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# Electrokinetic analysis of PES/PVP membranes aged by sodium hypochlorite solutions at different pH

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## ABSTRACT

This study focused on the impact of ageing solution pH (200 ppm TFC sodium hypochlorite) on the electrokinetic properties of a commercial PES/PVP UF membrane. PVP oxidation, leading to an increase in the negative charge density of aged membranes, was pointed out whatever the ageing solution pH although different mechanisms might be involved depending on the ageing pH. PES degradation was also demonstrated. Electrokinetic measurements highlighted the formation of functional groups with very weak acid properties on the surface of membranes aged in sodium hypochlorite at pH 8.0 and to a lesser extent at pH 6.0 and 11.5. These results were found to be consistent with the formation of phenol groups due to the

radical hydroxylation of PES aromatic rings. Moreover, the disappearance of the isoelectric point of membranes aged in sodium hypochlorite at pH 6.0 and 8.0 gave evidence for the formation of strong acid groups such as sulfonic acids. These results suggested some PES-chain scissions, which was confirmed by XPS measurements. The disappearance of the isoelectric point was not observed for membranes aged in sodium hypochlorite at pH 11.5, thus indicating that  $\text{ClO}^-$  was not involved in PES-chain scissions for the ageing conditions considered in this work. Finally, electrokinetic measurements performed ~~after ageing experiments performed in sodium hypochlorite solutions~~ with the addition of tertio-butanol ~~acting as a~~ (free radical scavenger) and thermo-oxidation experiments revealed for the first time that, although both  $\text{HClO}$  and free radicals species contributed to PES-chain scissions,  $\text{HClO}$  had the greater impact on PES degradation.

**Keywords:** ultrafiltration; ageing; sodium hypochlorite; electrokinetics; polymer membranes

## 1. Introduction

Polyethersulfone (PES) / Polyvinylpyrrolidone (PVP) membranes are widely used for ultrafiltration and microfiltration processes, mainly because of their stability in use and cleaning conditions [1]. PES exhibits excellent chemical and thermal resistances over a wide range of pH (from 2 to 12) [2-4] but is relatively hydrophobic. Hydrophilic additives such as PVP are therefore added to PES in order to obtain membranes suitable for industrial applications especially for fluids containing organic compounds such as proteins or polysaccharides [5, 6].

Despite the choice of hydrophilized organic membranes, membrane fouling by organic compounds remains a major problem in filtration units used in both food industry and water treatment. In order to restore the membrane initial flux and to prevent micro-organism development, cleaning-in-place (CIP) and disinfection processes are implemented in the various industries. For instance a typical daily CIP for dairy applications using spiral membranes consists of an alkaline cleaning step followed by an acid cleaning and finally a sanitation step using generally sodium hypochlorite (150 - 200 ppm in total free chlorine (TFC) at 50°C) at pH 11.0-11.5 [7,8]. For applications in water production, using hollow fibers, the most frequent procedures for cleaning membranes are (i) a back-washing process with a TFC concentration up to 20 ppm at pH 8.0 for up to 5 minutes every 6 hours of membrane operation and (ii) a chemical cleaning process with a TFC concentration up to 400 ppm at pH around 11 at room temperature for up to 2 hours monthly [4, 9].

Until now, there are considerably less publications dedicated to membrane ageing than to cleaning / disinfection [10]. Wienk et al. showed that sodium hypochlorite post-treatment of porous membranes prepared from PES / PVP blends led to a significant increase in water

permeability [2]. However, membrane performance are known to deteriorate progressively after contacting with oxidizing agents such as sodium hypochlorite. Delaunay [11] and Rabiller-Baudry et al. [12] compared the chemical resistance of dense films made either with pure PES or PES/PVP blends upon exposure to sodium hypochlorite and concluded to a higher degradation kinetics in the presence of PVP. The membrane autopsy carried out by Bégoïn et al. [13] with spiral-wound PES ultrafiltration membranes aged under industrial conditions revealed breakage of the PES C-S bond. A similar conclusion was drawn by Arkhangelsky et al. [3] by soaking PES-based membranes in bleach solutions containing 150 ppm TFC at pH 7.2 for various times corresponding to free chlorine doses up to 100 g h / L. Several studies showed that chlorine is more aggressive towards PES / PVP membranes at  $7 < \text{pH} < 9$  [4, 9], a pH range for which the coexistence of HClO and ClO<sup>-</sup> is believed to produce a significant amount of unstable radicals [14]. Yadav et al. [15] studied ageing of PES spiral-wound membranes by 700 ppm TFC sodium hypochlorite solutions at pH 9 and 12. They proposed a mechanism for PES-chain scission in which PES chains break in two parts, with one end terminated by a sulfonic acid group and the other chain end terminated by a phenyl chloride. The appearance of a new band at 1034 cm<sup>-1</sup> on the ATR-FTIR spectra of membranes aged at both pH 9 and 12 was attributed to the formation of sulfonic acid groups. However, although electron dispersion spectroscopy (EDS) highlighted the presence of chlorine on the surface of membranes aged at pH 9, no chlorine was detected on membranes aged at pH 12. Rabiller-Baudry et al. [12] and Bégoïn et al. [13] evidenced the presence of Cl element on PES/PVP membranes (no cationic species was detected) aged at both pH 8.0 and 11.5 at 50°C for a wide range of TFC concentrations and also confirmed the apparition of a new band located around 1030 cm<sup>-1</sup> on the aged membranes ATR-FTIR spectra.

Unlike Yadav et al. [15], Prulho et al. [16] attributed the appearance of a new band around 1030 cm<sup>-1</sup> in aged membranes ATR-FTIR spectra to the formation of phenol groups and not

to sulfonic acids, and they suggested that hydroxyl radicals formed in bleach solution provoke PES radical oxidation in PES / PVP blends leading to the hydroxylation of the PES component. The effect of HO\* radicals was also suggested by Gaudichet-Maurin and ThomINETTE [1] and Causserand et al.[17] to explain the degradation of polysulfone (PSf) membranes in contact with bleach solutions.

Hanafi et al. performed the electrokinetic characterization of ultrafiltration and nanofiltration PES/PVP membranes aged in 400 ppm TFC NaOCl at pH 8.0 and concluded that both phenols and sulfonic acid groups were present on aged membrane surface [18].

The complex effects of sodium hypochlorite on the degradation mechanisms of PES/PVP membranes and the contradictory results reported in the literature remain unclear and deserve complementary studies. The present work thus aimed at investigating the effect of sodium hypochlorite solution pH on the degradation molecular mechanisms of PES / PVP ultrafiltration membranes by means of advanced electrokinetic measurements, namely tangential streaming current measurements conducted in a nitrogen inert environment. This characterization technique detects changes in surface electrical properties of materials and we show in this study that it can provide important insight into the changes in membrane chemistry caused by exposure to bleach solution. The electrokinetic characterization of pristine and aged membranes was complemented by X-ray photoelectron spectroscopy (XPS), ATR-FTIR spectroscopy and filtration performance evaluation.

## 2. Theoretical background

Transversal (or through pores) [19-22] and tangential streaming potential [23-25] measurements are the most used techniques to determine membrane zeta potential. In the case of membranes composed of several layers or membranes with ion-rejection capability,

tangential streaming potential measurements is preferred because it is difficult to get a meaningful and reliable interpretation of data obtained from transversal measurements [26-29]. However, the contribution of the underlying support layer(s) to the system electric conductance gives rise to complications in the interpretation of tangential streaming potential data [30-32].

