

EXPERIMENTAL STUDY OF CONCENTRATION POLARIZATION IN A CROSSFLOW REVERSE OSMOSIS SYSTEM USING DIGITAL HOLOGRAPHIC INTERFEROMETRY

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Abstract

Digital Holographic Interferometry (DHI) has been used to visualize the polarization concentration layer during crossflow RO. This technique is based on the fact that changes in the concentration of the solution produce changes in its refractive index. Therefore, the concentration profile formed due to the polarization phenomenon can be visualized as interference fringes. Experiments with Na_2SO_4 and NaCl solutions have been carried out. Three variables of the process were studied: crossflow velocity, initial concentration and pressure applied. In each experiment, crossflow velocity was changed every 30 minutes, in an increasing or decreasing sequence. Few minutes after changing the crossflow velocity the steady-state was reached. Interference fringe patterns of the polarization layer and their corresponding concentration profiles, as well as the permeate flux in different experimental conditions, are presented. The major experimental result is the visualization for the first time in situ and in real time of the polarization layer in a process of cross flow by a non-invasive method. Experimental results show a close relationship among crossflow velocity, permeate flux and polarization layer. Furthermore, experimental maximum concentration values reached at the membrane surface were compared with values calculated by using the film theory approach and a good agreement was obtained.

Keywords: Crossflow reverse osmosis; Concentration profiles; Visualization polarization layer; Digital Holographic Interferometry.

1. Introduction

During the mass transfer through a membrane, in processes such as ultrafiltration (UF) and reverse osmosis (RO), the permeate flux drives solute to the membrane. The build-up of rejected solute in the boundary layer near the membrane surface generates a concentration gradient and as a consequence, a diffusive flow of solute back to the feed solution bulk appears. This phenomenon is known as concentration polarization and the study of its properties by means of measurements of the dissolved solute profiles is easier in an unstirred batch process than in crossflow processes, because, in crossflow processes the thickness of the boundary layer is limited by the flow parallel (especially if it is turbulent) to the membrane. In RO processes carried out in an unstirred batch cell or dead-end conditions, steady-state is not easily reached, concentrations near the membrane surface (C_m) reach a very high value and the thickness of the boundary layer (δ) grows continuously with time (Figure 1a). The process seems to reach a quasi-steady state only after a long period of time. When the concentration of the permeate solution (C_p) tends to the bulk concentration (C_o), the convective solute flow to the membrane surface is balanced by the solute flux through the membrane and the diffusive flow back to the bulk solution; as a consequence, no more accumulation of solute will occur. In crossflow, if steady-state is reached, the convective solute flux to the membrane surface is balanced by the solute flux through the membrane plus the diffusive and convective flow back to the bulk of the feed. The concentration profile near the membrane is usually stable and the maximum concentration is not very high (Figure 1b).

One of the earliest experimental research (1971) on concentration polarization in crossflow RO processes was developed by Hendricks and Williams [1]. They measured salt concentration profiles in brine adjacent to the membrane during reverse osmosis with electrical conductivity microprobes for a fully-developed two-dimensional channel in a closed-return water tunnel. Cellulose acetate membranes were employed with solutions of NH_4NO_3 , NaNO_3 , NaCl , NaSO_4 and MgSO_4 . In a relatively recent paper (2001), Sablani et al. [2] made a critical review about concentration polarization in UF and RO. More recent research of this subject has been basically focused on theoretical studies of simulation. Song and Yu [3] developed a new model for concentration polarization in the crossflow RO process in which the local variation of concentration polarization and the coupling between concentration polarization and permeate flux are

handled. In 2004, Fletcher and Wiley [4] applied a computational fluid dynamics (CFD) model to study the effect of buoyancy in reverse osmosis of salt–water separation in a flat sheet system. A mathematical model of reverse osmosis systems was published by Jamal et al. [5] in 2004. Kim and Hoek [6] (2005) modelled the concentration polarization in reverse osmosis. Geraldes and Afonso [7] (2006) proposed a generalize mass-transfer correction factor for nanofiltration and reverse osmosis. A finite element model to study pressure, flow, and concentration profiles in crossflow membrane filtration systems with open and spacer-filled channels was developed by Subramani et al. [8] in 2006. Ghidossi et al. [9] (2006) reviewed the state of the art on computational fluid dynamics (CFD) methods applied to membrane processes. In 2007, Alexiadis et al. [10] also used a CFD method to model the reverse osmosis membrane flow, validating the model with experimental permeate flux data. Lyster and Cohen [11] (2007) studied concentration polarization during reverse osmosis processes using a rectangular membrane channel. Chong et al. [12, 13] (2007) studied the fouling effect on polarization concentration in reverse osmosis. Wardeh and Morvan [14] (2008), developed CFD simulations of flow and concentration polarization in spacer-filled channels applied to water desalination. Cavaco Morão et al. [15] (2008) performed simulations of flow structure and solute concentration distribution in a nanofiltration/reverse osmosis plate-and-frame module by using CFD.

This review of the more recent literature shows that most of the papers are theoretical studies of the simulation, without experimental determination of the profiles of the concentration polarization layer (CPL) in crossflow RO processes. In some papers, experimental data of the permeate fluxes have been obtained, comparing them with those calculated with the model.

