Tailoring the Selective Permeation of Asymmetric Cellulose Acetate/Silica Hybrid Membranes by Pos-Formation Treatments

M. P. da Silva[1, 2] and M. N. de Pinho[1, 2]

[1] *Departamento de Engenharia Química (DEQ), Instituto Superior Técnico, Universidade de Lisboa, Lisbon, Portugal*
[2] *Centro de Física e Engenharia de Materiais Avançados (CeFEMA), Instituto Superior Técnico, Universidade de Lisboa, Lisbon, Portugal*

November 2019

Abstract

The cellulose acetate (CA) membranes, developed in the early 1960s by Loeb and Sourirajan for sea water desalination, are prepared by the wet phase inversion method which is responsible for creating an asymmetric structure. The structure is composed of a thin skin dense layer that determines the membrane selective characteristics and a porous sublayer providing mechanical support. The wet phase inversion method allows the synthesis of asymmetric membranes, from a myriad of polymers, with a diverseness of structures accountable for a broad spectrum of separation characteristics. Hence, the specific selective permeation properties of a membrane can be tailored through the formulation of the casting solutions conditions—in the polymer/solvent system—and control of the casting parameters—evaporation time and coagulation media. This versatility allows the synthesis of hybrid membranes of CA and silica (SiO_2), CA/SiO_2 membranes, by coupling the wet phase inversion with the sol-gel techniques. The present work addresses the synthesis of hybrid CA/SiO_2 membranes, which are submitted to a solvent exchange pos-formation treatment. The assessment of the effect of pos-treatment on membrane structure modification is performed by the membrane's characterisation in term of (1) selective permeation properties: hydraulic permeability, rejection to salts and neutral macro molecules, molecular weight cut-off and mean pore size; and (2) water order and dynamics by NMR. In conclusion, the pos-treatment by solvent exchange caused a shrinkage of the membrane porous structure leading to different permeation characteristics than those of untreated membranes.

Keywords: Cellulose Acetate; Asymmetric Membrane; Mixed Matrix Membrane; Characterisation of Selective Permeation Properties; NMR; Membrane Pos-Formation Treatments

1 Introduction

The development of cellulose acetate (CA) membranes for sea water desalination by Loeb and Sourirajan [1], in the early 1960s, was a technological breakthrough in the field of synthetic membranes that endorsed the widespread implementation of membrane technology in industrial processes. Its contribution, alongside the development of membrane modular configurations, set the stage for the industrial scale-up of reverse osmosis (RO) and made possible the implementation, at a large scale, of other pressure-driven membrane processes such as ultrafiltration (UF) and nanofiltration (NF)[2, 3]. These membranes are prepared by the wet phase inversion method [4] which is responsible for creating an asymmetric structure. The structure is composed of a thin skin dense layer that determines the membrane selective characteristics and a porous sublayer which provides mechanical support [2, 3]. The wet phase inversion method allows the synthesis of asymmetric membranes, from a myriad of polymers, with a diverseness of structures accountable for a broad spectrum of separation characteristics. Hence, the specific selective permeation properties of a membrane can be tailored through the formulation of the casting solutions composition — in the polymer/solvent system — and control of the casting parameters — evapora-

tion time and coagulation media [2].

This versatility allows the synthesis of hybrid membranes of CA and silica (SiO_2), CA/SiO_2 membranes [5], by coupling the wet phase inversion [4] with the sol-gel [6] techniques. The addition to the casting solution, CA/solvent system, of a SiO_2 precursor promotes the *in situ* condensation between silanols from the SiO_2 precursors and the C–OH or acetate groups from the CA polymer, resulting in monophasic CA/SiO_2 asymmetric hybrid membranes [5].

Moreover, the selective separation characteristics of a membrane are essentially attributed to molecular sieving mechanisms and solute(s)/solvent/membrane interactions in UF, and diffusion mechanisms in RO. However, in NF, the transport mechanisms are attributed not only to size exclusion mechanisms, but also to the solution-diffusion mechanism, solute(s)/solvent/membrane interactions and to membrane surface charge mechanisms [7, 8]. However, these separation mechanisms are not only determined by the structure of the active layer but also by the characteristics of the water clusters in their pores and of the polymer hydrophobicity/hydrophilicity [9].

It is generally considered that adsorbed water in membrane pores exhibit distinct structures: monomeric, weakly or strongly H–bonded clusters [9]. Specifically for asymmetric CA membranes, it has been observed that the relative amount of water existent in the active layer depends on the inherent skin layer morphology. Meaning that more permeable asymmetric membranes, in the UF range, contain more water when compared to less permeable NF/RO asymmetric membranes [10]. In addition, lightly clustered water species, weakly H–bonded to the polymer hydroxyl groups are predominant in the skin layer of RO membranes whereas the UF membranes mainly contain bulk-like water clusters [10]. This influence of the state of water demonstrates that a low degree of formation of clusters in the pores of membranes leads to weak solubility of salts in it and, therefore, to low permeability of the ions through the membrane [9, 11, 12].