Alternatively, it has been proposed to measure the streaming current along composite membrane skin-layers since its interpretation is not complicated either by the surface conductance or by the electrical conduction through the membrane porous sublayer(s) [33-35]. The measuring principle of tangential streaming current is relatively simple and can be summarized as follows. A hydrostatic pressure gradient is applied through a well-defined channel obtained by putting two identical solids (membranes) face to face. The channel is filled with a (background) electrolyte solution which moves tangentially to the walls under the action of the pressure gradient. If the channel walls bear a fixed charge density, then the excess of counterions in solution (balancing the fixed charge on the channel walls) is pulled towards the low-pressure side, thus inducing an electrical current referred to as the streaming current. If we consider a pressure-induced laminar flow between two rectangular membrane samples separated by a distance  $h_{ch}$  (referred to as channel height) much larger than the Debye length in the background solution, the zeta potential ( $\zeta$ ) can be inferred from the experimental streaming current ( $I_s$ ) as follows (considering conventionally that the streaming current and the zeta potential have the same sign):

$$I_s = \frac{Wh_{ch}\varepsilon_0\varepsilon_r\Delta P}{\eta L}\zeta \quad (1)$$

where  $L$  and  $W$  are the sample length and width, respectively,  $\Delta P$  is the pressure difference applied between the channel ends,  $\varepsilon_0$  is the vacuum permittivity,  $\varepsilon_r$  is the background solution dielectric constant and  $\eta$  its dynamic viscosity.

For channel heights ( $h_{ch}$ ) much larger than the background solution Debye length, the net (or effective) charge density  $\sigma_{net}$  (defined as the opposite of the electrokinetic charge density  $\sigma_{ek}$  so that  $\sigma_{net} + \sigma_{ek} = 0$ ) of the membrane samples can be determined from  $\zeta$  by means of the following relation derived from the Gouy-Chapman theory for flat interfaces [36]:

$$\sigma_{net} = -\sigma_{ek} = \text{sgn}(\zeta) \sqrt{2\varepsilon_0\varepsilon_r RT \sum_i c_i \left( \exp\left(-\frac{z_i F \zeta}{RT}\right) - 1 \right)} \quad (2)$$

where  $c_i$  and  $z_i$  are the concentration and the charge number of ion  $i$ , respectively,  $F$  is the Faraday constant,  $R$  is the ideal gas constant and  $T$  is the temperature.

### 3. Experimental

#### 3.1. Solutions

Hypochlorite solutions used for ageing experiments were prepared from dilution of a commercial bleach solution (NaOCl, La Croix, France – TFC: 96,000 ppm). Their pH was adjusted with 0.1 mol L<sup>-1</sup> HCl and NaOH solutions of analytical grade (Fischer Scientific).

Polyethylene glycol (PEG; Fluka) with different molecular weights of 10,000; 20,000 and 35,000 g mol<sup>-1</sup> were used for rejection tests.



Tertiobutanol (ACROS Organics, analytical grade) was used as a free radical scavenger [37] in some ageing experiments.

All electrokinetic measurements were conducted with  $0.001 \text{ mol L}^{-1}$  KCl background solutions the pH of which was adjusted with  $0.1 \text{ mol L}^{-1}$  HCl and KOH solutions (Fischer Scientific, analytical grade).

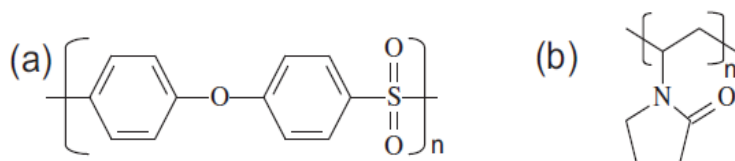
Ethanol (>99%; Fischer Scientific) was used to prepare water/alcohol mixtures used to remove membrane conservatives.

All solutions were prepared using deionized water (resistivity:  $18 \text{ M}\Omega \text{ cm}$ ).

### 3.2. Membranes

HFK-131 ultrafiltration membranes (Koch Membrane Systems, USA) with a molecular weight cut-off of  $5\text{-}10 \text{ kg}\cdot\text{mol}^{-1}$  were used in this work. According to the manufacturer these membranes are made of a skin layer in PES on top of a non-woven polyester support. Actually, it was shown that the HFK-131 skin layer is made of PES with PVP as additive (Figure 1) [12].

An NTR 7450 nanofiltration membrane (Nitto Denko, Japan) was used for complementary electrokinetic measurements (shown in the supporting information). According to the manufacturer this membrane has a skin layer made of sulfonated polyethersulfone.



**Figure 1:** Chemical structures of Polyethersulfone (a) and Polyvinylpyrrolidone (b).

Prior to ATR-FTIR and streaming current measurements, the membrane samples were soaked in a 75/25 (v/v) water/ethanol mixture and sonicated for 5 minutes in order to remove conservatives. The samples were further rinsed twice with deionized water and sonicated (2 x 2 minutes).

### 3.3. Ageing procedure

#### 3.3.1. Ageing by sodium hypochlorite

Static ageing experiments were performed by soaking membrane samples in 200 ppm TFC NaOCl solutions at room temperature ( $20 \pm 2$  °C). This concentration has been selected as it is fairly representative of on-site operations. Indeed, for the same hypochlorite dose, accelerated ageing experiments using higher concentrations and shorter ageing times as compared to on-site operations may exaggerate the membrane degradation [9]. The ageing pH was adjusted to 6.0, 8.0 or 11.5 and membrane samples were soaked in ageing solutions for 10 days. It is worth mentioning that small samples ( $10 \text{ cm}^2$ ) were soaked in 1 L NaOCl solutions that were renewed every day. Consequently, pH variation was negligible during the whole membrane ageing process. The pHs 6.0 and 11.5 correspond to HClO and  $\text{ClO}^-$  predominance, respectively, while, pH 8.0 corresponds to the coexistence of both HClO and  $\text{ClO}^-$  species ( $\text{ClO}^-$  representing about 75 % of the TFC against 25 % for HClO; see Figure S1 in the supporting information), a pH that is believed to produce the maximum amount of free radicals [14], according to the following reaction [2]:



Another mechanism leading to the formation of HO\* radicals without the involvement of ClO<sup>-</sup> has also been proposed in the literature [38]:



### 3.3.2. Ageing by sodium hypochlorite exposure in the presence of tertiobutanol

In order to study the effect of HO\* radicals on the PES/PVP membranes degradation mechanisms, additional ageing experiments were conducted with the addition of tertiobutanol (tBuOH; 2 g.L<sup>-1</sup>) as a free radical scavenger.

### 3.3.3. Thermo-oxidation

Thermo-oxidation of the pristine membrane was performed in order to investigate membrane ageing in the presence of HO\* radicals only [16]. These experiments were carried out by keeping the pristine membrane in a ventilated oven at 140°C for 15 days.

### 3.4. Membrane characterization

Prior to characterization membrane samples were rinsed thoroughly with deionized water, sonicated twice (2 x 2 minutes) and then dipped in deionized water for approximately 24

hours in order to remove all traces of bleach solution or possible soluble polymer degradation products.

### 3.4.1. Filtration performance

Pure water permeability and PEG rejections for pristine and aged membranes were carried out with a cross-flow filtration set-up equipped with a 10 L thermally controlled feed tank ( $T = 25 \pm 2^\circ\text{C}$ ).