Since the review made by Sablani et al. [2], only two papers [16, 17] presenting experimentally determined profiles of the CPL have been found. In both cases, experiments were developed on unstirred batch conditions. Chmiel and Fritz [16] constructed an experimental apparatus which allowed an *in situ* chemical sampling of a reverse osmosis system inside a high-pressure column. In it, a 101.3 mM sodium chloride solution was advected towards an uncompressed sodium-saturated bentonite membrane. Twelve small-diameter stainless steel tubes were fitted to run parallel to the length of the experimental column, each tube terminating at a different position within the concentration polarization layer. In the other paper [17], holographic interferometry

was used to visualize the appearance, evolution with time and disappearance of the concentration polarization layer in unstirred batch reverse osmosis.

Holographic interferometry is an optical technique of the so-called 'non-invasive' methods. A review of "non-invasive" experimental methods for the observation in-situ and in real-time of membrane processes has been made by Chen et al. [18]. The authors describe a wide range of optical and non-optical techniques.

In previous papers [17, 19-24], the optical holographic interferometry technique was used to visualize the evolution of the concentration polarization layer during UF of BSA and PEG solutions, as well as RO of salts. This technique, which has also been used to study diffusion processes [25-26], allows interferometric fringe patterns to be obtained, that are indicative of changes in the optical path followed by the light and are related to changes in the refractive index. In the case of the appearance of the concentration polarization layer during the RO process, changes in the concentration distribution, and therefore in the refractive index distribution, can be visualized as an interference fringe pattern.

In the present research, the technique used is Digital Holographic Interferometry (DHI), a variation of the conventional HI technique where the main difference is the change of the hologram recording element. In classical HI, a holographic plate, photographically developed, is used. In DHI, the holographic plate has been substituted for the CCD chip of a video camera. The technique is as valid as the classical HI, and has already been used in similar diffusion studies in transparent media [27-28]. Methodology for the digital reconstruction of the interferograms may vary depending on the process to be studied. Schnars and Jüptner [29] developed the methodology for numerically reconstructing a digital hologram, while maintaining the same advantages (or even extending them) as optical holography. Nevertheless, there are applications where these advantages are not necessary and therefore easier ways for the interferogram formation can be used. Such is the case of Electronic Speckle Pattern Interferometry (ESPI, or DSPI also TV Holography). By means of this method, two interferograms of two different states of the object are recorded and then subsequently subtracted digitally, creating an interferogram similar to that obtained with conventional holographic interferometry [29].

The aim of this study is to determine in situ and real-time concentration profiles during the crossflow RO of salts by using Digital Holographic Interferometry. This determination constitutes the first direct verification of the CPL under crossflow conditions. Along with the measurement of the interference fringe pattern by means of DHI to determine the polarization layer, the permeate flow was measured in each experiment. The close relationship between these two variables of the process could be observed. So, an increase of crossflow velocity causes a higher shear force that decreases the polarization layer and, consequently, increases the permeate flow.

2. Experimental

2.1. Experimental set-up

The experimental assembly associates two different systems: the optical set-up for the holographic interferometry and the reverse osmosis set-up. These two assemblies were coupled on the same work table, with the RO module as the common element.

The RO module, specially designed to carry out the RO process satisfying the holographic interferometry requirements, has been thoroughly described in a previous paper [23]. Since a crossflow process takes place in a low channel, a piece of Teflon was introduced in the RO module to reduce the channel height to its final dimension (3 mm). Dimensions of the module used were 100 x 10 x 3 mm.

In this paper, a digital holographic interferometric set-up (Figure 2) was used. This optical system is very similar to that explained in a previous paper [24], the main difference being that the holographic plate has been substituted by the CCD chip of a video camera. The chip is, therefore, the hologram recording device.

The laser beam is divided with a beam splitter (Bs1) into the reference beam and the object beam. After passing through the RO module (Ob), the object beam is re-joined with the reference beam and both are focused into the camera (CCD) by means of a lens system (Lens). The interferences between both beams form the hologram, which is electronically stored in the PC.

The crossflow RO system (Figure 3) is similar to that described in a previous paper [22]. The feed solution was pumped (1) from the tank (2) to the RO module (3). Pressure was visualized by means a pressure gauge (4), while the crossflow rate was

measured with a rotameter (5). A valve in the rotameter allowed both the pressure and the crossflow velocity of the system to be controlled. A fine regulation valve (6) also helped to regulate flow rate and pressure. Permeate flux was continuously measured by means of a balance (8) and its conductivity determined with a conductivity probe (Crison, model 5287) (7) and a conductimeter (Crison, model GLP 32) (9) connected to a PC (10).

2.2. Materials

Experiments were performed with a thin film membrane (TFM-50, from Hydro Water S.L.). Suitable pieces for the size of the module used (1x10 cm) were cut from the entire membrane. Each piece of membrane was changed after several experiments, so after each experiment the module was washed with distilled water. Washing was done by circulating water at high crossflow velocity to completely remove salts from the membrane surface. The membrane was considered to be clean when the permeate flux of water was recovered.

