Swelling of polymeric membranes in room temperature ionic liquids

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Abstract

This research work demonstrates how an optical technique, developed for studying the process of polymer swelling, is able to produce highly reproducible data of swelling of dense polymeric membranes exposed to liquid mixtures. This technique was applied for studying the swelling process of different polymeric membranes, from proton conducting polymers (Nafion) to non-charged hydrophobic polymers, such as a polyurethane–polybutadiene elastomer (PU/PBDO), polydimethylsiloxane (PDMS) and polyvinylidene fluoride membrane (PVDF).

Room temperature ionic liquids (RTILs) were chosen as solvents to be studied, due to the growing interest of using their unique physico-chemical properties in hybrid membrane processes. The results obtained show that the technique developed allows for studying the swelling and “deswelling” of polymeric membranes even when anisotropic phenomena take place. These results are discussed and interpreted from the perspective of the nanoscale properties of the polymers.

1. Introduction

1.1. The swelling phenomenon

Swelling is the process of dissolution of a polymer in a defined solvent. At first, the solvent molecules slowly diffuse into the polymer to produce a swollen gel. If the polymer–polymer intermolecular forces are high, thanks to crosslinking, crystallinity, or strong hydrogen bonding, this is all what happens. But, if these forces are overcome by the introduction of strong polymer–solvent interactions, a second stage, the dissolution of the polymer, can take place [1].

The process of swelling results actually from the balance between repulsive and attractive phenomena. These phenomena may include: the thermodynamic mixing between the net polymer and the solvent; the interaction between fixed charged groups and free ions as happens in proton-exchange membranes; the elastic force of the polymer and also inter-chain attractive forces.

The expansion of the polymer takes place due to the entropic diffusion of its constituent chains and their counterions [2]. On the other hand, swelling is countered by elastic forces within the polymer chain and inter-chain attractive forces. Overall, polymer–solvent systems tend to reach the minimum of the Gibbs energy of mixing, \( G_{\text{mix}} \), which is the driving force of the process.

1.2. Solvent–solute–polymer interactions

The process of sorption and diffusion of solutes into polymers is characterized by the interaction of molecules of all species among them and with the polymer. Their interaction with the polymer chains of the membrane can significantly modify the membrane properties [3–6]. Interaction among different molecules in mixtures, in which the presence of one component has a positive or a negative influence on the rate of transport of
another [7,8], may also have a significant effect on their sorption and penetration into the polymer. During transport into the membrane, two ways of mutual effecting of components may be considered [3]:

1. A free volume effect, which generally leads to increasing of the diffusivity of components (i.e., macroscopically perceived as a plasticizing effect).
2. A coupling effect, which results from interactions between different molecule species within the polymer that may increase or decrease their diffusivity within the membrane (i.e., retarded or accelerated diffusion due to interaction effects).

A careful choice of the solvent, solute and membrane material is therefore crucial for a successful and efficient transport process.

1.3. Methods for quantitative determination of membrane swelling

Membrane swelling has been described in the literature from two different perspectives: “macroscopic swelling”, which is defined as a large scale expansion of polymer membranes measured over an area of at least 1 mm², and is used synonymously with the term “bulk swelling”, and “microscopic swelling”, where the change in dimension is inferred from small-angle X-ray scattering (SAXS) data. The microscopic swelling observation is then defined as the increase in the equivalent Bragg spacing as a result of solvation [9,10].

The macroscopic swelling is usually measured gravimetrically, which in many situations is not very accurate, especially when volatile (methanol and toluene) or viscous (room temperature ionic liquids—RTILs) solvents are used. In the latter case difficulties, when using gravimetric methods, arise from a deficient removing of excess solvent from the membrane surface. In fact, several authors reported the difficulty of removing excess RTILs from the surface of polymeric membranes, even after careful cleaning and rinsing. This behaviour has been also demonstrated by XPS studies of the membrane surface after contact with RTILs. Under these circumstances, gravimetric techniques are rather limited and inaccurate for studying the swelling behaviour of polymeric membranes. Therefore, one of the major aims of our research work was the development and validation of an instrument, and an experimental technique, which allow for the continuous quantitative determination of macroscopic swelling kinetics and equilibrium of thin films.