Hydrophilic membranes, such as CA, synthesised *via* the wet phase inversion process, using water as a precipitating agent, have normally higher water content than membranes produced by other techniques [13, 14]. This state of water within the membrane is responsible both for water permeation and for solute rejection during pressure-driven membrane processes [12, 14].

In many cases the behaviour of the membranes will change upon dehydration, as observed for wet (or as cast) CA based membranes [14, 15]. The water within the CA membranes structures cannot be allowed to evaporate in air, under ambient conditions, because the asymmetric structure collapses [3, 16, 17]. During ambient drying, the membrane porosity is grossly reduced because, as the surface tension forces between the water and the polymer are strong, the water clusters within the membrane decrease in size and the pores around them collapse [15, 18]. As a result, CA membranes that undergo direct water evaporation suffer a nonrecoverable loss in permselectivity and in physical properties with increasing drying time [15]. To avoid this loss in performance due to water evaporation, several pos-treatments aimed to replace water in the membranes by water-soluble substances [15, 19] or by replacing the water completely [20].

However, membrane pos-treatments can serve very distinct purposes. For instance, a treatment that is commonly employed to CA membranes is thermal annealing [21, 22, 23]. This thermal pos-treatment is known to result in the densification of the porous structure of CA membranes [24]. By doing so, the permselectivity of the membrane is enhanced but, as a trade-off, the water permeation fluxes are decreased. The CA membranes are well known for their high selectivity, hydrophilic and high solubility characteristics in organic solvents and for their widespread application not only in RO and UF but also in gas separation (GS) [16, 25]. Generally, the synthesised (as cast) membranes must be dried before being used in GS operations [3]. CA membranes, when dried in a way to preserve their porosity and the surface pore structure, show high permeation rates and significant separation efficiency for gaseous mixtures [17, 20]. In that regard, the multiphase solvent exchange pos-treatment was developed by Lui et al. [20] to slow down the drastic changes in capillary forces that occur inside the membrane pores and, this way, avoid the collpase of the membrane porous structure.

In the multiphase solvent exchange technique, the water in the membrane is replaced by a water-soluble first solvent that is nonsolvent for the membrane material. The first solvent is then replaced by a second solvent that is volatile. The second solvent is subsequently air evaporated to obtain the dry membrane.

Lui et al. [20] studied the effect of the first and second solvent on the pore size at each step of solvent exchange and, ultimately, on the pore sizes of the dry membrane that was obtained.

Conversely, Vos and Burris [15] studied the outcome of soaking CA reverse osmosis membranes in aqueous solutions of different (non-ionic, anionic and cationic) surface active agents in their physical properties - such as appearance, brittleness and surface tension - and desalination properties – rejection to NaCl and pure water permeation fluxes. A method of reducing the interaction between the CA polymer matrix and the water, without collapsing the membrane pores, is to depress the surface tension of the pore water – i.e., the surface tension of the system CA-water-air. Regarding that, the study evaluated the concentration of surfactant in the immersion aqueous solution that upon obtaining a dry membrane, when re-wet and tested, would perform adequately. Despite this, membranes dried with most of the surface active agents exhibited loss in their physical properties, such as increased brittleness. To prevent this outcome, substances acting as plasticisers were introduced in the conditioning solution. It was also reported that the addition of these substances, such as glycerol or ethylene glycol, up to 60% (V/V%), increased the membranes hydraulic permeability (between 10 to 20%) at no expense to the salt rejection. Notably, glycerol is also considered as a surface active agent because it depresses the surface tension of water [26]. In addition to that, the experimental results revealed that the membranes treated with surfactant solutions containing a plasticiser content of 20% (V/V%) presented slightly higher hydraulic permeability and rejection to NaCl.

Later on, van Oss and Bronson [19] applied a drying pos-treatment on CA membranes for UF application in haemodialysis. Drying was made possible with prior impregnation of the membrane in aqueous solutions of 50% (V/V%) glycerol. A reported outcome of this treatment is the reduction of 20-25% of the membrane flux after drying. Glycerol has been further used as a surface coating agent either to prepare CA membranes for air drying [22, 14, 27, 28] to modify the surface of PVDF membranes [44], [198], or enhance the hydrophilicity of PES (UF) membranes [199]. A hydrophilic layer can be simply coated on the hydrophobic PVDF membrane surface to enhance both hydrophilicity and fouling resistance. This coating momentarily preserves the wettability of the membrane during transportation and storage and is, usually, washed away before operation [29, 30].

The process of membrane synthesis by phase inversion and its underlying mechanisms is not yet completely understood [31]. In fact, this technique is still rooted in empiricism. Additionally, some membrane posformation treatments are employed to further tune the membranes to a specific mass transfer task. Regarding that, treatments like thermal annealing [24], that result in the densification of the CA membranes porous structure, or solvent exchange [20], that is applied to prepare CA membranes to be used in gas separations, are used. Conversely, conditioning with surfactant mixtures [15], particularly glycerol, are employed in an attempt to conserve the membrane structure. These pos-formation treatments are also empiric and lack understanding.

In this study, the effect of the solvent exchange postreatment on asymmetric CA/SiO_2 membranes structure is investigated. This assessment is carried out by evaluating the selective permeation properties of treated membranes, in comparison to untreated ones, as well as the water order and dynamics within the porous structures in treated membranes by NMR [32].