Experiments were performed using solutions of two salts: Na₂SO₄ and NaCl (Panreac). Different feed concentrations (C₀), in the range of 3.5-8.5 kg/m³, were used to study the effect of the solute and feed concentration on the polarization layer. Physical properties of the solute solutions used (diffusion coefficient, density and osmotic pressure) were obtained from literature.

$$\text{Na}_2\text{SO}_4 \text{ [30]: } D \text{ (m}^2\text{/s)} = -3.9 \times 10^{-12} C \text{ (kg/m}^3\text{)} + 1.16 \times 10^{-9}$$

$$\text{NaCl [4]: } D \text{ (m}^2\text{/s)} = \max (1.61 \times 10^{-9} (1-14 m), 1.45 \times 10^{-9})$$

where m is the mass fraction of the solute

$$\text{Na}_2\text{SO}_4 \text{ [31]: } \rho \text{ (kg/m}^3\text{)} = 9.80 C \text{ (kg/m}^3\text{)} + 997.1$$

$$\text{NaCl [31]: } \rho \text{ (kg/m}^3\text{)} = 7.24 C \text{ (kg/m}^3\text{)} + 997.1$$

The osmotic pressure of both solutions was calculated using the van't Hoff equation for dilute solutions [32]

$$\text{Na}_2\text{SO}_4: \Pi \text{ (atm)} = 0.516 C \text{ (kg/m}^3\text{)}$$

$$\text{NaCl: } \Pi \text{ (atm)} = 0.835 C \text{ (kg/m}^3\text{)}$$

2.3. Experimental methodology

Three variables of the process were studied in each experiment: initial concentration (C_o), pressure applied (ΔP) and crossflow (CF) velocity. Four values of initial concentration (3.5, 5, 7 and 8.5 kg/m^3), two different transmembrane pressures (6 and 7.2 bar) and two combinations of crossflow rate were used. The use of glass windows limited the maximum pressure applied. Therefore, in order to prevent buckling of the windows (which could cause the appearance of spurious interference fringes) a maximum pressure of 7.2 bar was used. This limitation on the pressure applied determines the range of salt concentrations used (up to 8.5 kg/m^3), as the solution should not have an osmotic pressure greater than the pressure applied. The CF velocities used were 0.2, 0.7 and 1.7 cm/s ($Re = 10, 31$ and 77), combined in each experiment in two ways: upward or downward, and always returning to the initial velocity at the end of each experiment. Thus, the upward series (*Up Series*) had a sequence 0.2-0.7-1.7-0.2 cm/s, while the downward series (*Down Series*) followed the sequence 1.7-0.7-0.2-1.7 cm/s. Each crossflow velocity was maintained for 30 minutes. Each possible variables combination (C_o , ΔP and Series of crossflow velocity) was repeated twice to verify the reproducibility of the results.

Before each experiment, water flow (J_w) was measured to verify that it had not fallen very much and the membrane was not in bad condition. Once the water flux was checked, the solution was introduced into the system and remained in circulation at the intermediate velocity of 0.7 cm/s. With the solution circulating and the optical set-up correctly aligned, the hologram capture program was started thus beginning the calculation of the interferograms. Finally, pressure was applied and initial CF velocity was selected according to the crossflow series to be studied.

The video camera captures the images and sends them to the PC. The program, at a rate of 1 per second, converts these images to a matrix. The value of each element of the matrix is related to the intensity received by each light detector (pixel) of the camera CCD chip. Afterwards, the numerical subtraction of two different matrixes, corresponding to two different states of the object, provides the intensity of the interferogram desired. Therefore, as the reference state (the hologram) must be the object before undergoing any change, the first image captured by the camera will be the hologram. Next images will be subtracted from the hologram and the resulting matrix will be converted back to an image. This image is the interferogram finally studied.

When pressure was applied, a convective flux of solute to the membrane surface began, thus causing the accumulation of the solute in the vicinity of the membrane. The increase of the concentration on the membrane surface (C_m) changed the refractive index and caused the appearance of interference fringes when comparing the actual state and the reference state. Each interference fringe corresponds to a concentration step in the solution. This step depends on the relation between the concentration and the refraction index, measured at 25 °C with a refractometer (Leica, AR600):

$$\text{Na}_2\text{SO}_4: n = 1.54 \times 10^{-4} C \text{ (kg/m}^3\text{)} + 1.33299$$

$$\text{NaCl: } n = 1.76 \times 10^{-4} C \text{ (kg/m}^3\text{)} + 1.33299$$

Methodology to obtain the concentration profile from the interferograms was described in previous papers [19, 24].

The process was continuously recorded, even while the crossflow velocity was modified. Modifications were made every 30 minutes through a change in the position of the valves of the system, until a total time of experiment of 120 minutes.

Weight and conductivity data of the permeate solution were also continuously measured during the process. Permeate weight data were used to calculate the permeate flux as the curve derived from the weight. As the relation between conductivity and concentration was experimentally measured, permeate concentration was obtained from conductivity data of the permeate solution.

$$\text{Na}_2\text{SO}_4: \mu \text{ (}\mu\text{S)} = 1227.3 C \text{ (kg/m}^3\text{)} + 2.29$$

$$\text{NaCl: } \mu \text{ (}\mu\text{S)} = 1799.2 C \text{ (kg/m}^3\text{)} + 2.29$$

Conductivity of permeate solutions was very low, thus indicating a very high retention (higher than 90%).