Another advantage of the proposed technique over widely used gravimetric methods is that all data are obtained “in situ” and, therefore, there are no effects of the external atmosphere during transfer of the samples to the balance and highly volatile or very viscous liquids can be used. This method is also able to perceive rather small and slow membrane swelling, which is an added advantage over gravimetric methods where it is extremely difficult to ensure exactly the same experimental conditions for all measured samples.

Finally, it is worth mentioning that in case of anisotropic swelling of the membrane, as previously described for Nafion® membranes, this method offers the possibility to differentiate and quantify the swelling behaviour in the x and y directions at the membrane plane.

1.4. Membranes and room temperature ionic liquids

Four membranes were investigated in this study: Nafion®, which is a proton exchange membrane, and two non-charged hydrophobic membranes (a polyurethane–polybutadiene elastomer (PU/PBDO) and polydimethylsiloxane (PDMS)) and hydrophilic polyvinylidene fluoride (PVDF) membrane. In fact, we know from previous confocal Raman spectroscopic studies that the PVDF membrane does not solubilise any of the imidazolium-based ionic liquids we have been working with. Still, we decided to perform swelling measurements with hydrophilic PVDF membranes in contact with the “hydrophilic” RTIL, [C₄mim][BF₄]. These materials were chosen due to their commercial application and different physico-chemical properties.

The Nafion membrane is widely used as a reference material in fuel cell studies and is suitable for these experiments due to its high mechanical, thermal and chemical stability. These characteristics are coupled with a high ionic conductivity, which depends strongly on the water content of the membrane. This polymer consists of a polytetrafluoroethylene (PTFE) backbone with sulphonic acid side-groups arranged in intervals along the chain. These acid groups are aggregated into clusters [11,12].

It is widely believed that the properties of Nafion membranes can be derived from the microscopic phase separation of ionic material of the fluorocarbon matrix. In addition, by performing small angle X-ray scattering (SAXS) experiments on Nafion membranes with different water contents, it has been demonstrated that the discrete entities associated with ionic clusters increase in size as the water content of the membrane increases [12–14].

PU/PBDO, PDMS and are important hydrophobic polymers used in several separation processes, such as in vapour permeation and pervaporation processes, where organic solutes are removed/recovered from vapours and diluted aqueous media. PDMS has been also successively used in spray-drying micro-coating to protect powders from the oxidative action of the atmosphere [15]. The PVDF membrane selected has been used in supported liquid membrane studies with RTILs.

This work is focused on the study of membrane swelling when exposed to ionic liquids. This type of compounds has been frequently recognised as new promising “green solvents” [16,17] and their use in hybrid membrane processes has been proposed recently, namely in pervaporation [18–20], supported liquid membranes [21,22], solvent extraction [23] and nanofiltration [24] processes. Ionic liquids exhibit extremely interesting properties:

1. Due to their negligible vapour pressure they are not lost into the environment making possible their repeatedly use in downstream processing.
2. Ionic liquids can solubilize a large range of organic molecules and transition metal complexes, which may present reduced solubility in conventional solvents.

3. Due to selective solute-RTIL interactions it is possible to remove/recover defined target solutes from reaction media, while keeping other reactants or products.

4. Due to their good thermal stability, reactive processes may take place at high temperatures (up to around 250 °C), which leads to faster kinetics in the case of endothermic reactions;

Most RTILs solubilise water in defined amounts and therefore it is not possible to avoid some water dissolution during their use in most processes. For this reason it is extremely important to assess the effect of water content in RTILs, when studying their effect on membrane swelling.

