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Digital holographic interferometry visualization of PEG-10000 accumulation on an acetate cellulose membrane: assessment of polarization layer and adsorption phenomenon

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ABSTRACT

PEG-10000 accumulation on a cellulose acetate membrane was studied with digital holographic interferometry to determine if it was a reversible adsorption phenomenon. This optical technique allows concentration differences to be seen as interference fringes. Firstly, an inert and impervious surface was assessed in place of the membrane. When pressure was applied, no fringes appeared thus indicating there was no concentration gradient near the membrane surface. Therefore, no adsorption had occurred, pointing out that pressure did not necessarily generate a deposition of PEG-10000. In a second test, it was checked if adsorption could occur if only the solution was in contact with the acetate cellulose membrane, without pressure. As no fringes appeared, there was no adsorption on that surface. In the last test, a silicon sheet was placed under the membrane to prevent permeate flux when pressure was applied to the solution. A continuous appearance of fringes was observed, indicating a concentration distribution near the membrane surface. Since there was no permeate flux, the built-up of the concentration polarization layer was avoided. Therefore, the change in the concentration was due to a continuous deposition of solute on the membrane. In conclusion, the interaction of PEG-10000 and a cellulose acetate membrane when pressure is applied causes a reversible accumulation or adsorption of solute in the membrane, a phenomenon that simultaneously occurs with the accumulation of solute in the polarization layer.

Keywords: Reversible adsorption; Polarization; Visualization; Polyethylene glycol; Acetate cellulose membrane; Digital holographic interferometry

1. Introduction

Solute accumulation on the membrane surface during ultrafiltration (UF) processes can be caused by either concentration polarization (solute retained on the membrane) or fouling phenomena such as adsorption and pore blocking [1]. Both mechanisms lead to a reduction in the permeate flux and therefore, in the performance of the process. Gaining a better knowledge of these mechanisms can help in the design of membranes and filtration equipment.

A critical review on several aspects of the concentration polarization in UF and reverse osmosis (RO) was made by Sablani et al. [2]. In recent papers, several authors have used more or less complicated models trying to predict the reduction on the permeate flux in

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UF of polyethylene glycol (PEG) [3,4], Dextran [5] and bovine serum albumin (BSA) [6]. These models apply different mechanisms to explain the accumulation of solute on the membrane.

Another important issue in UF is how the fouling phenomenon is affected by the concentration polarization [7], and how that fouling phenomenon, which in some cases is irreversible and others reversible, occurs. Bacchin et al. proposed a unifying model for concentration polarization, gel layer formation and particle deposition in cross-flow membrane filtration of colloidal suspensions [8]. In their conclusions, the authors state a distinction between two possible mechanisms for the formation of irreversible layers: a gelation mechanism, which forms a loose layer simultaneously across the membrane, and a deposition mechanism, consisting on a formation of a compact deposit growing progressively from the outlet to the inlet of the membrane device. Churaev et al. studied dead-end UF of PEG of different molecular weights and found that experimental data were reproducible and, most importantly, adsorption was reversible [9].

In dead-end UF, models can theoretically predict the evolution with time of the solute concentration profiles in the vicinity of the membrane surface [10,11]. Unfortunately, they are not usually accompanied by a comparison with experimental results which could be used to validate the model. A shortage of knowledge about the polarized layer is mainly due to the experimental difficulties associated with making concentration profile determinations within a very thin layer. Chen et al. made a review of non-invasive experimental methods for the observation in-situ and in real-time of membrane processes, providing examples of their use and limitations for liquid-based membrane processes [12]. Holographic interferometry is one of these methods.

Holographic interferometry (HI) is an optical technique that allows visualizing changes in the refractive index of a solution as interference fringes. In the UF process, solute retained by the membrane (the polarization layer) causes a concentration gradient or a concentration profile, resulting in a variation of the refractive index of the solution. As a consequence, this concentration gradient will be seen as an interference fringe pattern. This technique has been used in previous papers, to visualize the appearance, evolution with time and disappearance of the concentration polarization layer during UF of BSA and PEG-2000 solutions [13,14], as well as RO of salts [15,16].

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 [17,18] as well as in the study of a crossflow reverses osmosis process [19]. The methodology for the digital reconstruction of the interferograms may vary depending on the process to be studied. By means of the electronic speckle pattern interferometry (ESPI, DSPI or also TV Holography) 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 HI [20].