After 120 minutes of experiment, the pump was stopped thus removing pressure and feed flow. It was observed that, in a few minutes, interference fringes of the polarization layer completely disappeared.

3. Results and Discussion

3.1. Na_2SO_4 experiments

Combining four initial feed concentrations (3.5, 5, 7 and 8.5 kg/m³ of Na₂SO₄) with two applied pressures (6 and 7.2 bar), a total of 8 experiments were run (Table 1). All the experiments were duplicated to check reproducibility. In each experiment, crossflow velocity was changed every 30 minutes, in an increasing sequence (*Up Series*). The

sequence of CF velocities was 0.2-0.7-1.7-0.2 cm/s ($Re = 10, 31, 77$ and 10). Permeate flux measurements showed that steady state was reached in a few minutes after the beginning of the experiment or after every change in the CF velocity. Interferogram recording was performed continuously.

In order to check if the CF velocity history has any effect on the results obtained, another series of experiments was made with a decreasing sequence (*Down Series*) of CF velocity. As the results obtained with the *Down Series* properly reproduced those obtained with the *Up Series*, only three concentrations ($3.5, 5$ and 7 kg/m^3) and a pressure of 6 bar were used (Table 1). The sequence of CF velocities was 1.7-0.7-0.2-1.7 cm/s ($Re = 77, 31, 10$ and 77) and all the experiments were duplicated. Some conditions ($\Delta P = 6$ bar, CF velocity = 1.7, 0.2 cm/s) were used 6 times, some of them with a different piece of the original membrane. Although it has been reported [33] that heterogeneities in the membrane can cause changes in its hydraulic permeability, no notable differences were observed in our experiments.

As an example, Figure 4 shows the complete results (permeate fluxes, interferograms and concentration profiles of the polarization layer) of experiment n° 8, corresponding to a concentration of 8.5 kg/m^3 of Na_2SO_4 , a pressure of 7.2 bar and an *Up Series* of crossflow velocity.

The top of the Figure shows the evolution of permeate flux (J) with time. Vertical lines have been included in the Figure to identify when the CF velocity changed. Thus, in the range of 0-1800 seconds the velocity was 0.2 cm/s; 0.7 cm/s during the 1800-3600 seconds interval; 1.7 cm/s during the 3600-5400 seconds interval and again 0.2 cm/s for the 5400-7200 seconds interval.

It can be seen that the permeate flux reaches a nearly constant value for each crossflow velocity. As feed flux at the inlet of the module was continuous and stationary, all the variables of the process reached a value which was stable with time. As a consequence, the solute concentration profile (polarization layer) at any point of the membrane channel also remained stable with time, and the same occurred with permeate flux which is conditioned by this polarization layer.

On the other hand, the higher the crossflow velocity, the higher the permeate flux. It can be observed (Figure 4) that when CF velocity is 0.2 cm/s, the permeate flux is $0.80 \times 10^{-6} \text{ m}^3/\text{s}\cdot\text{m}^2$; when CF velocity changes to 0.7 and 1.7 cm/s, the permeate flux is 1.08 and $1.39 \times 10^{-6} \text{ m}^3/\text{s}\cdot\text{m}^2$, respectively. At the end of the run, when velocity returns to the initial value (0.2 cm/s), permeate flux returns to $0.80 \times 10^{-6} \text{ m}^3/\text{s}\cdot\text{m}^2$. The reason is that

when the CF velocity increases, the shear effect is greater and the polarization layer decreases, thus increasing the permeate flux. The recovery of the permeate flux value when returning to the initial conditions shows that the permeate flux depends only on the pressure applied and on the CF velocity; therefore, concentration polarization can be considered a reversible phenomenon.

In Figure 4, it can also be seen that a steady state is easily reached after a few minutes. This period of time is necessary for the concentration polarization layer to become stable, which implies either a formation or a destruction process. The formation of the polarization layer will occur when crossflow velocity decreases, thus causing a less shear effect and increasing the accumulation of solute on the membrane surface. The destruction of the polarization layer will occur with the increase of CF velocities.

In the central part of Figure 4, four interferograms corresponding to the four crossflow velocities (0.2, 0.7, 1.7 and 0.2 cm/s) of Experiment 8 are shown. Holographic interferometry allows the appearance and evolution of the concentration polarization layer during crossflow RO experiments to be followed in real time. At the beginning of the process, some fringes appeared on the membrane surface, thus indicating that the concentration of solute at the membrane surface was increasing.

As has been noted when discussing the behaviour of the permeate flux, the stabilization of the polarization layer (appearance or disappearance of some fringes) occurred only during a few minutes after changing the crossflow velocity. Usually, the process needed around 10 minutes after each change of CF velocity to be stabilized. After this time of stabilization, the number of fringes remained constant, as well as their distance from the membrane surface. This fact indicates that C_m and the thickness of the boundary layer (δ) had reached the steady state. Usually, the process reached the steady state (the number of fringes and their appearance remained virtually immutable, and both the permeate flux and permeate concentration were constant) around 10 minutes after each change of CF velocity. Although a high number of images are available (video camera captures one image per second), in Figure 4 only four interferograms are shown. The interferograms were taken at the end of each steady state step, just before changing the crossflow velocity.