A plate and frame module (Ray-Flow X100, Novasep-Process, France) with an effective membrane area of  $127 \text{ cm}^2$  was used. Each sample was initially compacted at 2.5 bar until getting a steady permeation flux (this preliminary step took about 1 hour). After membrane compaction, the pure water permeate at different transmembrane pressures (TMP) ranging from 0.5 to 2.5 bar was collected for determining pure water flux ( $J_w$ ). The pure water permeability ( $L_p$ ) was then obtained from Darcy's law:

$$L_p = \frac{J_w}{TMP} \quad (3)$$

PEG rejection by pristine and aged membranes was also studied (using  $1.0 \text{ g.L}^{-1}$  feed solutions). Rejection experiments were carried out at a constant cross-flow velocity ( $0.26 \pm 0.01 \text{ m.s}^{-1}$ ) and at a constant TMP equal to 1 bar. Both permeate and retentate were recycled in the feed tank. Once the membrane had steady-state permeation (it took about 1 hour), permeate and retentate were collected for analysis. PEG concentrations were determined by total organic carbon analysis (TOC- $V_{\text{CPH/CPN}}$  Total Organic Analyzer, Shimadzu, Japan). PEG rejections ( $R_{\text{PEG}}$ ) were determined from the following equation:

$$R_{PEG} = 100 \left( 1 - \frac{C_P}{C_f} \right) \quad (4)$$

where  $C_P$  is the PEG concentration in permeate and  $C_f$  is the PEG concentration in the feed solution.

### 3.4.2. Streaming current measurements

A SurPass electrokinetic analyzer (Anton Paar GmbH, Graz, Austria) equipped with an adjustable-gap cell was used to measure tangential streaming current. Membrane samples were cut and adjusted to the sample holder dimensions (i.e.  $L = 2$  cm and  $W = 1$  cm) and fixed using double-sided adhesive tape. The distance between the membrane samples was set to  $100 \pm 2$   $\mu\text{m}$ .

The solution flow was created by a pair of syringe pumps and streaming current was measured with a pair of reversible Ag/AgCl electrodes (surface area:  $10$   $\text{cm}^2$ ). Using electrodes with a large surface area and alternating the direction of solution flow limits electrode polarization during streaming current measurements.

The streaming current was measured and recorded for increasing pressure differences up to  $300$  mbar, the flow direction being changed periodically.

Prior to the first measurement the electrolyte solution was circulated through the channel formed by the membrane samples for at least  $2$  hours in order to equilibrate the membrane samples with the background solution. All experiments were performed at room temperature ( $20 \pm 2$   $^\circ\text{C}$ ) under a controlled atmosphere (nitrogen gas) in order to allow accurate measurements at alkaline pHs, as described elsewhere [35].

### 3.4.3. ATR-FTIR spectroscopy

ATR-FTIR spectroscopy was performed with a Spectrum 100 Fourier Transform Infrared Spectrometer (Perkin Elmer, USA) equipped with a diamond crystal ATR element (single reflection; incidence angle: 45°). Each spectrum was averaged from 20 scans collected from 650 to 4000  $\text{cm}^{-1}$  at 2  $\text{cm}^{-1}$  resolution after background recording performed at ambient air. Membrane samples were carefully dried for two days under dynamic vacuum before performing ATR-FTIR spectroscopy experiments.

### 3.4.4. X-ray photoelectron spectroscopy (XPS)

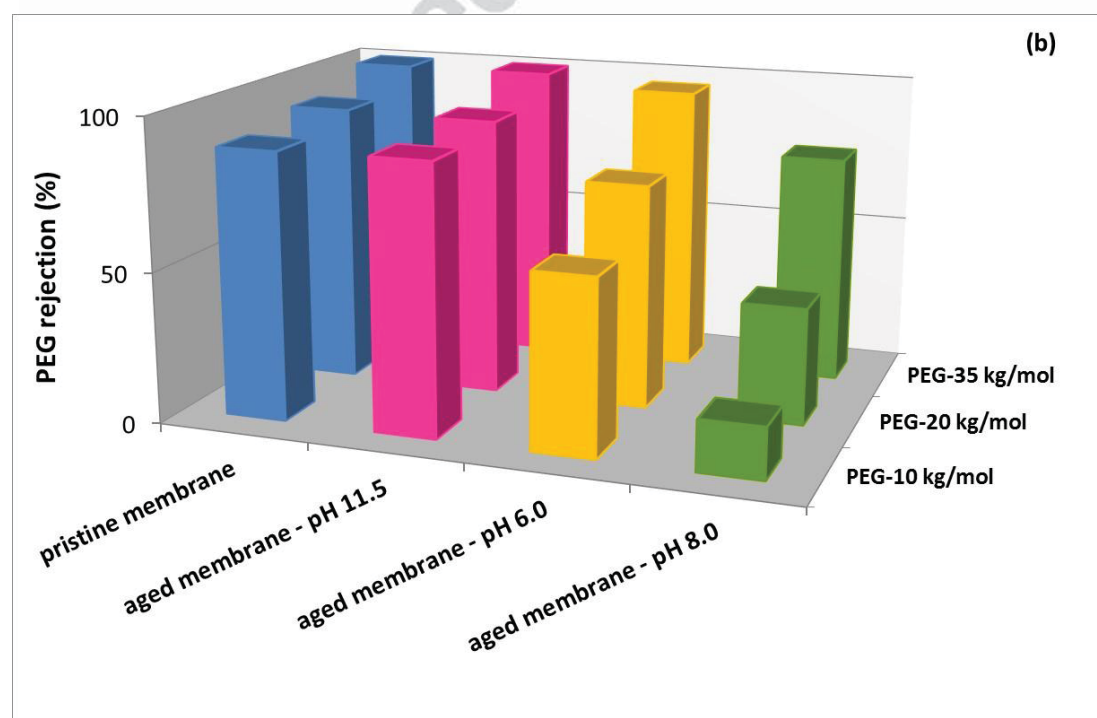
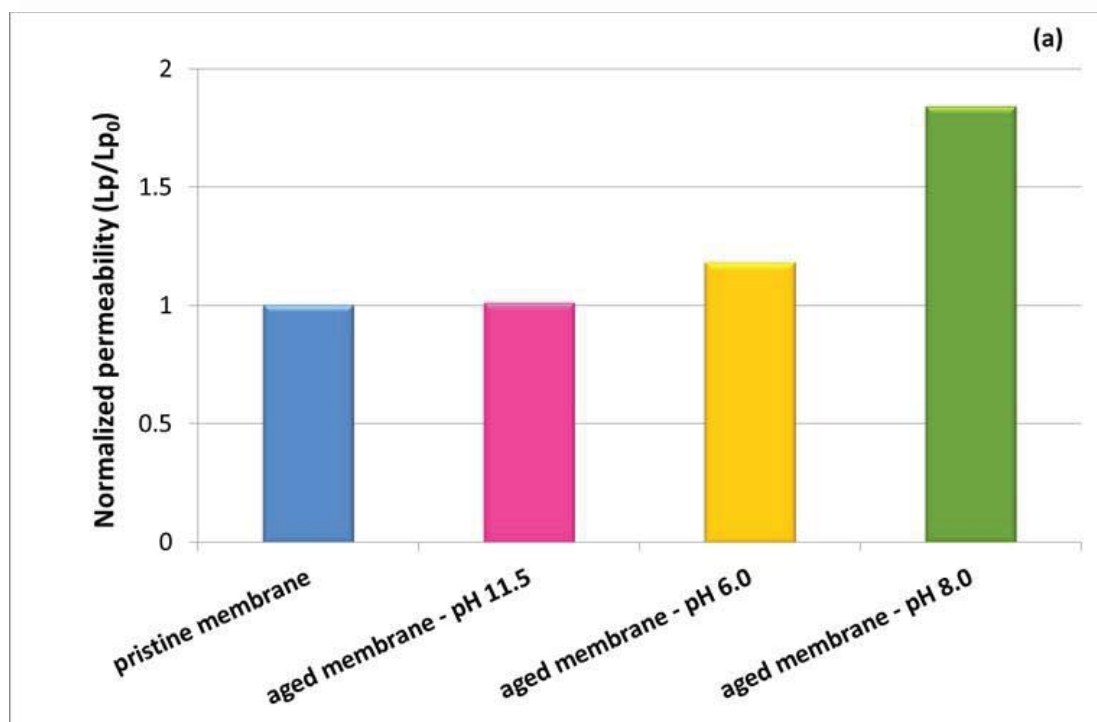
XPS measurements were carried out using a VSW HA100 photoelectron spectrometer (VSW Atomtech Ltd., UK) with a hemispherical photoelectron analyzer, working at energy pass of 22 eV. X-ray source used Mg  $K\alpha$  at 1254 eV. Spectral analysis included a Shirley background subtraction and peak separation using mixed Gaussian-Lorentzian functions. The take-off angle was 0° off normal.