In a recent paper, PEG-10000 accumulation on the surface of a cellulose acetate membrane was studied [21]. Results have shown evidence of a combination of both accumulation mechanisms: polarization layer formation and solute adsorption Fig. 1. Concentration polarization causes an increase of concentration, from the feed concentration (C_o) to the concentration in the membrane (C_m), in a boundary layer of thickness δ. Solute adsorption avoids a great increase in C_m as solute accumulates on the membrane, forming successive layers of solute deposited over each other (physical adsorption).

Solute accumulated in the polarization layer is still in solution and was directly visualized as interference fringes by HI [21]. Solute adsorpted was deposited on the membrane and no direct measurement was obtained. However, the adsorption phenomenon was indirectly observed through two ways by Fernández-Sempere et al. [21]. On the one hand, calculating the solute mass balance in the polarization layer, it was found that it was not fulfilled, as the amount of solute provided to the membrane by convection was greater than that accumulated in the polarization layer. Because of this inequality, it was assumed that the amount of

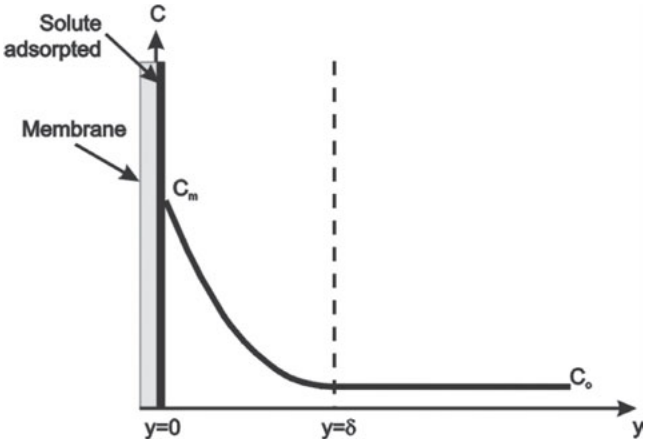

Fig. 1. Concentration polarization and solute adsorption on a membrane surface.

solute that does not close the balance was deposited or adsorpted on the membrane surface. Secondly, when pressure ceased, the appearance of new interference fringes near the membrane surface during the first minutes was observed. These fringes indicated that the polarization layer was growing, that is the amount of solute in solution was increasing. Moreover, since the fringes appeared on the membrane surface, the solute was moving from the membrane to the solution. Therefore, it was assumed that the solute was coming from the deposited or adsorpted layer on the membrane surface.

Fernández-Sempere et al. noted that these two phenomena were complementary [21]. The amount of solute that did not fulfil the mass balance, theoretically deposited on the membrane, was later observed, when the pressure ceased, as a new interference fringe pattern in the polarization layer. It was observed that the adsorpted layer was reversible, because when the driving force (the pressure) ceased, the solute deposited on the membrane surface disappeared. A totally reversible adsorption occurs when it is physical, that is an adsorption that takes place without any chemical solute–membrane interaction. It consists of a deposition of solute in consecutive layers on the membrane surface.

The aim of the current research was to check the influence of the variables that can cause this physical adsorption apart from the transmembrane flux, that is pressure and solute–membrane interaction.

2. Methodology

2.1. Equipment

The experimental assembly was made up of an optical system (DHI) and an UF system, coupled on the same work table. The UF set up could be easily adapted for the adsorption experiments. The common element to both systems was the UF cell, specially designed to carry out the UF or adsorption process satisfying the HI requirements.

The DHI optical set-up was described in a previous paper [19], using the CCD chip of a video camera as the holographic recording media. The UF system was also described in a previous paper [21]. The UF cell, provided with two windows thus allowing the membrane surface to be visualized, was horizontally placed on the optical table with the membrane surface facing upward. The UF cell used was also explained in a previous paper [22]. The active membrane dimensions were 10 × 1 cm with a 10 cm^2 effective area, a size chosen to satisfy the interferometric requirements. The distance from the membrane surface to the top of the cell was 40 mm, so the volume of solution in the cell was large enough to guarantee that concentration changes inside the cell would only take place near the membrane. Therefore, far from the membrane surface, the bulk concentration (C_o) remained unchanged during the process.