It can be seen that the greater the crossflow velocity, the lesser the number of fringes, thus indicating the polarization layer decreases due to the higher shear flow. As an example, the number of interference fringes in Figure 4 is 7-5-4-7 when the crossflow velocity is 0.2-0.7-1.7-0.2 cm/s, respectively.

Moreover, as the thin fringes close to the membrane are related to the thickness of the concentration polarization layer (δ), some qualitative conclusions about this thickness can be extracted from interferograms in Figure 4. 1) the lesser the crossflow velocity, the greater the polarization layer thickness (when the crossflow velocity is 0.2 cm/s, δ is around 1 mm and decreases to 0.8 mm when the crossflow velocity increases). 2) In RO crossflow processes, δ is much lesser than in unstirred batch RO processes, (where δ can be up to 5 or 6 mm, as stated in a previous paper [17]).

Finally, in the bottom part of Figure 4, four concentration profiles calculated from the four interferograms in the Figure are shown. As the relationship between refractive index and concentration of the solutions is known, interference fringes can be converted into a concentration profile. Methodology for this conversion has been described in previous papers [19, 24]. It can be observed that, the higher the CF velocity, the flatter the concentration profile and the lesser the concentration at the membrane surface.

Figures 5 and 6 show the effect of feed concentration on the permeate flux when an *Up Series* of experiments was carried out at 6 and 7.2 bar, respectively.

Not all experiments have been carried out with the same piece of membrane. Cleaning and regeneration of the membrane during repeated experiments caused a small deterioration that made it necessary to replace the membrane after several experiments. Nonetheless, a first interpretation allows it to be seen that in every experiment the permeate flux reaches a stable value a few minutes after a new crossflow velocity was fixed.

On the other hand, there is a clear influence of the feed concentration on the permeate flux. As the higher the feed concentration, the greater the osmotic pressure, an increase of feed concentration will reduce the driving force and therefore the permeate flux will decrease.

Finally, comparing Figures 5 and 6, it is possible to state that an increase of the applied pressure causes an increase of the permeate flux.

A second set of experiments, with decreasing crossflow velocities (*Down Series*), was carried out. Figure 7 shows the evolution of permeate flux in a *Down Series* when three feed concentrations of Na_2SO_4 (3.5, 5, and 7 kg/m^3) and a pressure of 6 bar were used.

As was previously stated when studying the results of experiment 8 (Table 1), the thickness and concentration profile of the polarization layer, and hence the permeate flux, depend on the crossflow velocity.

In order to study if there is any influence of the sequence of variation of the crossflow velocity (*Up Series* or *Down Series*), Figure 8 shows the permeate flux for two experiments carried out with the same conditions (pressure: 6 bar; feed concentration: 5 kg/m³) but with different CF velocity sequences. It can be observed that the steady state value of the permeate flux, with a particular crossflow velocity, is independent of the previous velocity used. For example, at the beginning and at the end of the *Down Series* (CF velocity = 1.7 cm/s) the permeate flux was 1.87 x 10⁻⁶ m³/s·m² and the same value was obtained in the range 3600-5400 seconds of the *Up Series*, when the CF velocity was 1.7 cm/s.

Figure 9 shows permeate flux, interferograms and concentration profiles corresponding to experiment n° 1 (pressure: 6 bars; feed concentration: 3.5 kg/m³). This experiment has been selected because it was carried out with the most different conditions to experiment n° 8 (pressure: 7.2 bar; feed concentration: 8.5 kg/m³). Comparing Figures 4 and 9, it can be seen that a decrease of the applied pressure and the feed concentration reduces the polarization layer thickness (δ) and the concentration in the membrane (C_m) (less interference fringes).

3.2. NaCl experiments

A total of 6 experiments (Table 1), combining three initial feed concentrations (3.5, 5 and 7 kg/m³ of NaCl) and two pressures (6 and 7.2 bar), were carried out. As with Na₂SO₄ experiments, crossflow velocity was changed after 30 minutes by regulating the valves of the system. Three CF velocities were used: 0.2, 0.7 and 1.7 cm/s (Re = 10, 31 and 77, respectively), combined in two series (*Up Series* and *Down Series*). With NaCl it has not been possible to use the greatest concentration (8.5 kg/m³) because with this concentration, the osmotic pressure of NaCl solution is greater than the pressure applied (7.2 bar).

As an example, Figure 10 shows permeate flux, interferograms and concentration profiles from experiment n° 17 (pressure: 7.2 bar; feed concentration: 7 kg/m³), when an *Upward Series* of crossflow velocity was carried out. Permeate fluxes for the three concentrations (3.5, 5 and 7 kg/m³ of NaCl) when a pressure of 6 and 7.2 bar were used are shown in Figures 11 and 12, respectively.

From a qualitative point of view, conclusions are similar to those obtained with Na₂SO₄ (paragraph 3.2). The effect of CF velocity, feed concentration and pressure on the thickness of the polarization layer and on the permeate flux is the same as with Na₂SO₄.

Some quantitative differences are evident: As the osmotic pressure of an NaCl solution is greater than that of an Na₂SO₄ solution with the same concentration, permeate fluxes, which depend on the difference $\Delta P - \Delta\pi$, are smaller with NaCl than with Na₂SO₄. On the other hand, the thickness of the polarization layer is smaller, as can be seen in Figures 10, 11 and 12.