Membrane samples were dried under dynamic vacuum for 2 days before being introduced in the ultra-high vacuum chamber and kept at  $10^{-6}$  Pa several hours before XPS analysis.

## 4. Results and discussion

### 4.1. Membrane permeability and rejection

Measurements of pure water permeabilities and PEG rejections for membranes exposed to 200 ppm TFC NaOCl solutions at pH 6.0, 8.0 and 11.5 for 10 days are shown in Figures 2a and 2b.



**Figure 2:** (a) Normalized permeability ( $L_p$  is the membrane permeability after ageing and  $L_{p0}$  is that of the pristine membrane) and (b) PEG rejection for the pristine HFK-131 membrane and membranes aged for 10 days in 200 ppm TFC NaOCl solutions at pH 6.0, 8.0 and 11.5.

The most significant change, in terms of both permeability and PEG rejection, was undergone by the membrane aged at pH 8.0. A slight increase in permeability accompanied with a significant decrease in PEG rejections were observed for the membrane aged at pH 6.0. On the other hand, the membrane sample aged at pH 11.5 showed no change either in pure water permeability or in PEG rejection after a 10-day ageing (free chlorine dose: 2000 ppm.day) at room temperature. These results agree with those published by Pellegrin et al. [9] who observed that modifications of the permeability and mechanical properties of PES/PVP hollow fiber membranes aged in 350 ppm TFC NaOCl solutions were most important for ageing carried out at pH 8.0.

The increase in the pure water permeability of PES/PVP membranes after exposure to bleach solutions was already reported by some authors [2, 39] and was attributed to the porous structure modification of membranes as a result of partial removal of PVP. Wolff and Zydney observed similar results with PSf/PVP membranes and noticed that the membrane permeability still increased even after complete removal of PVP, thus indicating chemical degradation of PSf itself [40].

#### *4.2. Physico-chemical characterization of membrane surfaces*

As mentioned in the experimental section, electrokinetic measurements carried out in the present work were conducted under controlled atmosphere by means of nitrogen gas, which is

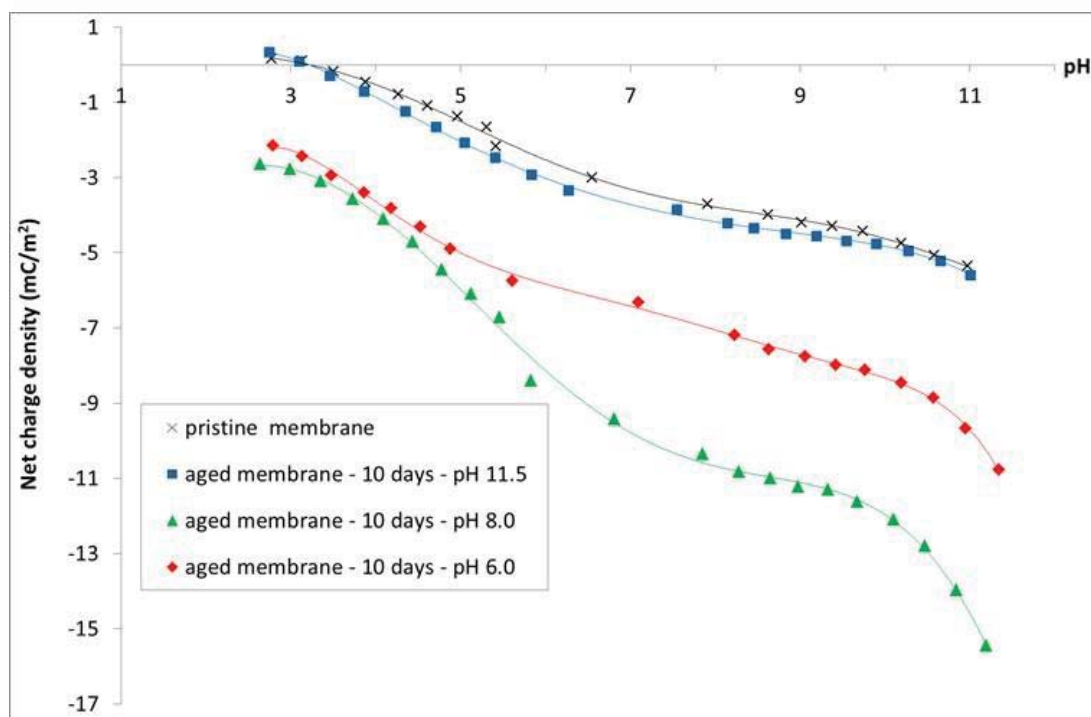


highly advisable for an accurate electrokinetic characterization since pH cannot be kept constant in the alkaline range in the presence of carbon dioxide. If working at ambient air, CO<sub>2</sub> dissolution in the electrolyte solution occurs leading to the formation of bicarbonate and carbonate ions depending on the pH. Consequently, pH has to be re-adjusted frequently during electrokinetic experiments, leading to progressive increase in the background-solution conductivity, which in turn impacts the electrokinetic measurements (typically, the zeta potential decreases as the background-solution concentration increases) [18].

However, even taking the precaution to work under inert atmosphere, the background-solution conductivity inevitably increases at low and high pH (as a result of the addition of non-negligible amounts of HCl and KOH solutions, respectively), which is likely to hide some important information. This issue can be overcome somehow by interpreting the electrokinetic data in terms of net charge density,  $\sigma_{net}$  (determined from equation 5), since this latter accounts for the variation of the background-solution conductivity by considering the actual concentrations of all ionic species in solution at a given pH [18].

Figure 3 shows the pH dependence of the net charge density for the pristine HFK-131 membrane as well as for membranes aged in 200 ppm TFC NaOCl solutions at pH 6.0, 8.0 and 11.5 for 10 days. Monitoring the pH dependence of the net charge density revealed that HFK-131 membranes became more negatively charged after exposure to sodium hypochlorite. For pH between 4 and 9 approximately, the trends of the different curves shown in Figure 3 are typical of the ionization of weak acids such as carboxylic acid groups. Such an increase in the negative charge was also reported for HFK-131 membrane aged in a 400 ppm TFC NaOCl solution at pH 8.0 [18], for PES/PVP hollow fiber membranes aged in 350 ppm TFC NaOCl solutions at pH 8 [39] and for PSf/PVP hollow fiber membranes aged in 2400 ppm TFC NaOCl solutions at pH 7.4 [40]. This increase in the negative charge density of aged membranes was attributed to the formation of carboxylic acids resulting from the PVP

degradation through pyrrolidone ring opening (see Figure S2 in the supporting information) as suggested by Wienk et al. [2].