2. Experimental

2.1. Chemicals

Room temperature ionic liquids: [C₄mim] [BF₄] (1-n-butyl-3-methyl-imidazolium tetrafluoroborate), [C₄mim] [PF₆] (1-n-butyl-3-methyl-imidazolium hexafluorophosphate), and [C₈mim] [PF₆] (1-octyl-3-methyl-imidazolium hexafluorophosphate) were prepared using generally reported procedures [25]. These ionic liquids were selected, because they are widely used and they exhibit different physical and chemical properties (see Table 1). The ionic liquid [C₄mim] [BF₄] is, in contrast to [C₄mim] [PF₆] and [C₈mim] [PF₆], totally miscible with water; therefore, it was possible to measure swelling kinetics of the mixture [C₄mim] [BF₄] and H₂O in the whole concentration range.

RTILs were dried under vacuum at 70 °C prior to experiments in order to reach a minimum water concentration, as reported in the Table 2. According to the literature, the hydrophilic [C₄mim] [BF₄] is considered “dried”, if its water content is kept below ~4500 ppm [25], whereas the more hydrophobic [C₄mim] [PF₆] and [C₈mim] [PF₆] are considered “dried” if the water content does not exceed ~600 and ~400 ppm, respectively [25].

2.2. Membranes

The flat non-porous PU/PBDO membrane (Fig. 1a) was prepared at the Department of Material Science of the Universidade Nova de Lisboa, by mixing PU (Mₐ = 3500 g mol⁻¹) and PBDO in a 3:2 ratio in toluene (60 wt% of polymer) at room temperature [26]. Both PU and PBDO were acquired from Sigma–Aldrich. One drop of cross-linking agent, dibutyltin dilaurate was also added. After 0.5 h of mixing with a rotation speed at 60 rpm, under nitrogen atmosphere, the solution was cast onto a glass plate at room temperature with a Gardner knife moving at a controlled speed of v = 5 mm s⁻¹. To complete the cross-linking, the polymer film was cured for 3.5 h in a vacuum oven at 75 °C and then for 3 days at room temperature at ambient atmosphere.

The PDMS membrane (Fig. 1b) was prepared in a similar way by mixing a solution of RTV 615A and RTV 615B (General Electric) in a 10:1 ratio in toluene (60 wt% of polymer) at 60 °C for 0.5 h. The dense membranes prepared were 60 ± 4 μm thick.

The PVDF membrane was provided by Pall Corporation (FP-Vericel membrane).

The Nafion® 112 membrane (Fig. 1c) provided by DuPont de Nemours, USA, was used as received. According to the manufacturer the membrane has the following properties: nominal thickness 51 μm, density 2000 kg m⁻³, ionic conductivity 8.3 S m⁻¹, acid capacity 0.89 mequiv. g⁻¹ and initial water content 5 wt%. This membrane was specifically referred to exhibit anisotropic swelling [27].

<table>
<thead>
<tr>
<th>Ionic liquid</th>
<th>[C₄mim] [BF₄]</th>
<th>[C₄mim] [PF₆]</th>
<th>[C₈mim] [PF₆]</th>
</tr>
</thead>
<tbody>
<tr>
<td>ρ (kg m⁻³) (25 °C)</td>
<td>1.420</td>
<td>1.409 [23]</td>
<td>1.423, 1.423 [23]</td>
</tr>
<tr>
<td>n (20 °C)</td>
<td>1.120 [23]</td>
<td>1.360 [23], 1.320 [20]</td>
<td>1.120 [23], 1.190 [20]</td>
</tr>
<tr>
<td>η (Pa s) (25 °C)</td>
<td>0.12</td>
<td>0.24 [20]</td>
<td>0.58 [20]</td>
</tr>
<tr>
<td>Water solubility in the RTIL (gwater/IL) (25 °C)</td>
<td>Water miscible</td>
<td>27.84 [20]</td>
<td>15.73 [20]</td>
</tr>
</tbody>
</table>