2.2. Materials

A cellulose acetate membrane, YC05 from Millipore with nominal molecular weight limit (NMWL) 500, was used. Suitable pieces for the size of the cell used were cut from the whole membrane. As each piece of membrane was used for several runs, after each experiment the membrane was washed, in cross-flow, with water flowing through the UF module until the solute was completely removed from the membrane surface.

In order to test the effect of the pressure without the membrane, pieces of an impervious and inert plastic were used. The plastic piece was cut to suit the cell space.

To study the effect of the feed concentration on the solute adsorption, the experiments were carried out using solutions of PEG-10000 (Sigma) with two different initial concentrations (C_o): 5 and 12.5 kg m^{-3}.

2.3. Experimental

Three different sets of experiments were developed to confirm the influence of the pressure applied and the material of the membrane. In the first one, pressure was applied to the solution but, instead of the membrane, an inert and impervious surface was used. In the second test, the cell with the membrane was filled with the solution and no pressure was applied. In the last set of experiments, pressure was applied to the solution after placing, under the membrane, a silicon sheet to prevent the permeate flux. The appearance of interference fringes in each experiment would indicate a concentration gradient, showing that solute was adsorpted on the membrane surface.

Adsorption experiments of PEG-10000 were carried out using two different feed concentrations (5 and 12.5 kg m^{-3}). All the experiments were performed in batch conditions applying three different pressures (1, 2 and 3 bar). Prior to each experiment, the system and the membrane were washed five times with water flowing through the module, in crossflow. After these washing runs and with the system filled of water, a pressure of 2 bar was applied to clean the membrane pores. The membrane was considered to be damaged when the water permeate flux decreased more than a 10% of the permeate flux before any experiment. Therefore, membrane was replaced.

Once the membrane was cleaned, the cell was aligned with the optical system, it was filled with the PEG solution and the solution remained in circulation for a few minutes. Then, the hologram capture program was started thus beginning the calculation of the interferograms. The methodology to obtain the interferograms was explained in a previous paper [19]. However, since the hologram is the reference state of the system without undergoing any change, in the second experiments with no pressure, the hologram was recorded before filling the system, to take the empty module as a reference state.

After that, depending on the experiment, the cell was filled or the pressure was applied and the changes in the concentration of the solute near the membrane surface (C_m) began. A decrease of C_m occurred and so did the refraction index, causing the appearance of interference fringes when comparing the actual state (with a different concentration distribution) and the reference state (the hologram). Each interference fringe corresponds to a concentration step in the solution. The methodology to obtain the concentration profiles from the interferograms has been previously described [13]. In this paper, from one interference fringe to the next one, the concentration change of PEG-10000 is 0.48 kg m^{-3}.

After 1 h of experiment, pressure was removed and the interference fringes began to disappear.

3. Results and discussion

3.1. Experiments with pressure and an impervious surface instead the acetate cellulose membrane

The first experiment was carried out to check if the pressure causes a deposition of PEG-10000 in every surface in contact. Therefore, instead of the acetate cellulose membrane, an inert and impervious surface was placed in contact with the solution. This surface avoided adsorption of solute and, consequently, no concentration distribution near the membrane (no interference fringes) should appear.

As expected, the PEG-10000 solution was pressurized but no fringes appeared, indicating that there was no concentration gradient near the membrane. This result indicated that pressure do not necessarily generates a deposition of PEG-10000 on the surface that is in contact with; it depends on the type of surface.

3.2. Experiments with no pressure and the acetate cellulose membrane

A second test was carried out to clarify whether interaction between PEG-100000 and the acetate cellulose