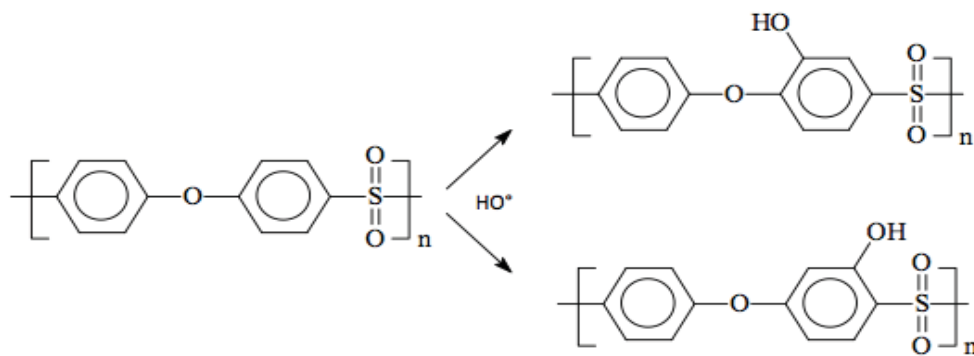
**Figure 3:** pH dependence of the net charge density of the pristine HFK-131 membrane and membranes aged for 10 days in 200 ppm TFC NaOCl solutions at pH 6.0, 8.0 and 11.5.

Figure 3 shows that the membrane aged in a 200 ppm TFC NaOCl solution at pH 8.0 exhibits a much more negative charge density over the whole pH range compared with membranes aged at pH 11.5 and 6.0, which indicates that more carboxylic acid groups are present at the surface of the membrane aged at pH 8.0, i.e. PVP degradation is more important at pH 8.0. Indeed at pH 8.0, PVP degradation is likely to occur not only through the ring opening mechanism caused by  $\text{ClO}^-$  (Figure S2 in the supporting information) but also through a radical mechanism. Indeed, Prulho et al [16] showed that hydroxyl radicals formed in bleach

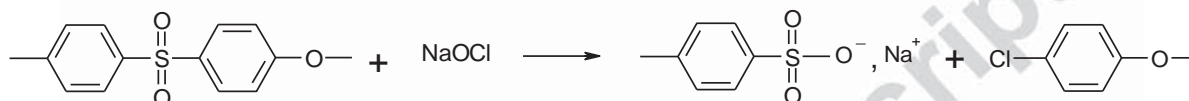
solution provoke PVP radical oxidation after a sufficiently long exposure time, leading to the formation of succinimide groups (see Figure S3 in the supporting information). These latter are sensitive to hydrolysis and are likely to form carboxylic acid functions (see Figure S4 in the supporting information) [41].

In Ref. [18] it was shown that two mechanisms were involved in PES degradation in a 400 ppm TFC NaOCl solution at pH 8.0: (i) the formation of phenol groups as a result of PES aromatic rings oxidation by hydroxyl radicals (Figure 4) and (ii) the formation of sulfonic acid groups resulting from PES-chain scission (Figure 5). Figure 3 gives evidence that both mechanisms also occur in a less concentrated NaOCl solution (200 ppm) at pH 8.0. Indeed, the steep increase in the negative charge density of the aged HFK-131 membrane observed for pH higher than ca 10 is consistent with the ionization of surface groups having very weak acid properties such as phenols. Moreover, the disappearance of the membrane isoelectric point (iep) is the signature of the presence of strong acids such as sulfonic acids. This conclusion was supported by additional electrokinetic measurements performed with a pristine NTR 7450 membrane, which is a sulfonated PES membrane. Indeed, as shown in Figure S5 in the supporting information, this sulfonated PES membrane exhibits a similar electrokinetic behavior to that of the HFK-131 membrane aged in NaOCl at pH 8.0.

To the best of our knowledge, advanced electrokinetic measurements such as those carried out in the present work are currently the only way to reveal unambiguously the presence of both strong acids and very weak acids on the surface of PES-based membranes degraded by bleach solutions.



**Figure 4:** Mechanism of phenol formation through PES radical oxidation [16].

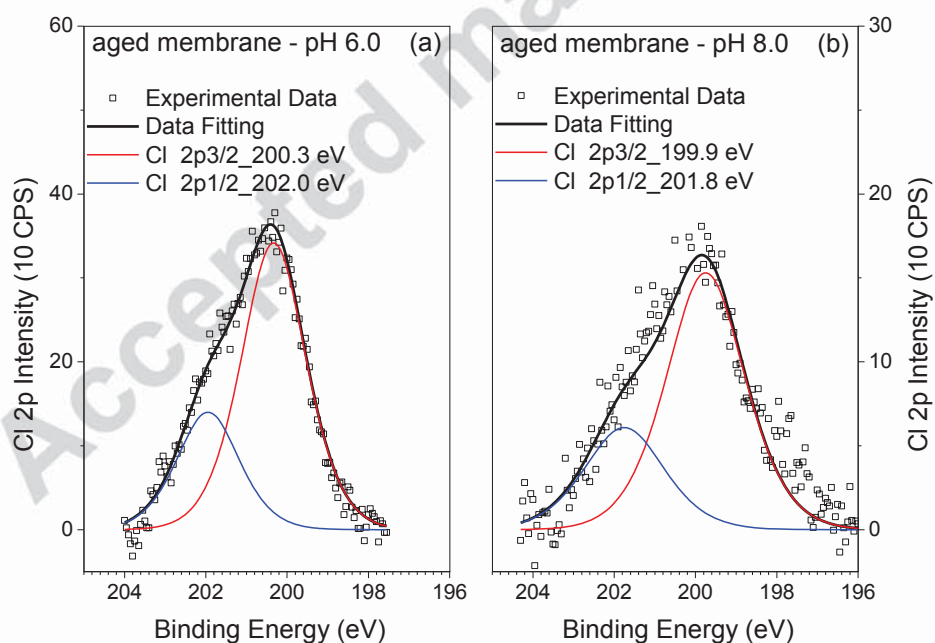


**Figure 5:** Formation of sulfonic acid groups as a result of PES-chain scission

For the membrane aged at pH 6.0, a significant increase in the negative net charge density was also observed, although this increase was less important than for the membrane aged at pH 8.0. This result may be explained by the fact that PVP degradation at pH 6.0 is provoked primarily by HO\* radicals (Figures S3 and S4 in the supporting information) and not by ClO<sup>-</sup> (the amount of which is negligible at pH 6.0; see figure S1 in the supporting information). Moreover, HClO does not react significantly with PVP in the present ageing conditions as it will be shown in section 4.3.

The increase in the net charge density of aged membranes for pH higher than ca 10, which was attributed to phenol groups ionization, was less important for the membrane aged at pH 6.0 than for the membrane aged at pH 8.0 (see Figure 3), which suggests that less free radicals are produced at pH 6.0 than at pH 8.0.