2 Materials and Methods

2.1 Materials

The asymmetric CA/SiO_2 hybrid membranes were prepared with cellulose acetate ($C_6H_7O_2(OH)_3$, $\sim 30.000\, g\, mol^{-1}$, $\geq 97\%$, acetyl content 38.9%) supplied by Sigma-Aldrich, tetraethyl orthosilicate (TEOS) (($Si(OC_2H_5)_4$, $208.33\, g/mol$, reagent grade, 98%) from Sigma-Aldrich, formamide (CH_3NO, $45.04\, g\, mol^{-1}$, $\geq 99.5\%$) purchased from Carlo Erba Reagents, acetone (C_3H_6O, $58.8\, g\, mol^{-1}$, $\geq 99.5\%$) from Valente e Ribeiro, Lda. and nitric acid (HNO_3, $63.01\, g\, mol^{-1}$, $\geq 65\%$ supplied by JMGS, Lda.

The reagents utilised in the membrane post-treatment by solvent exchange were 2-propanol (C_3H_8O, $60.10\, g\, mol^{-1}$, $\geq 99.8\%$) supplied by Riedel-de Haen and n-hexane ($CH_3(CH_2)_4CH_3$, $86.18\, g\, mol^{-1}$, $\geq 95\%$) purchased from Carlo Erba reagents.

Additionally, the solutes used in permeation experiments were sodium chloride (NaCl, $\geq 99.9\%$) from AnalaR NORMAPUR, magnesium chloride ($MgCl_2$, $\geq 99.0\%$) from Merck, sodium sulphate (Na_2SO_4, $\geq$

3

98.5 %) from Scharlau, magnesium sulphate ($MgSO_4$, $\geq$ 99.9 %), polyethylene glycols (PEGs) from $200\,Da$ to $35000\,Da$ from Merck, and Dextran $40000\,Da$ (DT) from Pharmacia. The deionised water used in all experiments had a conductivity of $\kappa_{25^\circ C} \leq 10\mu S/cm$. All chemicals used in the synthesis and characterisation of the hybrid CA/SiO_2 membranes were employed without further purification.

2.2 Membrane Preparation

Hybrid CA/SiO_2 membranes were prepared by coupling the wet phase inversion [4] with the sol-gel techniques [6]. The phase inversion method requires the preparation of a polymer casting solution containing cellulose acetate (CA, polymer), acetone (stronger solvent) and formamide (poorer solvent). Next, the acid catalysed hydrolysis of the SiO_2 alkoxide sol-gel precursors is promoted *in situ* by adding water, tetraethyl orthosilicate (TEOS) and nitric acid to the polymer solution. The procedure for the preparation of hybrid CA/SiO_2 membranes from casting solutions with 30% formamide and varying SiO_2 contents is described by Mendes et al.[5]. Table 1 shows the compositions of the casting solutions for the prepaparation of three membranes with very distinct asymmetric porous structures, $CA22/SiO_2$, $CA30/SiO_2$ and $CA34/SiO_2$, both with a SiO_2 content of 5% ($wt\%$) and formamide contents of 21.26%, 29% and 32.87%, respectively.

Table 1: Film casting solutions compositions and casting conditions of hybrid CA/SiO_2 membranes.

Casting Solution Composition ($wt\%$)			
Membrane	$CA22/SiO_2$	$CA30/SiO_2$	$CA34/SiO_2$
CA	16.4	16.4	16.4
Formamide	21.26	29	32.87
Acetone	58.84	51.1	47.23
TEOS	3	3	3
H_2O	0.5	0.5	0.5
HNO_3	4 drops ($pH \approx 2$) (for all membranes)		
Casting Conditions			
Temperature of Solution	20–25°C		
Room Temperature	20–25°C		
Air Relative Humidity	$40 - 50\%$		
Solvent Evaporation Time	$0.5\,min$		
Coagulation Medium	Ice cold water ($\approx 0°C$) (2 h)		

2.3 Membrane Pos-Formation Treatment

The hybrid CA/SiO_2 membranes were dried by solvent exchange, denoted as [SE], using isopropanol/n-hexane combinations, as described by Lui et al. [20]. After membrane preparation by phase inversion, the samples were immersed in aqueous solutions of successively higher alcohol contents (25, 50, 75 and 100 $V/V\%$ isopropanol) for at least 24 h at each successive step in order to remove water. The membranes were then immersed in isopropanol/n-hexane solutions of successively higher hexane contents (i.e., 25, 50, 75 and 100 $V/V\%$ n-hexane) for 24 h at each successive step in order to remove the alcohol. The n-hexane was then removed by evaporation in a desiccator at ambient temperature for 24h.

To compare the effect of pos-treatment on membrane structure and permeation properties, two hybrid CA/SiO_2 membranes were kept wet, or as cast, in deionised water, after being prepared by phase inversion and are denoted as [C].