Table 2

Swelling equilibrium data of membranes exposed to “pure” RTILs at 25 °C

<table>
<thead>
<tr>
<th>Membrane</th>
<th>[C₄mim] [BF₄]</th>
<th>[C₄mim] [PF₆]</th>
<th>[C₈mim] [PF₆]</th>
</tr>
</thead>
<tbody>
<tr>
<td>ΔX (%)</td>
<td>ΔY (%)</td>
<td>ΔX (%)</td>
<td>ΔY (%)</td>
</tr>
<tr>
<td>PU/PBDO</td>
<td>0.14</td>
<td>0.25</td>
<td>0.39</td>
</tr>
<tr>
<td>Nafton</td>
<td>4.59</td>
<td>3.68</td>
<td>2.14</td>
</tr>
<tr>
<td>PDMS</td>
<td>0.05</td>
<td>0.00</td>
<td>–</td>
</tr>
<tr>
<td>PVDF</td>
<td>0.14</td>
<td>0.31</td>
<td>–</td>
</tr>
</tbody>
</table>
2.3. Apparatus for measurement of the swelling of membranes

A new optical apparatus for measurement of the swelling kinetics of flat polymer membranes in liquid mixtures was developed and constructed at the Department of Physical Chemistry of the Institute of Chemical Technology, Prague, Czech Republic. The scheme of the apparatus is shown in Fig. 2. This equipment allows for taking images in short sequences by using an optical digital camera with high resolution. The main advantage of this apparatus lies in the possibility of measuring very slow and minute swelling of flat polymers. The accuracy of this optical method is also better than that of gravimetric methods, usually used for swelling equilibrium determination. On the other hand, by this method it is not possible to measure the change of the thickness of the polymer (z direction). This limitation is not relevant if changes of thickness (z) are identical to those in the transverse direction (x and y directions) as happens in isotropic swelling processes.

The digital camera Olympus Camedia 5050 (C) and the magnifying glass (MG-2×) are fixed at a stand with holders (SH). A square (either 0.5 cm × 0.5 cm or 1.0 cm × 1.0 cm) of a dry flat membrane is pierced by the spike of a circle Teflon cell (TCS), threaded onto the spike and put on the bottom of the hollow. To prevent lifting of the membrane after addition of the liquid, the membrane is slightly tacked by two stainless steel wires that do not prevent the extension of the membrane. The cell with the membrane is then placed into a thermostated vessel (TV), controlled by a thermostat (Medingen U8). The camera (C) is then switched on, together with its infra-red remote control and
timer (RCT). The remote control and timer allow to take images at regular intervals. Time intervals can be chosen from 10 to 80 s. For each experiment, the time interval was chosen according to the swelling rate of the particular membrane and liquid mixture.

To exclude the influence of the liquid meniscus distortion in the Teflon cell, blank experiments with a square Teflon film (which does not swell in the liquid mixtures under study) were performed for each mixture and pure solvents. The highest distortion caused by the meniscus was observed with water, which behaved like a magnifying glass. We measured the apparent change of the width $x$ and of the length $y$ of the square Teflon film caused by pouring the liquid mixture into the cell. This change was then subtracted from the length and the width of the wet membrane (typically 2 pixels, i.e. ±0.6%, where 1 pixel is 13 μm). After taking an image of the dry membrane, from which we determined the initial width $x_0$ and length $y_0$ of the polymer, 1 ml of liquid mixture was added with a micropipette 200–1000 μl into the hollow of the Teflon cell. The time between addition of the liquid and the first image of the wet membrane in the liquid mixture was recorded. The images of the membrane extension were then taken automatically until the swelling equilibrium was reached.