As previously noted in the Introduction, in 1971 Hendricks and Williams [1] measured profiles of the polarization layer in cross-flow experiments in RO. using a technique based on the variation of solution conductivity with concentration. The salts tested by these authors (NH₄NO₃, NaNO₃, NaCl, NaSO₄ and MgSO₄) included the two salts used in this study, NaCl and NaSO₄. A comparison between results from both papers is difficult: Most of the experimental data of concentration profiles in the polarization layer presented in graphical form in [1] concern the NH₄NO₃ and no profile of Na₂SO₄ is presented. On the other hand, although experimental results with NaCl are presented, they were obtained with very different experimental conditions ($\Delta p = 21.6$ atm and $Re = 137$) to those used in this research; furthermore, these conditions were not suitable for a reverse osmosis process. As the authors themselves say, "That in Figure 8 is for NaCl at sea water concentration, in this case the osmotic pressure, 35.9 atm, exceeded the pressure applied, and therefore water could be transported out the brine only because of imperfect rejection".

3.3. Comparison between experimental and theoretical results

The film theory approach is commonly used as a starting point for many simplified laws used in membrane science. It simplifies a complex transport problem to a one-dimensional mass transfer problem by assuming axial solute convection near the membrane negligible. To describe concentration polarization, one-dimensional flow and a fully-developed boundary layer is assumed. As a consequence, the relationship between concentration polarization and permeate flux can be expressed as [34]:

$$\frac{C_m - C_p}{C_o - C_p} = \exp\left(\frac{J}{k}\right) \quad (1)$$

where k is the mass transfer coefficient.

There are several empirical relationships that attempt to estimate the value of k depending on the hydrodynamics of the system. These equations are of the type:

$$Sh = \frac{k \cdot d_h}{D} = f(Re, Sc) \quad (2)$$

where Re is the Reynolds number and Sc is the Schmidt number

Mass transfer coefficient can be calculated by using the correlation of the Sherwood number for a laminar flow [34].

$$Sh^o = 1.85 \left(Re \cdot Sc \cdot \frac{d_h}{L} \right)^{0.33} \quad (3)$$

However, this correlation was developed for impermeable walls and low mass-transfer rates. Geraldes and Afonso [7] obtained a correction factor for conventional mass-transfer coefficients to account for the suction effect in nanofiltration (NF)/reverse osmosis (RO) membrane modules. They defined the correction factor as $\Xi = \frac{Sh}{Sh^o}$, where Sh is the average Sherwood number taking into account the suction effect and Sh^o is the Sherwood number at impermeable walls and low mass-transfer rates.

This correction factor depends only on the ratio $\phi = \frac{Pe}{Sh^o}$, where Pe is the permeation average Peclet number $\left(Pe = \frac{J \cdot h}{D} \right)$. Once the relation $\Xi(\phi)$ is known [7], the corrected mass transfer coefficients can be calculated and the concentration at the membrane surface obtained.

The intrinsic rejection (R) is defined by equation 4:

$$R = 1 - \frac{C_p}{C_m} \quad (4)$$

By introducing the mass transfer coefficient and the expression of the intrinsic rejection (R) in equation 1:

$$\frac{C_m}{C_o} = \frac{\exp(J/k)}{R + (1-R)\exp(J/k)} \quad (5)$$

The ratio $\frac{C_m}{C_o}$ is called the concentration polarization modulus. This ratio increases (C_m increases) as the permeate flux and the rejection rate does, or when the mass transfer

coefficient decreases. Equation (5) shows that there is a close relationship between J and R , the main parameters related to the membrane performance.

Experimental values of membrane concentration ($C_{m,e}$) have been compared with calculated membrane concentration values ($C_{m,c}$). $C_{m,c}$ has been calculated with equation (5), using experimental values of C_o , R , J , the geometrical parameters of the channel and the diffusion coefficient of the solution (D). The correction factor proposed by Geraldés and Afonso [7] was used to calculate the mass transfer coefficients, under the experimental conditions used in this work. Using the height of the channel used ($h = 3$ mm) and the permeate fluxes obtained with the pressure and CF velocity conditions applied, the Peclet number was calculated, values ranging between 1.55 and 6.03 for Na_2SO_4 solutions and between 0.98 and 4.63 for NaCl solutions. With these values of Pe and with the Sh^o values obtained with equation (3), parameter ϕ was calculated (ranging between 0.06 and 0.36). Finally, the correction factor $\Xi(\phi)$ was determined, values being in the range 1.03-1.20.

Table 2 shows, as an example, the comparison between 12 of the experimental and calculated values of concentrations at the membrane surface (C_m), corresponding to each of the three CF velocities used (0.2, 0.7 and 1.7 cm/s) in the experiments 7, 8, 16 and 17. Experimental values of R used for the calculation were obtained from the C_p measured. In all the experiments with the same solute, the mean value for R was very similar, resulting in 0.97 for Na_2SO_4 and 0.9 for NaCl .

In general, as can be observed, there is a good agreement between experimental and theoretical values with 2.0 % average error.

