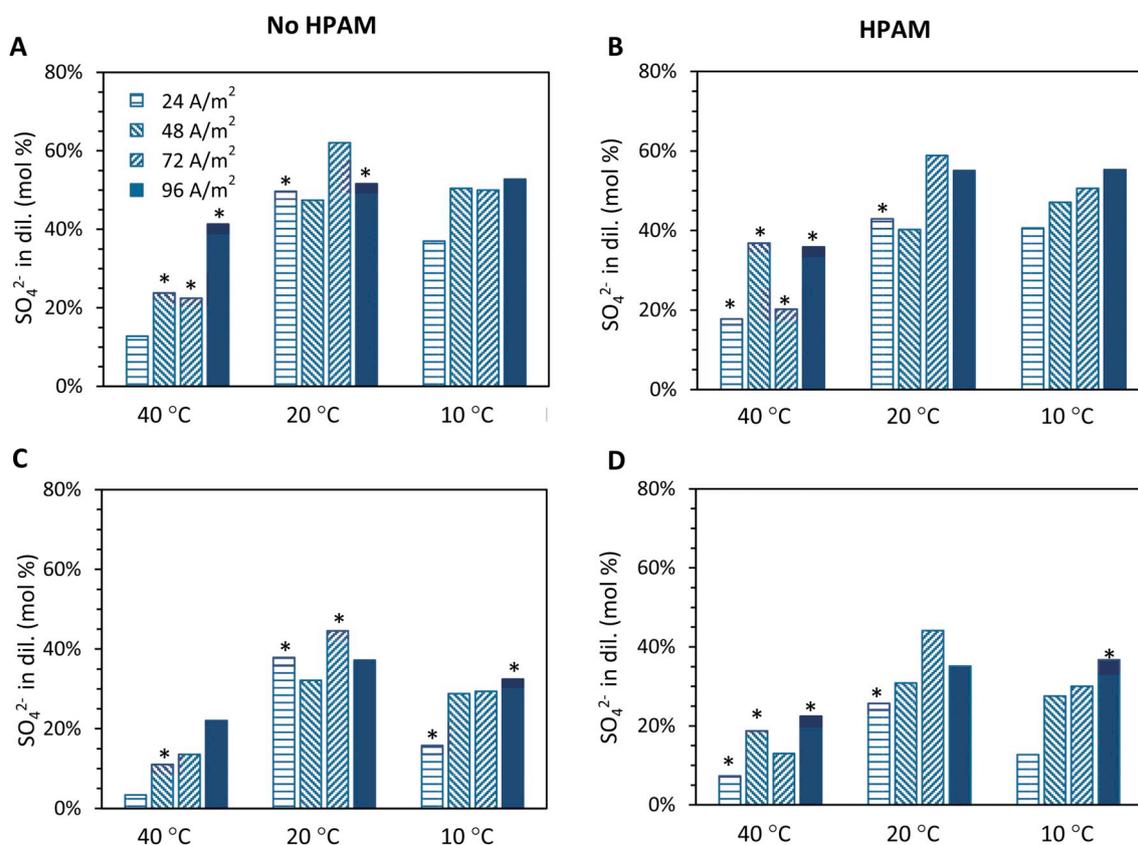
As shown in Fig. 9, the four solutions prepared with water desalted through electro dialysis presented higher viscosities than the solutions prepared with diluted seawater, the differences ranging between 22 and 43%. These results demonstrate that even though the preferential removal of multivalent ions seemed minor, it can have measurable effects in the properties of the viscous solution, which would be potentially reflected as savings of fresh polymer and chemicals. If less polymer is required, the impact is also favorable in terms of chemical procurement, transportation, storage and handling (mixing and hydration) requirements and operating costs [14].

Regarding the sulfate removal, the desulphation level needed to minimize the scaling would greatly depend on the amount of hardness in solution. As a reference, a sulfate reduction plant based on nanofiltration can decrease sulfate concentrations from 3000 to 40 mg/L, but even at this concentration there may still be a scaling potential [55]. However, it is also known that SrSO<sub>4</sub> precipitation is inhibited when [SO<sub>4</sub>] is below 1000 mg/L; and for [Ba] = 80 mg/L, like in seawater [42], the precipitation of BaSO<sub>4</sub> starts when [SO<sub>4</sub>] > 175 mg/L [55]. Then, since the experiments run at 24 A/m<sup>2</sup> and 40 °C achieved a final sulfate concentration under 10 mg/L when no HPAM was present (and 60 mg/L when it was), obtained results also seem promising in this aspect.

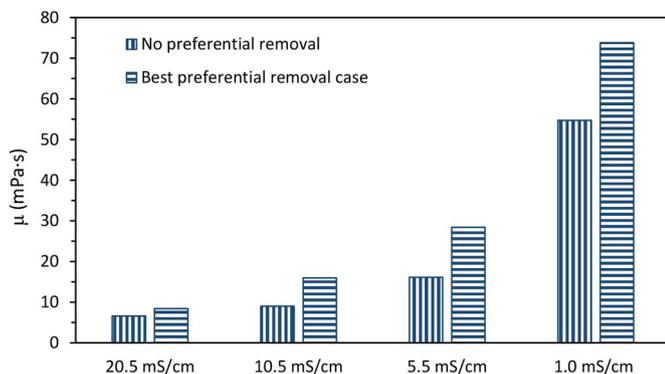
## 4. Conclusions

To be reused, polymer-flooding produced water needs to be partially desalted, and desirably stripped of its multivalent ions. For the composition studied in this article, it was identified that divalent cations, accounting for less than 10% of all the cations in solution, have the most significant effect in reducing the viscosity of polymer-flooding solutions.

Our results demonstrate that it is possible to achieve preferential removal of divalent cations through electro dialysis, especially when employing low current densities (24 A/m<sup>2</sup>) and high temperature (40 °C). The removal of sulfate, a divalent anion, is also accelerated in these conditions. The presence of the polyelectrolyte HPAM does not significantly affect the removal rate of divalent ions. Thus, meticulous application of ED to minimize concentrations of divalent ions in PFPW is a potential effective way for water and polymer recycling in cEOR



**Fig. 8.** Percentage of sulfate remaining in the diluate. **A)** Samples taken at 10.5 mS/cm from experiments without HPAM; **B)** At 10.5 mS/cm with HPAM; **C)** At 5.5 mS/cm from experiments without HPAM; **D)** At 5.5 mS/cm from experiments with HPAM. Each bar is the average calculated from 2 independent experiments, and the star (\*) indicates that the individual values differed above 10%.



**Fig. 9.** Viscosity of HPAM solutions prepared with desalted water. For the “no preferential removal” case, the sea water solution was diluted with demi water until reaching the desired conductivity. The “best preferential removal case”, was prepared according to the ionic compositions attained during the runs at 40 °C, 24 A/m<sup>2</sup> and without polymer. All solutions were prepared with 1.0 g/L of high MW HPAM, and their viscosities measured at 40 °C and 7.3 s<sup>-1</sup>. Values measured at other shear rates are included in the Supplementary material.

situations, as an alternative to the use of other non-selective desalination technologies. However, understanding permselectivity of ions and the phenomena affecting it, including the effects of the boundary layers, remains a topic for further clarifying research.

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#### Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.memsci.2019.117251>.

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