The analysis of the data acquired was performed by using the commercial software Zoner Media Explorer 6, Czech Republic. Dimensions of the membrane in dry and wet state were measured in pixels and the extension was evaluated as a relative change of the width $\Delta x$ and of the length $\Delta y$ compared to the initial “dry” membrane ($\Delta x = (x' - x^0)/x^0 \times 100\%$ and $\Delta y = (y' - y^0)/y^0 \times 100\%$, where $x'$ and $y'$ are dimensions of the swelled membrane). The absolute error in determining the membrane extension is 1 pixel i.e. ±0.5% or ±13 μm. The overall absolute error of the measurements including software determination and subtraction of the blank experiment with Teflon square can be as high as 3 pixels i.e. ±0.9%. On the other hand, reproducibility was always better than ±0.9% i.e. ±39 μm in the $x$ and $y$ direction.

![Diagramme of the apparatus developed for determination of swelling kinetics of membranes](image)

Fig. 2. Schematic diagramme of the apparatus developed for determination of swelling kinetics of membranes—C: digital camera Olympus Camedia 5050; MG: magnifying glass; TCS: circle Teflon cell; TVL: thermostated vessel; SH: stand with holders; RCT: infra-red remote control and timer.

### 3. Results and discussion

#### 3.1. Swelling equilibrium

Table 2 presents the swelling equilibrium data measured for the selected membranes, when exposed to the different RTILs under study. In the case of the dense polymeric membranes of PU/PBDO, PDMS and PVDF it was not possible to observe a measurable swelling behaviour. The results obtained for their relative swelling are below 1%, or slightly above, i.e. within the experimental error. These results were confirmed by independent confocal Raman spectroscopy studies using a PVDF and PDMS [27] membrane and various RTILs. It was shown that RTILs are not able to penetrate and “dissolve” inside the structure of non-charged, PDMS and PVDF films.

However, when we evaluate the swelling behaviour of the Nafion membrane exposed to the different RTILs, we can conclude that swelling is taking place even if extremely dried ionic liquids are used. From confocal Raman spectroscopy studies [28] we know that the cation of the RTILs can penetrate and solubilise within the structure of the Nafion membrane, where they interact with negatively charged sulfonic groups and water molecules. Oppositely, the corresponding anions are not able to solubilise due to an efficient Donnan exclusion mechanism.

Additionally, as it can be observed from Table 2, the degree of swelling of the Nafion membrane seems also to include a contribution from the residual water present in these dried ionic liquids. In fact, the relative swelling observed may be related with the water activity of the ionic liquids used (given by the ratio between the water concentration in a given RTIL and the corresponding water saturation concentration), which controls the competitive partitioning of the residual water from the RTIL phase to the membrane.

Fig. 3 shows the swelling equilibrium behaviour of a Nafion membrane when exposed to a binary mixture of deionised water and the RTIL [C₄mim][BF₄]. The first striking observation is the fact that when exposed to “pure” water the Nafion mem-
brane exhibits a clear anisotropic swelling, i.e. it swells much significantly in the transverse direction (x) than in the casting direction (y). Interestingly, when exposed to “pure” ionic liquid the membrane swells isotropically. To understand this behaviour it is necessary to know the structure of a Nafion membrane and how that structure may regulate the process of solute penetration and solvation [29]. Oppositely, the PU/PBDO and PDMS membranes swell in an isotropic ways; irrespectively to the solvent/solute mixtures they are exposed to (see Tables 2–4).

Gierke et al. [30] concluded that the water-swollen morphology of Nafion was best described by a model of ionic clusters ~40 Å in diameter that were approximately spherical in shape with an inverted micellar structure. Taking into consideration the high ionic permselectivity and the requirement of a percolation pathway for ionic transport in Nafion membranes, the ionic clusters were further proposed to be interconnected by narrow channels ~10 Å in size [29]. This presence of ionic clustering in Nafion was supported on SAXS and neutron scattering experiments [12]. Using the SAXS data of Gierke and co-workers over a limited range of water contents, Litt showed that the d spacing are proportional to the volume of absorbed water [31]. Based on this observation, a lamellar model, which is consistent with the bilayer structure suggested by Starkweather [32] was proposed for the morphology of Nafion. In this model, the ionic domains are defined as hydrophilic “micelle” layers separated by thin, PTFE-like crystallites. As water absorbs among these PTFE domains and separates them, then the increase in d spacing between ionic domains is expected to be proportional to the volume fraction of the water in the polymer.