2.4 Membrane Characterisation

The permeation properties of both dried and wet membranes were assessed in terms of hydraulic permeability, L_P, apparent rejection coefficients to salts and neutral macromolecules, f, as well as determination of their molecular weight cut-off ($MWCO$) and mean pore radius, r_p, at the surface of the membrane. A UF unit comprised of a flat cell unit with two detachable parts separated by a porous plate (membrane support) with a membrane surface area of $13.2 \times 10^{-4} m^2$ was used in the permeation experiments. The laboratory UF crossflow unit used in the permeation experiments has been previously described elsewhere [33]. Before the experiments, the membranes were compacted for 2 h with deionised water at a transmembrane pressure of $4.2\,bar$. This procedure minimises the effects of compression in the cell on membrane structure in subsequent experiments. The L_P was measured with a transmembrane pressure ranging from 0.5 to $3.5\,bar$, at $25°C$, and with a flow rate of $2.5\,L\,min^{-1}$.

In order to determine the apparent rejection coefficients, $MWCO$ and r_p, permeation experiments of salts and neutral reference solutes were performed. The apparent rejection coefficient, f, is defined as

$f = (C_b - C_p)/C_b$, where C_b and C_p are the feed bulk and the permeate concentrations, respectively. The apparent rejection coefficients were determined in total re-circulation mode, at maximum circulating flow, for solutions with a solute concentration of $600\,ppm$. For salts, the solute rejection was calculated from electrolytic conductivity measurements using a conductometer from Crison, model GLP 32. As for neutral solutes, the rejection is computed in terms of total organic carbon (TOC) using a Shimadzu TOC V Analyser. In all the permeation experiments, the feed temperature was kept at $25\,^{\circ}C$ and the stabilisation time for each experimental run was $30\,min$. Between experimental runs the membranes were washed with deionised water.

The MWCO is based on the results of permeation experiments of solutions of neutral macromolecules, i.e., PEGs ranging from 0.2 to 35 kDa and DT 40 kDa. It refers to the molecular weight of the solute that is 95 % retained by the membrane. The MWCO is determined from the intersection of the linearized curve of $\log(f/(1-f))$, as a function of the organic solutes molecular weight, and the $f = 95\,\%$ rejection line $(\log(f/(1-f)) = 1.28)$.

The mean pore radius in the active layer of the membrane was calculated through an algorithm that incorporates the steric pore flow model developed by Rosa [34], following the fundamental assumptions of Deen [35] and Tam et al. [36]. This model assumes that the permeation of neutral solutes in membrane pores is governed by steric hindrance mechanisms and allows for the determination of the intrinsic membrane rejection coefficients, f', through eq. (1):

$$f' = 1 - \frac{W}{1 - (1 - W)e^{-Pe}} \tag{1}$$

where W is the hindrance factor for convection and Pe is the Peclet number defined as (2):

$$Pe = \frac{W r_p^2 \Delta P}{8 \mu H D_{AW}} \tag{2}$$

where r_p is the mean pore radius of the membrane, ΔP is the transmembrane pressure, μ is the viscosity, H the hindrance factor for diffusion and D_{AW} the solute diffusivity. Through this model, the intrinsic rejection coefficients of neutral solutes with known molecular weights and sizes were calculated for a membrane with an arbitary pore radius. The rejection coefficients were compared to the experimental values and the sum of the square of the deviations between the calculated rejection coefficients and the experimental ones was minimised leading to the determination of the membrane mean pore radius.

2.5 Characterisation of Molecular Order and Dynamics of Water by NMR

^{2}H NMR spectroscopy and ^{1}H NMR relaxometry and diffusometry were used to characterise water order and dynamics of CA22/SiO$_2$ and CA34/SiO$_2$ membranes that were treated by solvent exchange, as described by Beira et al. [32].

3 Results and Discussion

3.1 Membrane Hydraulic Permeability

Figure 1 represents the variation of pure water flux, J_w, versus the transmembrane pressure, ΔP, for the wet CA22/SiO$_2$ [C] membrane. The slope of this linear variation, $J_w = (7.78 \pm 0.13)\Delta P$, is the membrane hydraulic permeability of $7.78 \pm 0.13\,kg\,h^{-1}\,m^{-2}\,bar^{-1}$.
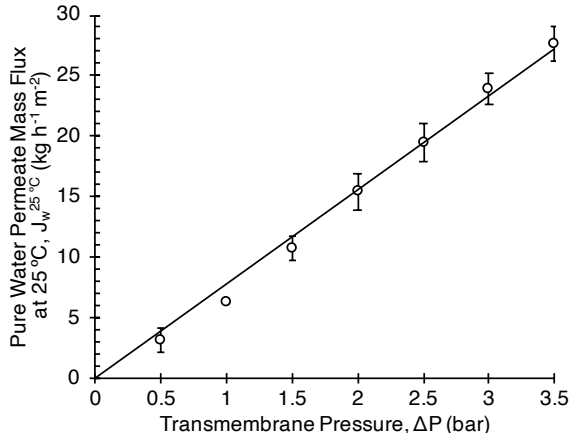

Figure 1: Pure water permeate flux vs. applied transmembrane pressure for the CA22/SiO$_2$ [C] membrane. The vertical error bars represent the standard deviation of the sample (SD) around the mean, with $n_{SD} = 3$.

Table 2 shows the hydraulic permeabilities of the four membranes that were studied.