The disappearance of the membrane iep was also observed for the membrane aged at pH 6.0, which demonstrates that PES-chain scission also occurs when ageing is performed at this pH. According to Figure 5, PES chains break into two parts, with one end terminated by a sulfonic acid group (detected by electrokinetic measurements) and the other chain end terminated by a phenyl chloride. The presence of chlorine on the surface of membranes aged at both pHs 6.0 and 8.0 was confirmed by XPS experiments (Figure 6) while no chlorine was detected on the pristine membrane surface. The Cl 2p spectra of membranes aged at pH 6.0 and 8.0 were deconvoluted into two peaks, Cl 2p<sub>3/2</sub> and Cl 2p<sub>1/2</sub> at 200.1±0.2 eV and at 201.9±0.1 eV respectively, corresponding to C-Cl covalent bond [42] (and not to chloride adsorption). These results are consistent with the presence of sulfonic acid groups highlighted by electrokinetic measurements (Figure 3) and confirm that PES-chain scissions occur at both pHs 6.0 and 8.0, which, to the best of our knowledge, has not been reported before.



**Figure 6:** High resolution XPS and deconvoluted peak assignments of Cl 2p<sub>1/2</sub> 2p<sub>3/2</sub> for HFK-131 membranes aged in 200ppm TFC NaOCl solution at pH 6.0 (a) and pH 8.0 (b).

It is worth mentioning that Prulho et al. performed size-exclusion chromatography with PES/PVP blends before and after ageing by sodium hypochlorite and put in evidence PES degradation with the formation of lower molecular weight products [16]. The combination of streaming current and XPS experiments reported in the present work gave additional information since it highlighted the presence of strong acid groups as well as the formation of C-Cl covalent bonds, thus giving credit to the chain-scission scheme shown in Fig. 5.

The membrane aged in NaOCl at pH 11.5 exhibited only a slight increase in its negative net charge density with respect to the pristine membrane (Figure 3), which indicates that PVP was only weakly attacked at pH 11.5 by  $\text{ClO}^-$  after a 10-day ageing in 200 ppm TFC NaOCl. According to reactions (1) and (2) no significant radical attack (and then no substantial PES aromatic rings hydroxylation) is expected at this pH as it was confirmed by the absence of steep increase in the membrane charge density at high pH. It can be noted, however, that PES hydroxylation was detected after longer exposure times (up to 60 days, see Fig. S6 in the supporting information), thus suggesting that PES could actually be degraded by NaOCl at pH 11.5 but that the kinetics of PES degradation is much slower at pH 11.5 than at pH 6.0 and 8.0.

Electrokinetic measurements also revealed that no sulfonic acid groups were formed on the surface of the membrane aged at pH 11.5 since no significant lowering of the membrane iep was detected (Figure 3). This finding therefore indicates that the PES-chain scission mechanism (Figure 5) does not occur when ageing is conducted at pH 11.5 for 10 days (note that no significant shift of the iep was detected even for membrane samples aged for 60 days, as shown in Fig. S6 in the supporting information). The absence of PES-chain scission was confirmed by XPS since no chlorine was detected on the surface of the membrane aged at pH 11.5 (see Fig. S7 in the supporting information).

Results discussed in the previous section allow drawing the following conclusions: (i) PVP can be attacked by  $\text{ClO}^-$  and/or  $\text{HO}^*$  radicals depending on the ageing solution pH, (ii) PES aromatic rings hydroxylation can be provoked by  $\text{HO}^*$  radicals, and (iii) PES-chain scission occurs for membranes aged at pH 6.0 and 8.0 but not at pH 11.5 (at least for ageing conditions applied in this work, i.e. immersion in 200 ppm TFC NaOCl solutions at room temperature for times up to 60 days). This last result suggests that  $\text{ClO}^-$  is not responsible for PES-chain scission.

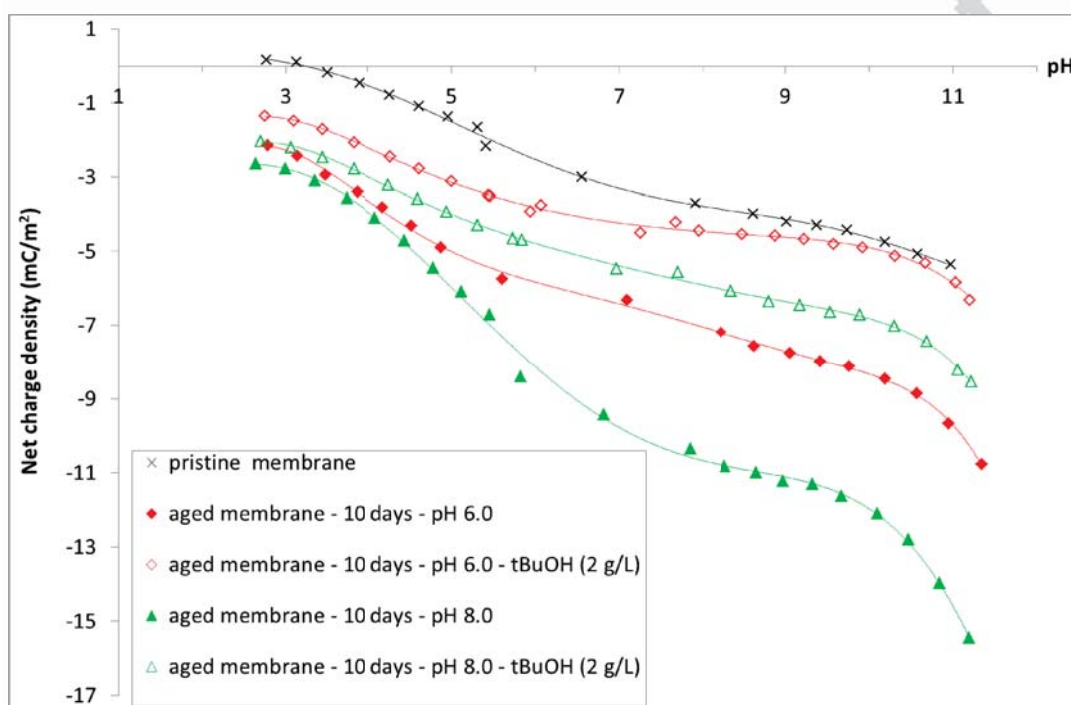
#### *4.3. Role of $\text{HO}^*$ and $\text{HClO}$ species in PES-chain scission*

In order to investigate the effect of  $\text{HO}^*$  radicals and  $\text{HClO}$  on PES-chain scission, a series of additional ageing experiments were conducted at pH 6.0 and 8.0 (for which both species are present in the ageing solution) with the addition of tertibutanol (tBuOH), acting as a free radical scavenger, in sodium hypochlorite solutions. A complementary ageing experiment based on membrane thermo-oxidation was also performed as ageing experiment involving only  $\text{HO}^*$  radicals.

Figure 7 shows the pH dependence of the net charge density of membranes aged at pH 6.0 and 8.0 with and without tBuOH. Interestingly, membranes aged at both pHs lost their iep even when tBuOH was added into the ageing solution. This finding demonstrates that  $\text{HClO}$  is involved in PES-chain scission (as stated previously,  $\text{ClO}^-$  cannot play a significant role since no iep lowering was observed for membranes aged at pH 11.5).