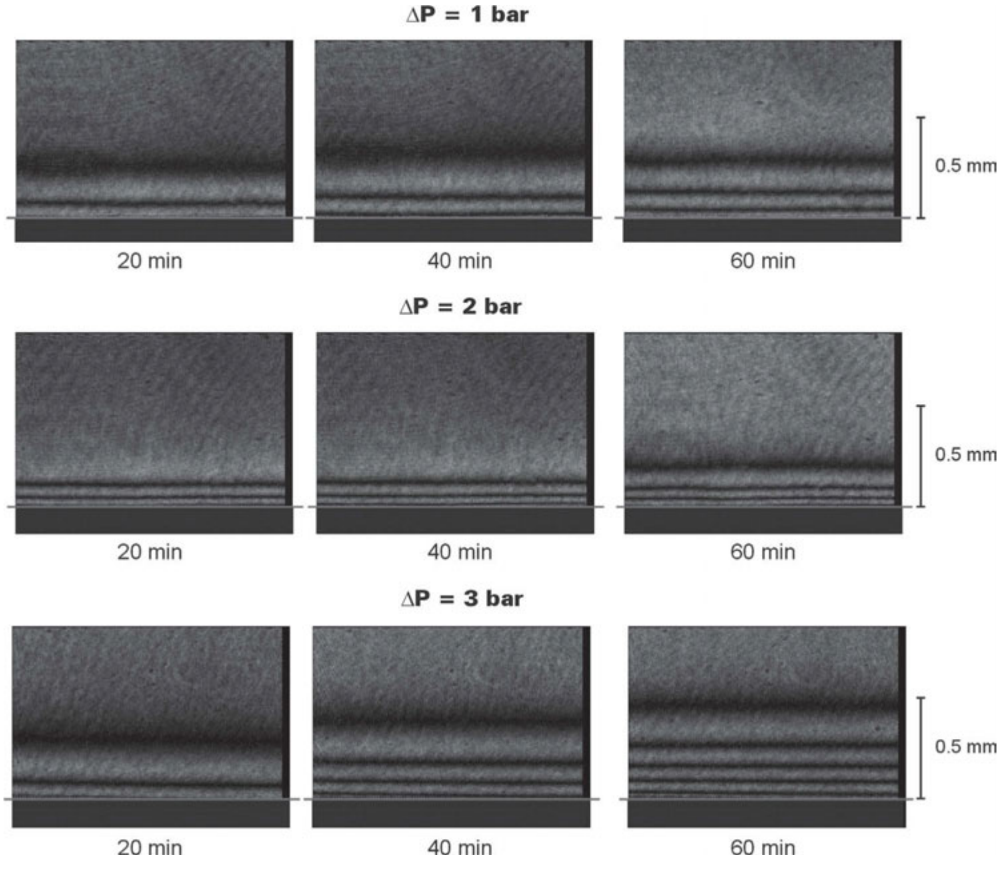

Fig. 2. Interferograms at 20, 40 and 60 min of the experiment with $C_o = 5$ kg m^{-3} for each pressure applied.

membrane causes necessarily the adsorption of solute, regardless of the applied pressure. Then, this experiment was to check any change in the concentration on the membrane surface just when the solution reached the membrane, without pressure. This phenomenon would have shown that there was an interaction membrane-solute that caused the adsorption of the solute on the membrane with no pressure. The change in C_m could have been seen with the appearance of fringes near the membrane.

Since the empty module was the reference state, the filling of the system should have done very carefully, to avoid any agitation of the solution that would lead to the appearance of fringes spurious to the adsorption process. When the cell was filled without pressure no fringes were visualized, thus indicating that concentration had not changed. Then, there was no chemical interaction between the membrane and PEG-10000, which caused the adsorption of solute on the acetate cellulose membrane.

3.3. Experiments with pressure (1–3 bar) and the acetate cellulose membrane

Finally, a third set of experiments similar to previous one were performed, but pressure was applied to the solution to check its influence in the deposition of solute. The acetate cellulose membrane and PEG-10000 were used and pressure was applied. Moreover, a silicon sheet was placed under the membrane to prevent the permeate flux. In this way, the convective flux of solute into the membrane was also prevented and the built-up of the concentration polarization layer was avoided. Therefore, the appearance of fringes indicating a concentration distribution would not have been caused by the solute accumulated in the polarization layer, but only by the deposition of solute on the membrane surface.

Interferograms at 20, 40 and 60 min, corresponding to each pressure applied and both feed concentrations used (5 and 12.5 kg m^{-3}) are shown in Figs. 2 and 3.

All these experiments, regardless of the pressure applied, showed a continuous appearance of fringes, indicating that a concentration decrease was taking place. A few minutes after the pressure was applied, some interference fringes near the membrane surface appeared. The amount of fringes continuously increased throughout the process, thus indicating that concentration at the membrane surface (C_m) was decreasing because of the solute adsorption. Moreover, the thickness (δ) of the layer, where concentration was not homogeneous, increased.