The results indicate that the [SE] treatment caused a reduction in the membrane's pure water permeate

Table 2: Hydraulic permeabilities of CA/SiO$_2$ membranes. The statistical uncertainties represent the 95% confidence intervals.

Membrane	L_P at 25°C ($kg\,h^{-1}\,m^{-2}\,bar^{-1}$)
CA22/SiO$_2$ [C]	7.8 ± 0.3
CA22/SiO$_2$ [SE]	1.29 ± 0.12
CA34/SiO$_2$ [C]	62 ± 3
CA34/SiO$_2$ [SE]	1.59 ± 0.09

fluxes. This reduction is of the same magnitude for both treated membranes whereas the L_P values for untreated membranes are much different. The difference in fluxes for the (CA22/SiO$_2$ and CA34/SiO$_2$) untreated membranes is owed to the formamide (pore-former) content in the casting solutions. As the CA34/SiO$_2$ casting solution has higher formamide content, the porosity of the membrane is increased. This is an indication that the two membranes have very distinct porous structures.

3.2 Apparent Rejection Coefficients to Salts

Figure 2 displays the apparent rejection coefficients to a monovalent salt, NaCl, and bivalent salts, MgCl$_2$, Na$_2$SO$_4$ and MgSO$_4$.
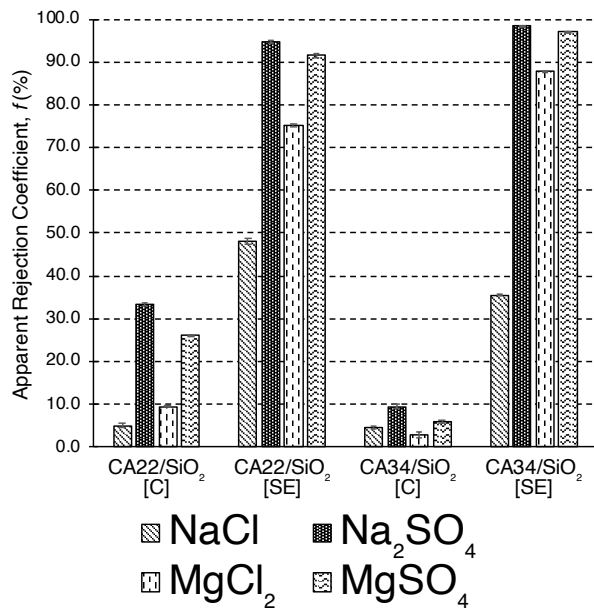

Figure 2: Apparent rejection coefficients to salts of CA/SiO$_2$ membranes. The statistical uncertainties were determined by error propagation.

The obtained rejection data shows that the treated [SE] membranes exhibit close to total rejections to the bivalent salts Na$_2$SO$_4$ and MgSO$_4$, comparing to untreated [C] membranes. In addition, it is possible to verify that the hybrid CA22/SiO$_2$ untreated [C] membrane rejects, although partially, the same solutes with an apparent rejection coefficient of $33.4 \pm 0.4\%$ and $26.02\pm0.15\%$, respectively. This means that both membranes retain, to more or less extent, the sulphate ion, SO$_4^{2-}$, that is common in both salts. This permselectivity, specially for CA22/SiO$_2$ [C] membranes, may be attributed to a separation mechanism characteristic of NF based on electrostatic interactions — repulsion/attraction — between the membrane and the ions [37]. Since the membrane fixed charge is also negative [38], an increase in co-ion charge and/or a decrease in counter-ion charge results in an increase of the salt rejection by the membrane [39]. It is then clear that for a negatively charged membrane, a higher anion charge leads to a higher exclusion and thus, a higher salt retention. However, regarding treated membranes, information on the pore radius of the membranes is necessary to draw further conclusions.

3.3 Determination of the MWCO

Figure 3 represents the determination of the $MWCO \approx 10\,kDa$ by the intersection of the curve of $log(f/(1-f))$ vs. solute molecular weight and the $f = 95\,\%$ rejection line ($log(f/(1-f)) = 1.28$).

Table 3 shows the MWCO of the hybrid CA/SiO$_2$ membranes.

Table 3: Molecular weight cut-off, MWCO, of hybrid CA/SiO$_2$ membranes.

Membrane	MWCO (kDa)
CA22/SiO$_2$ [C]	≈ 10
CA22/SiO$_2$ [SE]	2
CA34/SiO$_2$ [C]	21
CA34/SiO$_2$ [SE]	1

The determined values for the MWCO of the membranes are concordant with the pure water permeation data. To elaborate, the membranes with higher L_P also display higher values of MWCO. In practice, the cut-off of the membranes that were treated by solvent exchange, [SE], can be considered the same.
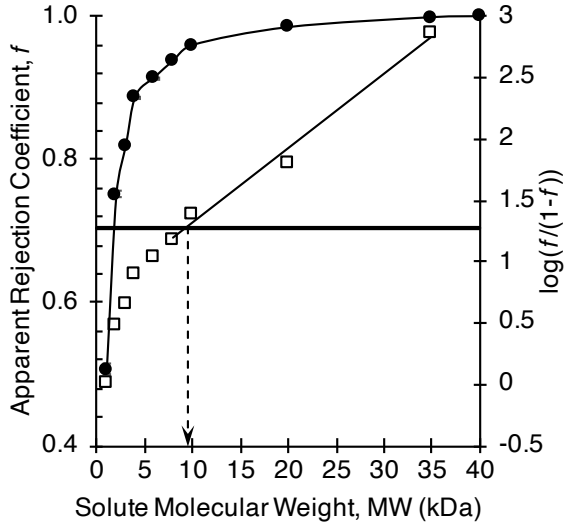
6