Overall, membranes aged in the presence of tBuOH were found to be less negatively charged than membranes aged without tBuOH, which can be explained by the inhibition of PVP radical oxidation (Figures S3 and S4 in the supporting information) resulting from the addition of the free radical scavenger into the ageing solution. It should be stressed that the

net charge density of the pristine membrane and that of the membrane aged at pH 6.0 in the presence of tBuOH were found to be close over a wide range of pH (except at low pHs because of the presence of sulfonic acid groups onto the aged membrane surface), which suggests that HClO does not substantially attack PVP. Moreover, the steep increase in the negative charge density for pH higher than ca 10 (attributed to the deprotonation of very weak acid functions) was found to be limited when tBuOH was added into the ageing solution, which is explained by the inhibition of the PES aromatic rings hydroxylation in the presence of the free radical scavenger.

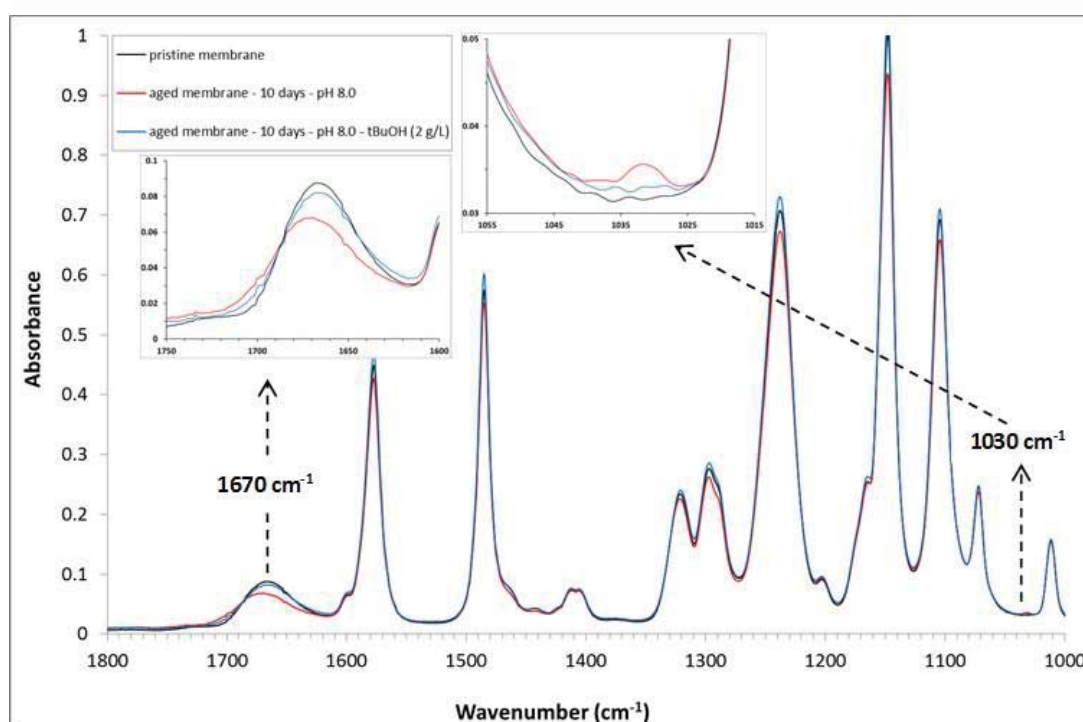


**Figure 7:** pH dependence of the net charge density of HFK-131 membranes aged for 10 days in 200 ppm TFC NaOCl solutions with and without tBuOH at pH 6.0 and 8.0.

Conclusions drawn from Figure 7 are supported by results obtained from ATR-FTIR spectroscopy, which give additional evidence for the inhibition of membrane oxidation by HO\* radicals in the presence of tBuOH (see in Figure 8 the more important modification of



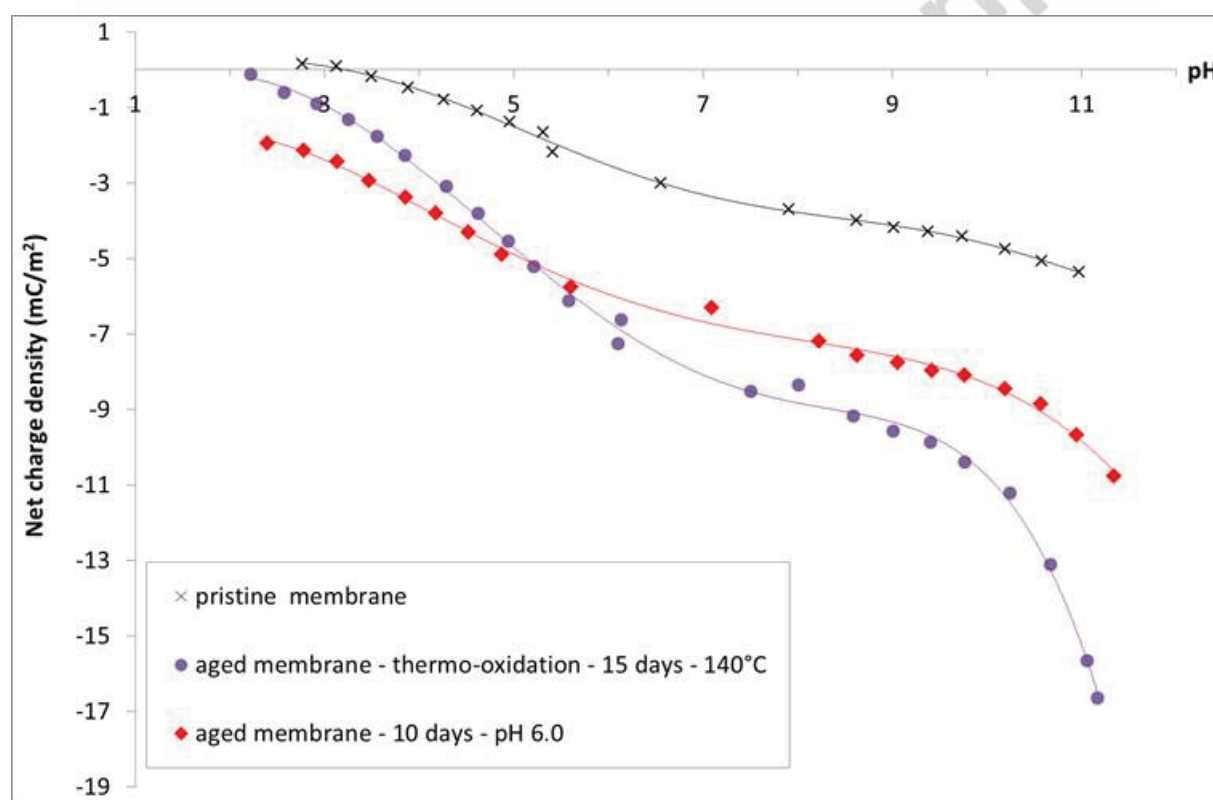
the band corresponding to the C=O vibration of the PVP amide group (band located at  $1670\text{ cm}^{-1}$  for the pristine membrane) for the membrane aged without tBuOH). It is also worth noting that the band of weak intensity observed around  $1030\text{ cm}^{-1}$  for the membrane aged without tBuOH was not detected when ageing was carried out in the presence of tBuOH, thus confirming the inhibition of PES aromatic rings hydroxylation by  $\text{HO}^*$  radicals. Similar results were obtained with the membrane aged at pH 6.0.