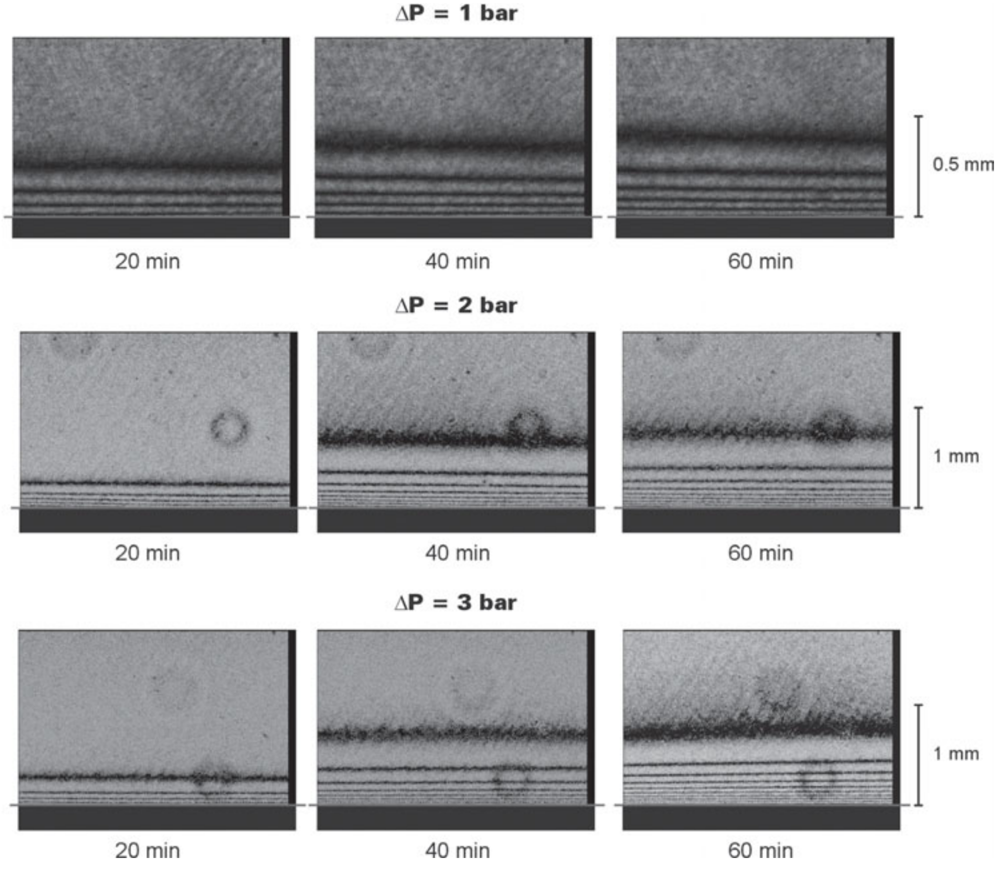

Fig. 3. Interferograms at 20, 40 and 60 min of the experiment with C_o = 12.5 kg m^{-3} for each pressure applied.