Figure 3: (1) Apparent rejection coefficients ($\bullet$) vs. solute molecular weight and (2) $log(f/(1-f))$ ($\square$) vs. solute molecular weight for the untreated CA22/SiO$_2$ [C].

3.4 Determination of the Mean Pore Radius of the Membranes

Table 4 indicates the computed mean pore radius at the surface of the membranes.

Table 4: Mean pore radius, r_p, of hybrid CA/SiO$_2$ membranes.

Membrane	r_p (nm)
CA22/SiO$_2$ [C]	1.9
CA22/SiO$_2$ [SE]	0.9
CA34/SiO$_2$ [C]	3
CA34/SiO$_2$ [SE]	0.8

Comparably to the untreated membranes [C], the results obtained allow to conclude that the solvent exchange [SE] treatment caused a shrinkage of the membranes pores to the NF pore range ($\leq 1\,nm$) [8]. This shrinkage lowers the pure water permeability of the treated membranes, as well as their MWCO.

One should note, however, that based on Donnan-exclusion [39] for a membrane with a negative fixed charge, the retention for MgCl$_2$ is expected to be lower than for NaCl, if the achieved separation is based purely on charge effects. In this case, for treated membranes, the rejection to MgCl$_2$ is higher than to NaCl. Regarding these results, the separation

that occurs cannot be ascribed to charge effects alone [8]. Comparing the hydrated radii of ions [40] to the membrane pore radius indicates that the effect of the ion size cannot be entirely neglected.

3.5 Water Order and Dynamics by NMR in CA/SiO$_2$ [SE] Membranes [32]

Figure 4 and 5 shows the deuterium spectra obtained for the treated CA22/SiO$_2$ and CA34/SiO$_2$, respectively.
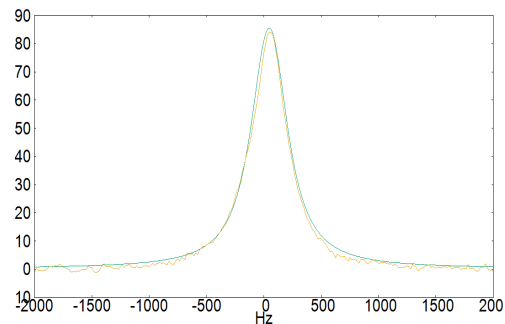

Figure 4: Deuterium spectrum for the treated D$_2$O+CA22/SiO$_2$ [SE] membrane, showing one water population [32].
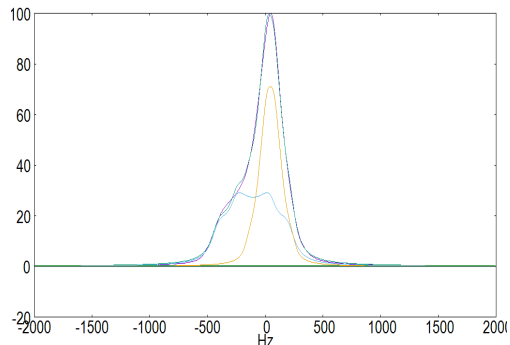

Figure 5: Deuterium spectrum for the treated D$_2$O+CA34/SiO$_2$ [SE] membrane, showing two water populations [32].

The deuterium spectra, obtained for both membrane samples, shows additional ordering of the water molecules above that of bulk water, which denotes interaction with an ordered environment. In addition, it was possible to identify extra ordering in the water molecules and the presence, in both membranes, of up to two spectral components with different degrees

of order and different T_1 values. Regarding that, the single spectral component from the CA22/SiO$_2$ [SE] membrane, observed in Figure 4, suggests a smoother variation of structure between the dense layer and the porous sublayer when compared to the two spectral signatures depicted in Figure 5, found in the CA34/SiO$_2$ [SE] membrane.

From ^{1}H NMR diffusometry, it was verified that the two water populations in the CA34/SiO$_2$ [SE] membrane have very distinct diffusion patterns. In that regard, the estimated self-diffusion coefficient in one of the populations is close to that observed in bulk water.

Additionally, the ^{1}H NMR relaxometry results suggest a less pronounced confinement of water inside the pores of the CA34/SiO$_2$ [SE] membrane, as opposed to the CA22/SiO$_2$ [SE] membrane.

The differences observed in the water dynamics between the two membranes are in agreement with the selective permeation properties reported for UF membranes with extreme MWCO [10]. Although the CA22/SiO$_2$ membrane operates in the UF range, it is characterised by a lower MWCO which enables its application in NF. This behaviour seems to be associated with very distinct porous structures leading to the diverse water dynamics that were characterised.