The Nafion membranes were fabricated in a way that induces an anisotropic distribution of ionic domains inside the membrane or their anisotropic shape (lamellae or cylinders) and preferential orientation in the casting (machine) direction y. Therefore, the swelling of Nafion is remarkably higher in the transverse direction x (where elastic forces are weaker), which is perpendicular to the casting direction y.

Clearly, the Nafion membrane used in this work behaves anisotropically. Cleghorn et al. [33] also reported observation of a similar anisotropic swelling of a Nafion membrane in water vapour. The anisotropic swelling of the Nafion membrane, when exposed to water, may be explained by the fact that small water molecules are able to fill up the ionic lamellae domains of the Nafion network much easily than larger and bulkier ionic liquid cations, such as [C4mim]+.

Another interesting feature of the water–[C4mim][BF4] swelling equilibrium is the maximum swelling observed in the mid concentration range (Fig. 3). The maximum swelling occurs when the contribution of both the [C4mim]+ cation and water are relevant. Taking into consideration the structure of the Nafion membrane we may assume that the ionic liquid cation is solvated by water molecules and together they form large clusters that expand the Nafion network. The swelling equilibrium studies were also extended to the use of mixtures of a RTIL with a non-charged, hydrophobic solute able to solubilise in non-charged membranes (hexyl acetate). As the liquid binary mixtures of [C4mim][BF4] and hexyl acetate are only partially miscible we prepared solutions with a maximum concentration of 7% (w/w) in hexyl acetate. The results obtained show a high and isotropic swelling of the hydrophobic membranes due to the solubilisation of the hexyl acetate, which confirms previous observations obtained during vapour permeation and pervaporation studies; they also show that hexyl acetate swells the Nafion membrane significantly, as it would be expected, in an anisotropic mode. This result could be anticipated if we take into consideration that hexyl acetate is a relatively small and mobile molecule, in comparison with the ionic liquids tested.

This experimental work was performed repeatedly and, for the specific situations referred, temperature seems to have no significant effect on the observed swelling behaviour. Still, we have to keep in mind that temperature changes may induce a multitude of effects, which may add or cancel between them: effect on the activity coefficients of the feed components, effect

### Table 3
Swelling equilibrium data of membranes exposed to binary mixtures of [C4mim][BF4] and hexyl acetate at 25 °C

<table>
<thead>
<tr>
<th>Membrane</th>
<th>Hexyl acetate</th>
<th>1.5% (w/w)</th>
<th>7% (w/w)</th>
<th>100% (w/w)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>ΔX (%)</td>
<td>ΔY (%)</td>
<td>ΔX (%)</td>
<td>ΔY (%)</td>
</tr>
<tr>
<td>PU/PBDO</td>
<td>1.06</td>
<td>1.53</td>
<td>2.79</td>
<td>2.81</td>
</tr>
<tr>
<td>PDMS</td>
<td>1.49</td>
<td>1.58</td>
<td>5.10</td>
<td>4.70</td>
</tr>
<tr>
<td>Nafion</td>
<td>12.3</td>
<td>7.00</td>
<td>12.5</td>
<td>7.20</td>
</tr>
</tbody>
</table>

### Table 4
Swelling equilibrium data of membranes exposed to binary mixtures of [C4mim][BF4] and hexyl acetate at 60 °C

<table>
<thead>
<tr>
<th>Membrane</th>
<th>Hexyl acetate</th>
<th>0% (w/w)</th>
<th>1.5% (w/w)</th>
<th>7% (w/w)</th>
<th>100% (w/w)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>ΔX (%)</td>
<td>ΔY (%)</td>
<td>ΔX (%)</td>
<td>ΔY (%)</td>
<td>ΔX (%)</td>
</tr>
<tr>
<td>PU/PBDO</td>
<td>1.02</td>
<td>1.02</td>
<td>1.99</td>
<td>1.71</td>
<td>2.91</td>
</tr>
<tr>
<td>Nafion</td>
<td>4.78</td>
<td>3.47</td>
<td>13.8</td>
<td>7.30</td>
<td>14.0</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>15.9</td>
</tr>
</tbody>
</table>
on the viscosity and diffusion coefficients of the feed components (less important when equilibrium conditions are attained) and effects on the membrane polymer matrix.