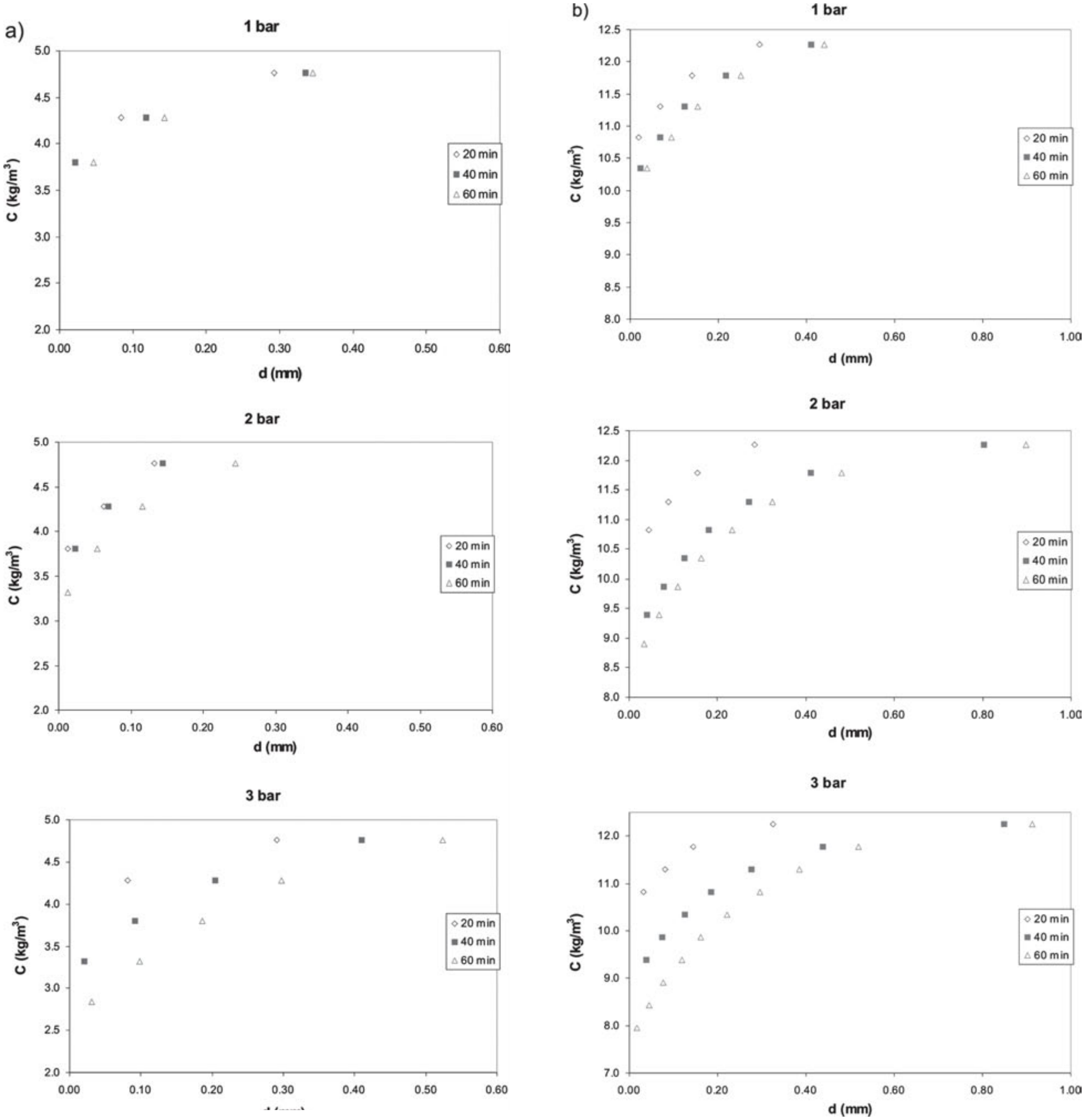

Fig. 4. (a) Concentration profiles at 20, 40 and 60 min for the experiment with C_o = 5 kg m^{-3}. (b) Concentration profiles at 20, 40 and 60 min for the experiment with C_o = 12.5 kg/m^3.

During the first minutes of the experiment, the rate of appearance of new interference fringes was relatively high. Later on, this rate decreased and nearly stopped. It can be seen that the last two interferograms (at 40 and 60 min) are very similar for all the experiments. For example, with a pressure of 1 bar and an initial concentration of 5 kg m^{-3}, at 20 min there were two fringes, that increased only to three fringes at 40 and 60 min. Using a greater feed concentration, the evolution is more evident. When C_o = 12.5 kg m^{-3} and pressure is 2 bar, the number of fringes was 4, 7 and 8 (at 20, 40 and 60 min, respectively). This behaviour points out that the amount of solute adsorpted is reaching a limit, which can be caused by two phenomena. On the one hand, membrane could be nearly saturated of solute and, on the other hand, the fall of C_m leads to a decrease in the driving force for the deposition, and consequently the rate of adsorption decreases.

A similar behaviour of the polarization layer thickness can be observed in Figs. 2 and 3, it rapidly increased during 30 min and then increased more slowly. The growth of the thickness of the inhomogeneous layer shows that the deposition process is faster than the diffusion of the solute from the bulk solution to the membrane.