4 Conclusions

The effects of pos-formation treatment by solvent exchange on the structure modification of CA/SiO$_2$ membranes was studied. Based on the characterisation of the permeation properties, it can be concluded that the solvent exchange treatment alters the membranes porous structures by shrinking the pores. This evidence is associated to a decrease in the pure water permeate fluxes, a total rejection to bivalent salts, lower MWCO and subsequently smaller mean pore sizes when compared to untreated membranes.

The study of water order and dynamics by NMR of the treated membranes shows agreemnt with the permeation results.

In conclusion, the treatment by solvent exchange can be considered as a method of annealing, as it alters the porous structures of membranes typically in the UF range to membrane structures with permeation properties associated to NF.

References

[1] S. Loeb and S. Sourirajan, "Sea Water Demineralization by Means of an Osmotic Membrane," *Advances in Chemistry*, vol. 38, pp. 117–132, jan 1963.

[2] P. M. Bungay, H. K. Lonsdale, and M. N. de Pinho, eds., *Synthetic Membranes: Science, Engineering and Applications*. Dordrecht: Springer Netherlands, 1986.

[3] K. Khulbe, C. Y. Feng, and T. Matsuura, *Synthetic Polymeric Membranes*. Springer Laboratory, Berlin, Heidelberg: Springer Berlin Heidelberg, 2008.

[4] B. Kunst and S. Sourirajan, "An approach to the development of cellulose acetate ultrafiltration membranes," *Journal of Applied Polymer Science*, vol. 18, no. 11, pp. 3423–3434, 1974.

[5] G. Mendes, M. Faria, A. Carvalho, M. C. Gonçalves, and M. N. de Pinho, "Structure of water in hybrid cellulose acetate-silica ultrafiltration membranes and permeation properties," *Carbohydrate Polymers*, vol. 189, pp. 342–351, jun 2018.

[6] C. J. Brinker and G. W. Scherer, *Sol-Gel Science*. San Diego: Academic Press, 1990.

[7] C. R. Dias, M. J. Rosa, and M. N. de Pinho, "Structure of water in asymmetric cellulose ester membranes — and ATR-FTIR study," *Journal of Membrane Science*, vol. 138, pp. 259–267, jan 1998.

[8] J. Schaep, B. Van der Bruggen, C. Vandecasteele, and D. Wilms, "Retention Mechanisms in Nanofiltration," in *Chemistry for the Protection of the Environment 3*, pp. 117–125, Boston, MA: Springer US, 1998.

[9] D. F. Stamatialis, C. R. Dias, and M. N. de Pinho, "Structure and Permeation Properties of Cellulose Esters Asymmetric Membranes," *Biomacromolecules*, vol. 1, pp. 564–570, dec 2000.

[10] D. Murphy and M. N. de Pinho, "An ATR-FTIR study of water in cellulose acetate membranes prepared by phase inversion," *Journal of Membrane Science*, vol. 106, pp. 245–257, oct 1995.

[11] Y. Ogawa and S. Suzuki, "On the nature of free and bound water in water permeation of cellulose acetate membranes in reverse osmosis," *Desalination*, vol. 42, pp. 57–61, jul 1982.

[12] C. R. Dias and M. N. de Pinho, "Water structure and selective permeation of cellulose-based membranes," *Journal of Molecular Liquids*, vol. 80, pp. 117–132, may 1999.

[13] R. E. Kesting, *Synthetic Polymeric Membranes: A Structural Perspective*. New York: Wiley, 2nd ed., 1985.

[14] E. Staude and J. Passlack, "Characterization of ultrafiltration membranes by drying," *Journal of Membrane Science*, vol. 28, pp. 209–223, sep 1986.

[15] K. D. Vos and F. O. Burris, "Drying cellulose acetate reverse osmosis membranes," *Industrial and Engineering Chemistry Product Research and Development*, vol. 8, no. 1, pp. 84–89, 1969.

[16] Z. Jawad, A. Ahmad, S. Low, T. Chew, and S. Zein, "Influence of solvent exchange time on mixed matrix membrane separation performance for CO2/N2 and a kinetic sorption study," *Journal of Membrane Science*, vol. 476, pp. 590–601, feb 2015.

[17] X. Jie, Y. Cao, J.-J. Qin, J. Liu, and Q. Yuan, "Influence of drying method on morphology and properties of asymmetric cellulose hollow fiber membrane," *Journal of Membrane Science*, vol. 246, pp. 157–165, jan 2005.

[18] D. J. Miller, D. R. Dreyer, C. W. Bielawski, D. R. Paul, and B. D. Freeman, "Surface Modification of Water Purification Membranes," *Angewandte Chemie International Edition*, vol. 56, pp. 4662–4711, apr 2017.

[19] C. J. van Oss and P. M. Bronson, "Separation of Blood Serum Proteins by Ultrafiltration," in *Membrane Science and Technology* (J. E. Flinn, ed.), pp. 139–149, Boston, MA: Springer US, 1970.