3.2. Swelling kinetics

As mentioned before, one of the interesting advantages of the swelling method developed is the fact that it allows to perform not only equilibrium measurements but also in situ kinetic studies. The first observation from Fig. 4 where a PU/PBDO membrane is exposed to pure hexyl acetate is the fact that swelling is fast (from a process point of view), being completed in 2–3 min, and isotropic. This figure is also a good example of the quality of the experimental data that this method allows to achieve.

As can be seen in Fig. 5 the Nafion membrane swells anisotropically when exposed to water, as previously discussed. A fully reversible process is supposed to occur inside the Nafion membrane during dehydration, which was experimentally confirmed. From Fig. 5 it may be concluded that the swelling process is fully reversible when the membrane is exposed to “deswelling” conditions; as it can be observed, after “deswelling” the $\Delta x$ and $\Delta y$ values came to zero.

However, the kinetics of “deswelling” observed is extremely interesting: in first place it is worth to notice that the “deswelling” process is much slower than swelling, which can be explained by the fact that the water inside the Nafion membrane is partially involved in solvation processes inside ionic clusters making their molecules more bounded and structured; secondly, it seems clear that “deswelling” in the $x$ direction starts immediately, while in the $y$ direction it starts only when $\Delta x \approx \Delta y$ (see grey arrow in Fig. 5). Actually, this behaviour suggests that contraction of Nafion in the casting ($y$) direction is only possible when the initial membrane spatial coherence is reacquired. Due to the elastic forces present in the Nafion network, contraction in the $x$ direction proceeds when it starts in the $y$ direction.

On the other hand, “deswelling” of the Nafion membrane exposed to a binary mixture of water and \([\text{C}_4\text{mim}]\) [BF$_4$] is not reversible at all (see Fig. 6). In this case the term “swelling” must be used with care because, in fact, an ion-exchange process is taking place when Nafion uptakes the ionic liquid cation. Even after a period of 100 days under “deswelling” conditions, swelling of the Nafion membrane was not reversed. Taking into consideration the knowledge gathered in this work, we interpret this result as a consequence of the highly bounded situation of the water inside the membrane matrix. As we know RTILs exhibit an extremely low vapour pressure, which explains why swelling due to RTIL solubilisation inside the membrane is not reversible. Additionally, it seems that all water uptaken during the swelling process is most likely strongly solvating the cation from the RTIL inside the Nafion structure. The interactions established are sufficiently strong and stable to impede water to leave the Nafion membrane.

4. Conclusions

This work demonstrates that the equipment designed and constructed for measurement of membrane swelling is a reliable and powerful tool to follow the kinetics and equilibrium of solute/solvent uptake by flat membranes. This technique reveals to be particularly adequate for studying situations where anisotropic swelling occurs; other techniques based on the over-
all volume or mass change are not able to account for this effect and to quantify it.

The results obtained, when studying the swelling of Nafion membranes, show also how the process of molecular solubilisation and swelling can be influenced by the fabrication conditions used during the manufacturing process. This aspect is particularly important if we take into consideration that the swelling process itself may also reflect on the transport properties of the polymer. When considering the Nafion membranes under study, with applications in low resistance devices such as fuel cells and transducers, their transport properties are obviously of high importance and may determine their performance under operating conditions.

The understanding of the swelling behaviour of thin films is therefore essential for a comprehensive design of membrane processes, from a better control of the nanoscale properties of materials towards membrane macroscale applications.

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