4. Conclusions

Digital Holographic Interferometry has proved to be a valid technique to observe the appearance and stabilization of the polarization layer. Evidence has been experimentally obtained to show that, in a crossflow reverse osmosis system, the hydrodynamics of the process has a great influence on the polarization layer.

Permeate flux drives solute to the membrane and increases the polarization layer; at the same time, fluid flow exerts a shear effect that reduces the concentration polarization layer.

Moreover, permeate flux and concentration polarization are completely dependent parameters. Thus, the contribution of solute towards the membrane increases the polarization layer and at the same time, the permeate flux is limited because of the build-up of this polarization layer.

Experimental results show a close relationship between these three significant parameters: permeate flux, polarization layer and crossflow velocity.

At high CF velocities, the number of fringes in the polarization layer decreased (and δ decreased) and permeate flux increased. This phenomenon was due to the greater shear force caused with the increase of the fluid flow. This shear force swept the solute away from the polarization layer, reducing the concentration on the membrane (C_m) and consequently, increasing the permeate flux. Moreover, the higher the CF velocity, the lesser the polarization layer thickness, because shear force itself avoided the growth of the polarization layer. Therefore, the crossflow velocity determines the thickness and concentration profiles of the polarization layer and hence, the permeate flux.

During the process, each time that the CF velocity changed, a steady state was reached after a few minutes. This period was necessary to obtain the stabilization of the polarization layer after changing the crossflow velocity. As a result, permeate flux also reached a steady value after a few minutes.

In the steady state, the number of fringes remained constant as well as their distance from the membrane surface. Furthermore, it was observed that the steady state value of the permeate flux for any velocity was independent of the previous velocities used.

On the other hand, the influence of the feed concentration on the permeate flux has been clearly proved. Independently of the crossflow velocity, the greater the feed concentration, the greater the reduction of the permeate flux. The reason is that when the feed concentration increases, so does the osmotic pressure, thus reducing the driving force and therefore, the permeate flux decreases.

The applied pressure also had an important effect on the polarization layer and the permeate flux. The lesser the applied pressure, the smaller the polarization layer thickness and the concentration in the membrane. A reduction of the concentration polarization causes a lesser resistance, thus increasing the permeate flux. However, a lesser pressure also causes the driving force to decrease. The global result of both effects is that permeate flux decreases.

In a qualitative way, no significant differences were observed with the two salts studied (NaCl and Na_2SO_4). The effect between all the significant variables studied was similar.

Nevertheless, some quantitative differences were observed as the osmotic pressure of NaCl solutions is greater than that of Na₂SO₄ solutions with the same concentration. This higher osmotic pressure caused a smaller permeate flux and consequently, the amount of solute moving to the membrane was lesser, so the polarization phenomenon was less important.

A good agreement between experimental and theoretical values of membrane concentration has been obtained.

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References

- [1] T. J. Hendricks and F. A. Williams, *Desalination* 9 (1971), pp. 155-180.
- [2] S. S. Sablani, M. F. A. Goosen, R. Al-Belushi and M. Wilf, *Desalination* 141 (2001), pp. 269-289.
- [3] L. Song and S. Yu, *AIChE J.* 45 (1999), pp. 921-928.
- [4] D.F. Fletcher and D.E. Wiley, *J. Membr. Sci.* 245 (2004), pp. 175-181.
- [5] K. Jamal, M.A. Khan and M. Kamil, *Desalination* 160 (2004), pp. 29-42.
- [6] S. Kim and E. M.V. Hoek, *Desalination* 186 (2005), pp. 111-128.
- [7] V. Geraldes and M. D. Afonso, *AIChE J.* 52 (2006), pp. 3353-3362.
- [8] A. Subramani, S. Kim and E. M.V. Hoek, *J. Membr. Sci.* 277 (2006), pp. 7-17.
- [9] R. Ghidossi, D. Veyret and P. Moulin, *Chem. Eng. Process.* 45 (2006), pp. 437-454.
- [10] A. Alexiadis, D.E. Wiley, A. Vishnoi, R.H.K. Lee, D.F. Fletcher and J. Bao, *Desalination* 217 (2007), pp. 242-250.
- [11] E. Lyster and Y. Cohen, *J. Membr. Sci.* 303 (2007), pp. 140-153.
- [12] T. H. Chong, F. S. Wong and A.G. Fane, *J. Membr. Sci.* 287 (2007), pp. 198-210.
- [13] T. H. Chong, F. S. Wong and A.G. Fane, *Desalination* 204 (2007), pp. 148-154.
- [14] S. Wardeh and H.P. Morvan, *Chem. Eng. Res. Des.* 86 (2008), pp. 1107-1116.
- [15] A. I. Cavaco Morão, A. M. Brites Alves and Vítor Geraldes, *J. Membr. Sci.* 325 (2008), pp. 580-591.
- [16] G. Chmiel and S. J. Fritz, *J. Membr. Sci.* 285 (2006), pp. 214-224.
- [17] J. Fernandez-Sempere, F. Ruiz-Bevia, R. Salcedo-Diaz and Pedro Garcia-Algado, *Ind. Eng. Chem. Res.* 45 (2006), pp. 7219-7231.
- [18] V. Chen, H. Li and A. G. Fane, *J. Membr. Sci.* 241 (2004), pp. 23-44.