[20] A. Lui, F. D. F. Talbot, A. Fouda, T. Matsuura, and S. Sourirajan, "Studies on the solvent exchange technique for making dry cellulose acetate membranes for the separation of gaseous mixtures," *Journal of Applied Polymer Science*, vol. 36, no. 8, pp. 1809–1820, 1988.

[21] H. Schwarz, K. Richau, and H. Hicke, "Annealing effect in porous cellulose acetate membranes," *Journal of Membrane Science*, vol. 34, pp. 283–296, jan 1987.

[22] J. Su, S. Zhang, H. Chen, H. Chen, Y. Jean, and T.-S. Chung, "Effects of annealing on the microstructure and performance of cellulose acetate membranes for pressure-retarded osmosis processes," *Journal of Membrane Science*, vol. 364, pp. 344–353, nov 2010.

[23] T. D. Kusworo, N. Aryanti, M. M. H. Firdaus, and H. Sukmawati, "Surface modification of cellulose acetate membrane using thermal annealing to enhance produced water treatment," in *AIP Conference Proceedings*, vol. 1699, p. 040014, 2015.

[24] M. N. de Pinho, T. Matsuura, T. D. Nguyen, and S. Sourirajan, "Reverse Osmosis Separation of Glucose-Ethanol-Water System by Cellulose Acetate Membranes," *Chemical Engineering Communications*, vol. 64, pp. 113–123, feb 1988.

[25] P. K. Gantzel and U. Merten, "Gas Separations with High-Flux Cellulose Acetate Membranes," *Industrial & Engineering Chemistry Process Design and Development*, vol. 9, pp. 331–332, apr 1970.

[26] E. W. Washburn, *International Critical Tables of Numerical Data, Physics, Chemistry and Technology, Vol. IV*. Washington, D.C.: National Academies Press, 1928.

[27] L. Yurong, L. Kongmon, C. Yiming, and C. Bangxiao, "Effect of heat-treating and dry conditions on the performance of cellulose acetate reverse osmosis membrane," *Desalination*, vol. 54, pp. 185–195, jan 1985.

[28] S. Singh, K. C. Khulbe, T. Matsuura, and P. Ramamurthy, "Membrane characterization by solute transport and atomic force microscopy," *Journal of Membrane Science*, vol. 142, no. 1, pp. 111–127, 1998.

[29] F. Liu, N. A. Hashim, Y. Liu, M. M. Abed, and K. Li, "Progress in the production and modific-

ation of PVDF membranes," *Journal of Membrane Science*, vol. 375, pp. 1–27, jun 2011.

[30] L.-Y. Yu, Z.-L. Xu, H.-M. Shen, and H. Yang, "Preparation and characterization of PVDF–SiO2 composite hollow fiber UF membrane by sol–gel method," *Journal of Membrane Science*, vol. 337, pp. 257–265, jul 2009.

[31] W.-L. Hung, D.-M. Wang, J.-Y. Lai, and S.-C. Chou, "On the initiation of macrovoids in polymeric membranes – effect of polymer chain entanglement," *Journal of Membrane Science*, vol. 505, pp. 70–81, may 2016.

[32] M. J. Beira, M. P. Silva, M. Condesso, P. Cosme, P. L. Almeida, M. C. Corvo, P. J. Sebastião, J. L. Figueirinhas, and M. N. de Pinho, "Molecular order and dynamics of water in hybrid cellulose acetate–silica asymmetric membranes," *Molecular Physics*, vol. 117, no. 7-8, pp. 975–982, 2019.

[33] A. R. Costa and M. N. De Pinho, "Effect of membrane pore size and solution chemistry on the ultrafiltration of humic substances solutions," *Journal of Membrane Science*, vol. 255, no. 1-2, pp. 49–56, 2005.

[34] M. João Rosa and M. N. de Pinho, "Separation of organic solutes by membrane pressure-driven processes," *Journal of Membrane Science*, vol. 89, pp. 235–243, apr 1994.

[35] W. M. Deen, "Hindered transport of large molecules in liquid-filled pores," *AIChE Journal*, vol. 33, pp. 1409–1425, sep 1987.

[36] C. Tam and A. Tremblay, "Membrane pore characterization—comparison between single and multicomponent solute probe techniques," *Journal of Membrane Science*, vol. 57, pp. 271–287, apr 1991.

[37] C. K. Yeom, S. H. Lee, and J. M. Lee, "Effect of the ionic characteristics of charged membranes on the permeation of anionic solutes in reverse osmosis," *Journal of Membrane Science*, vol. 169, no. 2, pp. 237–247, 2000.

[38] G. Mendes, *Novas Membranas Assimétricas de Matriz Mista de Acetato de Celulose e Sílica*. Msc thesis, Instituto Superior Técnico, Universidade de Lisboa, 2016.

[39] K. Boussu, Y. Zhang, J. Cocquyt, P. Van der Meeren, A. Volodin, C. Van Haesendonck, J. Martens, and B. Van der Bruggen, "Characterization of polymeric nanofiltration membranes for systematic analysis of membrane performance," *Journal of Membrane Science*, vol. 278, pp. 418–427, jul 2006.

[40] Y. Marcus, "Ionic radii in aqueous solutions," *Journal of Solution Chemistry*, vol. 12, pp. 271–275, apr 1983.