Figs. 4a and b show the concentration profiles corresponding to the interferograms from Figs. 2 and 3, respectively. It can be observed that, in the first part of the experiment, concentration decreased considerably; then, the decline was slower. When $C_o = 12.5$ kg m^{-3} and $\Delta P = 2$ bar, concentration on the membrane decreases to 10.5, 9.2 and 8.5 kg m^{-3} after 20, 40 and 60 min of experiment, respectively. Likewise, thickness of the inhomogeneous layer increased faster in the first minutes (δ was 0.3 mm at 20 min), whereas at 40 and 60 min was almost equal (δ ~ 0.85 mm).

The effect of the initial concentration can also be observed. The higher the feed concentration, the greater the decrease of the concentration in the membrane. When $\Delta P = 3$ bar, at 60 min, concentration on the membrane is 2.5 kg m^{-3} when C_o is 5 kg m^{-3}, and 7.5 kg m^{-3} when C_o is 12.5 kg m^{-3}. This phenomenon points out that a higher C_o causes greater deposition of solute on the membrane surface. Therefore, the driving force for the deposition is related to the concentration near the membrane (C_m) and as a consequence saturation concentration is related to the concentration in the bulk solution.

The effect of the initial concentration on the inhomogeneous layer thickness is similar. The higher the feed concentration, the greater the layer thickness. When $\Delta P = 3$ bar, δ is 0.55 mm for $C_o = 5$ kg m^{-3}, and 0.90 mm for $C_o = 12.5$ kg m^{-3}.

Finally, the effect of the pressure applied on C_m and δ is similar than the effect of the initial concentration. Then, a higher pressure causes an increase in the inhomogeneous layer thickness and an increase of the solute adsorpted (C_m decreases). Therefore, the saturation concentration or the driving force for the adsorption process is also related to the pressure applied.

In all the experiments, when pressure ceased, the interference fringes began to disappear. The disappearance of the interference fringes showed that the concentration distribution near the membrane was disappearing, that is, the solute deposited on the membrane was coming back to the bulk solution. Therefore, the adsorption process was reversible.

4. Conclusions

When pressure was applied to a system were a silicon sheet was placed under the membrane, to prevent the permeate flux, concentration changes (visualized as interference fringes) were observed. This suggested that the concentration changes observed were exclusively due to solute deposition. The interference fringes disappeared once the pressure ceased, suggesting that adsorption is a physical and reversible phenomenon. When the inert surface was used, in place of the membrane, no fringes appeared, indicating that pressure did not cause deposition of PEG-10000 on the inert surface.

In the experiments using a cellulose acetate membrane, the higher the pressure applied, the more fringes appeared, thus indicating more solute adsorption. Likewise, the higher the feed concentration, the more solute deposited. Therefore, this physical adsorption depends on the pressure applied and on the membrane concentration. In fact, the adsorption rate decreased as the experiment went on. This behaviour could be caused by two phenomena: membrane could be nearly saturated of solute, and the fall of C_m because of the solute adsorption would lead to a decrease in the driving force for the deposition.

It was concluded that the interaction PEG-10000 and cellulose acetate membrane, with a certain pressure, causes a reversible accumulation or adsorption of solute in the membrane, which occurs simultaneously to the accumulation of solute in the polarization layer.

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References

[1] G.B. Van den Berg and C.A. Smolders, Flux decline in ultrafiltration processes, Desalination, 77 (1990) 101–133.
[2] S.S. Sablani, M.F.A. Goosen, R. Al-Belushi and M. Wilf, Concentration polarization in ultrafiltration and reverse osmosis: a critical review, Desalination, 141 (2001) 269–289.
[3] C. Bhattacharjee and S.Datta, Analysis of polarized layer resistance during ultrafiltration of PEG-6000: an approach based on filtration theory, Sep. Purif. Technol., 33 (2003) 115–126.
[4] M. Cinta Vincent-Vela, S. Álvarez-Blanco, J. Lora-García and E. Bergantiños-Rodríguez, Prediction of ultrafiltration permeate flux decline by means of a shear induced diffusion model with empirical estimation of the gel layer concentration, Desalin. Water Treat., 10 (2009) 139–143.
[5] J.P.F. De Bruijn, F.N. Salazar and R. Bohórquez, Membrane blocking in ultrafiltration. A new approach to fouling, Food Bioprod. Process., 83 (C3) (2005) 211–219.
[6] R. Ghosh and D.M. Kanani, A constant flux based mathematical model for predicting permeate flux decline in constant pressure protein ultrafiltration, J. Membr. Sci., 290 (2007) 207–215.
[7] S. Vulf, I. Sutzkover-Gutman, D. Hasson and R. Semiat, Effect of the concentration polarization on the fouling driving force of UF membranes, Desalin. Water Treat., 31 (2011) 54–58.
[8] P. Bacchin, D. Si-Hassen, V. Starov, M.J. Clifton and P. Aimar, A unifying model for concentration polarization, gel-layer