- [19] M.J. Fernández-Torres, F. Ruiz-Beviá, J. Fernández-Sempere, M. López-Leiva, *AIChE J.* 44 (1998), pp. 1765-1776.
- [20] J. Fernández-Sempere, F. Ruiz-Beviá, R. Salcedo-Díaz, *J. Membr. Sci.* 229 (2004), pp. 187-197.
- [21] F. Ruiz-Beviá, J. Fernández-Sempere, R. Salcedo-Díaz, P. García-Algado, *Ind. Eng. Chem. Res.* 46 (2007), pp. 1794-1802.
- [22] J. Fernández-Sempere, F. Ruiz-Beviá, P. García-Algado, R. Salcedo-Díaz, *J. Membr. Sci.* 342 (2009), pp. 279-290.
- [23] J. Fernández-Sempere, F. Ruiz-Beviá, R. Salcedo-Díaz, P. García-Algado, *Ing. Quim.* 438 (2006), pp. 147-154.
- [24] F. Ruiz-Beviá, J. Fernández-Sempere, R. Salcedo-Díaz, P. García-Algado, *Opt. Lasers Eng.* 46 (2008), pp. 877-887.
- [25] F. Ruiz-Beviá, J. Fernández-Sempere, J. Colom-Valiente, *AIChE J.* 35 (1989), pp. 1895-1898.
- [26] J. Fernández-Sempere, F. Ruiz-Beviá, J. Colom-Valiente, F. Mas-Pérez, *J. Chem. Eng. Data* 41 (1996), pp. 47-48.
- [27] A. Anand, V. K. Chhaniwal and C. S. Narayanamurthy. *Applied Optics* 45 (2006), pp. 904-909.
- [28] J. Richter, A. Leuchter and N. Großer. *J. Mol. Liq.* 103-104 (2003), pp. 359-370.
- [29] U. Schnars and W. Juptner, *Digital holography*, Springer Verlag, Berlin Heidekberg, 2005.
- [30] S. Sourirajan, *Reverse Osmosis*; Academic Press: New York, 1970.
- [31] R. H. Perry, W. D. Green, *Perry's Chemical Engineers' Handbook*, (7th Ed.), McGraw-Hill: New York, 1997.
- [32] G. B. Van den Berg and C. A. Smolders, *Desalination* 77 (1990), pp. 101-133.
- [33] C. Rosén, and C. Trägårdh, *J. Membr. Sci.* 85 (1993), pp. 139-156.

[34] M. Mulder, Basic Principles of Membrane Technology, Kluwer Academic Publishers, Dordrecht, 1991, pp. 281-289.

Figure captions

Figure 1. Schematic concentration profiles: a) unstirred batch cell at three different times; b) crossflow cell at steady state

Figure 2. Digital holographic interferometry set-up.

Figure 3. Reverse osmosis crossflow system: (1) pump; (2) feed and water tanks; (3) RO module; (4) pressure gauge; (5) rotameter, (6) regulation valve; (7) conductivity probe; (8) balance; (9) conductimeter; (10) computer.

Figure 4. Permeate flux, interferograms and concentration profiles for each CF velocity used (experiment 8).

Figure 5. Permeate flux of Na_2SO_4 experiments at 6 bar with different feed concentration (*Up Series*).

Figure 6. Permeate flux of Na_2SO_4 experiments at 7.2 bar with different feed concentration (*Up Series*).

Figure 7. Permeate flux of Na_2SO_4 experiments at 6 bar with different feed concentration (*Down Series*).

Figure 8. Comparison between permeate flux of *Up and Down Series* in experiments with the same pressure and feed concentration (6 bar; 5 kg/m^3).

Figure 9. Permeate flux, interferograms and concentration profiles for each CF velocity used (experiment 1).

Figure 10. Permeate flux, interferograms and concentration profiles for each CF velocity used (experiment 17).

Figure 11. Permeate flux of NaCl experiments at 6 bar with different feed concentration (*Up Series*).

Figure 12. Permeate flux of NaCl experiments at 7.2 bar with different feed concentration (*Up Series*).

Tables

Table 1. Experiments carried out

Salt	Series	Experiment	C_o (kg/m ³)	ΔP (bar)
Na ₂ SO ₄	<i>Up series</i>	1	3.5	6
		2		7.2
		3	5	6
		4		7.2
		5	7	6
		6		7.2
		7	8.5	6
		8		7.2
	<i>Down series</i>	9	3.5	6
		10	5	6
		11	7	6
NaCl	<i>Up series</i>	12	3.5	6
		13		7.2
		14	5	6
		15		7.2
		16	7	6
		17		7.2

Table 2. Comparison between experimental and calculated values of C_m

Experiment n ^o	CF velocity (cm/s)	$C_{m,e}$ (kg/m ³)	$C_{m,c}$ (kg/m ³)
7	0.2	10.25	9.842
	0.7	9.84	9.68
	1.7	9.43	9.50
8	0.2	11.07	10.49

	0.7	10.25	10.21
	1.7	9.84	10.14
16	0.2	7.79	7.71
	0.7	7.43	7.49
	1.7	7.43	7.43
17	0.2	8.34	8.35
	0.7	7.99	8.12
	1.7	7.99	8.04