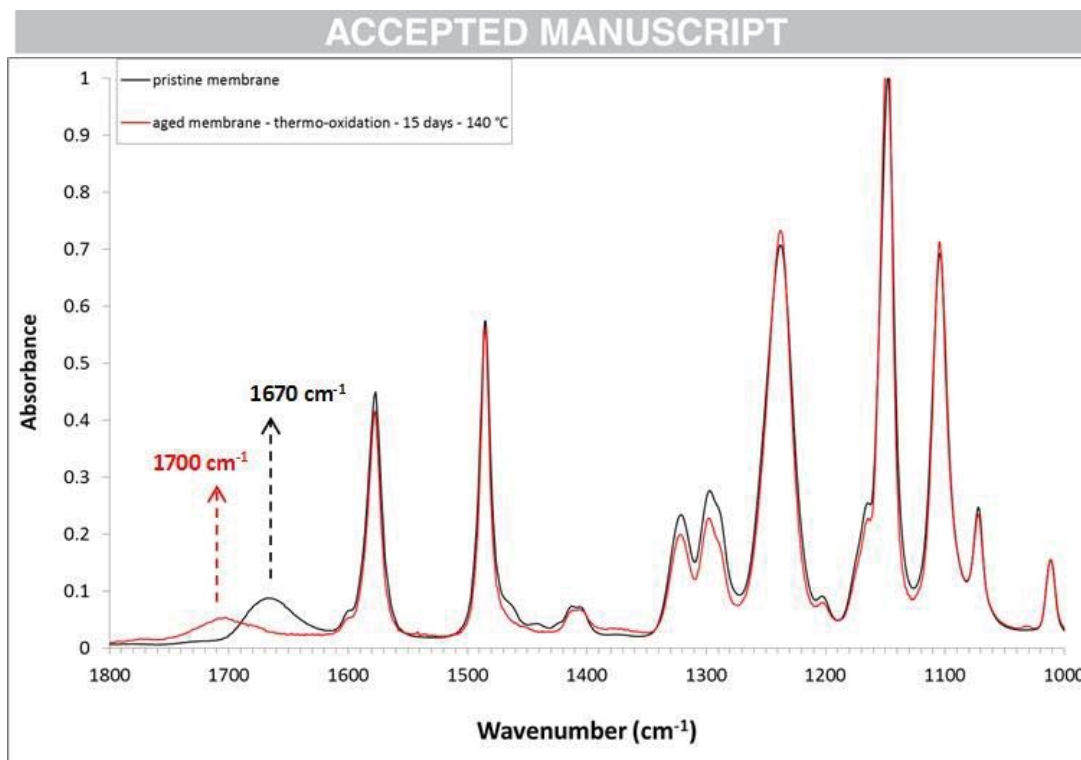
**Figure 8:** Evolution of ATR-FTIR spectra of HFK-131 membranes aged for 10 days in 200 ppm TFC NaOCl solutions with and without tBuOH at pH 8.0.

The impact of  $\text{HO}^*$  radicals was investigated by membrane thermo-oxidation at  $140^\circ\text{C}$  for 15 days. The interest of this additional experiment is to age the membrane in an environment containing only free radicals and no  $\text{HClO}$  species. As observed with the membrane aged in

sodium hypochlorite solution at pH 6.0 (for which HClO is the dominant species), HFK-131 membrane thermo-oxidation led to an increase in the membrane negative charge density (Figure 9). The dramatic increase occurring for pH higher than ca 10 (attributed to ionization of phenol groups as discussed in section 4.2) indicates that a substantial amount of HO\* radicals was produced in the course of the thermo-oxidation experiment, which was confirmed by the presence of succinimide groups (formed by PVP radical attack according to Figure S3 in the supporting information) detected by ATR-FTIR (see Figure 10 showing the appearance of a band around  $1700\text{ cm}^{-1}$  that can be attributed to succinimide groups).



**Figure 9:** pH dependence of the net charge density of the HFK-131 membrane before and after ageing by thermo-oxidation at  $140^{\circ}\text{C}$  for 15 days and by immersion for 10 days into 200 ppm TFC NaOCl at pH 6.0.



**Figure 10:** ATR-FTIR spectra of the HFK-131 membrane before and after ageing by thermo-oxidation at 140°C for 15 days.

Interestingly, Figure 9 shows that the membrane iep was shifted towards lower values after thermo-oxidation (around pH 2.2 vs. 3.2 for the pristine membrane), which indicates a more acidic feature for the aged membrane surface. Nonetheless the membrane aged by thermo-oxidation kept an iep unlike membranes aged in sodium hypochlorite at pHs 6.0 and 8.0. This finding suggests that HO\* radicals might contribute to PES-chain scission but considering results obtained by ageing membranes in 200 ppm TFC NaOCl solutions in the presence of tBuOH (Figure 7), it can be concluded that HClO has more impact than HO\* radicals on PES-chain scission (at least for the ageing conditions considered in this work) since membranes lost their iep when the free radical scavenger was added to the ageing solution.

## 5. Conclusion

The influence of the pH of 200 ppm TFC sodium hypochlorite solutions on PES/PVP ultrafiltration membrane degradation was analyzed on the basis of a static ageing procedure at pH 6.0, 8.0 and 11.5 at room temperature. By means of streaming current measurements, complemented with ATR-FTIR and XPS analysis, it was possible to characterize modifications in membrane chemistry due to membrane ageing and to gain insight into the chemical species involved in the membrane degradation.

Overall modifications of membrane electrokinetic properties after ageing were correlated to the change of filtration performance, i.e. the most significant change being observed for membranes aged at pH 8.0 while membrane charge density, rejection performance and water permeability of samples aged at pH 11.5 were comparatively much less impacted than for membranes aged at pH 6.0 and 8.0.

PVP was degraded by sodium hypochlorite whatever the ageing solution pH. The weakest degradation was observed at pH 11.5 and attributed to PVP attack by  $\text{ClO}^-$  while electrokinetic and ATR-FTIR measurements suggested that PVP chemical degradation occurred mainly through radical attack when ageing was carried out at pH 6.0. Both mechanisms were shown to occur at pH 8.0.

Moreover, electrokinetic measurements gave evidence for PES degradation upon exposure to sodium hypochlorite. The interpretation of electrokinetic data in terms of net charge density allowed showing the formation of phenol groups on the surface of membranes aged in sodium hypochlorite at pH 8.0 and to a lesser extent at 6.0 and pH 11.5. The formation of these groups was attributed to the radical attack of PES aromatic rings as no significant phenol formation was observed in the presence of a free radical scavenger. Moreover, when membranes were aged at pHs 6.0 and 8.0, the disappearance of the membrane iep was

observed and attributed to some PES-chain scissions leading to the formation of sulfonic acid functions on one chain end and to covalent bonding between chlorine and aryl radical on the other chain fragment. This phenomenon was not observed at pH 11.5 which means that  $\text{ClO}^-$  was not involved in PES-chain scissions (in the present ageing conditions). Thanks to ageing experiments performed (i) in sodium hypochlorite solutions in the presence of a free radical scavenger and (ii) by thermo-oxidation, it was demonstrated for the first time that both  $\text{HClO}$  and  $\text{HO}^*$  species contributed to PES-chain scissions. The advanced electrokinetic characterization carried out in this work also revealed that  $\text{HClO}$  had a greater impact on PES degradation than free radicals.

#### **Appendix A. Supporting information**

Supplementary data associated with this article can be found in the online version.

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### Highlights

- **Advanced electrokinetic characterization of PES/PVP membranes aged in NaOCl at different pH**
- **Physico-chemical modification of both PVP and PES was highlighted**
- **PES degradation at pH 6.0 and 8.0 led to the formation of both sulfonic acid and phenol groups**
- **Sulfonic acid groups were not detected on the surface of membranes aged at pH 11.5**
- **HClO played a major role in PES-chain scission**