formation and particle deposition in crossflow membrane filtration of colloidal suspensions, Chem. Eng. Sci., 57 (2002) 77–91.

[9] N.V. Churaev, R.G. Holdich, P.P. Prokopovich, V.M. Starov and S.L. Vasin, Reversible adsorption inside pores of ultrafiltration membranes, J. Colloid Interface Sci., 288 (2005) 205–212.

[10] S. Nicolas, I. Boulanouar and B. Balou, Unstirred dead-end ultrafiltration: a method to determine diffusion coefficient or osmotic pressure for non-charged macromolecular solutions, J. Membr. Sci., 103 (1995) 19–30.

[11] C. Bhattacharjee, A numerical simulation for the prediction of flux and rejection during ultrafiltration in unstirred batch cell using variable diffusivity concept, Sep. Purif. Technol., 24 (2001) 13–22.

[12] V. Chen, H. Li and A.G. Fane, Non-invasive observation of synthetic membrane processes – a review of methods, J. Membr. Sci., 241 (2004) 23–44.

[13] M.J. Fernández-Torres, F. Ruiz-Beviá, J. Fernández-Sempere and M. López-Leiva, Visualization of the UF polarizad Layer by holographic interferometry, AIChE J., 44 (1998) 1765–1776.

[14] J. Fernández-Sempere, F. Ruiz-Beviá and R. Salcedo-Díaz, Measurements by holographic interferometry of concentration profiles in dead-end ultrafiltration of polyethylene glycol solutions, J. Membr. Sci., 229 (2004) 187–197.

[15] J. Fernández-Sempere, F. Ruiz-Beviá, R. Salcedo-Díaz and P. García-Algado, Measurements of concentration profiles by holographic interferometry and modelling in unstirred batch reverse osmosis, Ind. Eng. Chem. Res., 45 (2006) 7219–7231.

[16] J. Fernández-Sempere, F. Ruiz-Bevia, R. Salcedo-Díaz and P. García-Algado, Diffusion studies in polarized reverse osmosis processes by holographic interferometry, Opt. Lasers Eng., 46 (2008) 877–887.

[17] A. Anand, V. K. Chhaniwal and C. S. Narayanamurthy, Diffusivity studies of transparent liquid solutions by use of digital holographic interferometry, Appl. Opt., 45 (2006) 904–909.

[18] C. Wylock, S. Dehaeck, T. Cartage, P. Colinet and B. Haut, Experimental study of gas–liquid mass transfer coupled with chemical reactions by digital holographic interferometry, Chem. Eng. Sci., 66 (2011) 3400–3412.

[19] J. Fernández-Sempere, F. Ruiz-Beviá, P. García-Algado and R. Salcedo-Díaz, Experimental study of concentration polarization in a crossflow reverse osmosis system using digital holographic interferometry, Desalination, 257 (2010) 36–45.

[20] U. Schnars and W. Jüptner, Digital Holography, Springer Verlag, Berlin Heidekberg, 2005.

[21] J. Fernández-Sempere, F. Ruiz-Beviá, P. García-Algado and R. Salcedo-Díaz, Visualization and modelling of the polarization layer and a reversible adsorption process in PEG-10000 dead-end ultrafiltration, J. Membr. Sci., 342 (2009) 279–290.

[22] J. Fernández-Sempere, F. Ruiz-Beviá, R. Salcedo-Díaz and P. García-Algado, Equipo experimental para visualizar la formación de la capa de polarización durante el proceso de ósmosis inversa, Ing. Quim., 438 (2006) 147–154.