

# DETERMINATION OF WATER VAPOR SORPTION AND SOME TRANSPORT PARAMETERS FOR THE AROMATIC POLYAMIDE LAYER OF RO MEMBRANES

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## **ABSTRACT**

This paper reports the isolation of individual layers in a thin composite reverse osmosis membrane. Unlike previous studies where the active layer has always been isolated on top of a solid support, we were able to obtain layers of unsupported active layer. These layers were characterised for their thickness, water vapour sorption and salt transport properties.

## **INTRODUCTION**

Since their introduction in the early 1970s, thin film composite membranes have dominated over cellulose acetate membranes for reverse osmosis processes. Thin film composite membranes are usually formed by depositing a thin layer of aromatic polyamide on top of a porous polysulfone support which is further strengthened by a non-woven polyester backing. It is the thin polyamide layer that is responsible for the high water flux and salt rejection properties of the membrane. Isolation and characterisation of the individual layers is difficult. In particular the polyamide active layer, with a thickness of a few hundred nanometers, becomes physically difficult to handle without any support. However, characterization of the individual layers is warranted as they will provide important information that will further the understanding as well as improve the performance of thin film composite membranes.

Recently, Freger (Freger 2004) have reported a method of dissolving the polysulfone support and isolating the active layer directly onto a solid electrode. The ion transport through the active membrane was then characterised using electrochemical impedance spectroscopy (EIS). Although they have demonstrated that it is possible to characterise the ion transport in the active layer without the porous supporting layer, careful interpretation of the EIS data and identification of possible artifacts is required for the data to be meaningful. Following Freger's recipe to remove the supporting layer, this paper will report our attempts to isolate the active layer onto an orifice and directly perform transport measurements in a diffusion cell. The characterisation of the active layer for its water vapour sorption and thickness using AFM will also be reported.

## **EXPERIMENTAL DETAILS**

### **Chemical reagents and membranes**

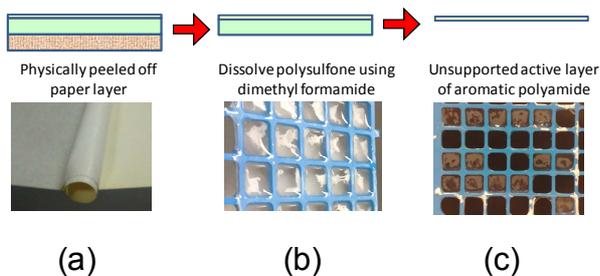
A commercial polyamide membrane Dow Filmtec SW30 and a porous polysulfone membrane support were kindly supplied by Dow Filmtec and GE Water, respectively. N,N-dimethyl formamide (DMF) (98 %, Chemsupply), 1,3-phenylenediamine (MPD) (99+%, Aldrich), trimesoyl chloride (TMC) (98 %, Aldrich), sodium chloride (NaCl) (99 %, Chemsupply) calcium chloride (CaCl<sub>2</sub>) (98+ %, Merck) and n-hexane (95 %, BDH) were used as received.

### **Membrane preparation**

The individual layers of the SW30 membrane were separated following the method reported by Freger (Freger 2004). The steps are illustrated in Figure 1. The nonwoven polyester paper backing was physically peeled away leaving the polysulfone with the active layer (Figure 1 (a)). The polysulfone layer was dissolved and washed away from the active layer using DMF. The washing procedure was repeated several times until all the polysulfone was removed. The active layer was then washed a few times with Milli-Q water. The active layer ( $\approx$  200 nm) is too thin to exist free from any support. Therefore, the polysulfone with active layer was rested over a plate with an array of 1 x 1 cm square holes while the polysulfone was being removed by DMF (Figure 1 (b)). The result is an array of 1 x 1 cm squares of free standing layer of aromatic polyamide. Figure 1 (c) shows a few squares of partially dried active layer that have survived the washing process.

The porous membrane support from GE consisted of the polyester and polysulfone support without the active layer. Similar to Figure 1 (a), the polyester paper backing can be peeled away to give only a single layer of polysulfone support.

In situ-prepared thin film composite membranes were made by interfacial polymerization (Cadotte 1981). GE polysulfone was soaked in a solution of 2 % w/v MPD in water for 15 min. The excess MPD solution was removed from the surface of the polysulfone support before immersing in a solution of 0.1 % w/v TMC in hexane. The contact time for the interfacial reaction was 10 seconds. The membrane was then washed with hexane to removed any excess TMC, followed by Milli-Q water for the removal of any excess MPD. The membrane was then kept in Milli-Q water.



**Figure 1: Isolation of SW30 active polyamide layer from its support. (a) Non-woven polyester support is peeled away. (b) The polysulfone is removed by washing it with DMF and (c) drying of free standing aromatic polyamide active layer.**

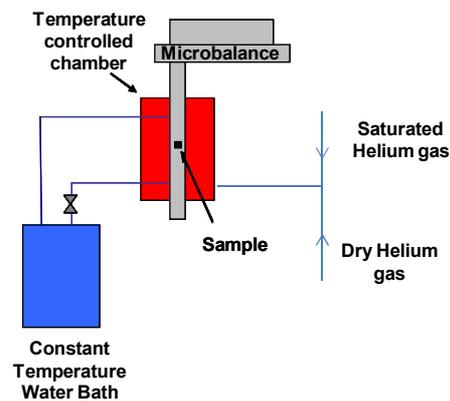
For the salt diffusion experiments, membranes with porous polysulfone support were soaked in Milli-Q water over night before compaction at 1000 Psi in a deadend filtration system overnight. The membrane was then flushed with Milli-Q water at 600 Psi. This ensured that there were no trapped air in the porous support. It was found that membranes that was not compacted or flushed floated; whereas membranes which were compacted and flushed sank in the water, indicating that entrapped air had been removed.

#### Membrane thickness:

The thickness of the polysulfone support was measured using a micrometer. For the thin polyamide layer, the thickness was measured using AFM (Digital Instruments Dimension 3100) in tapping mode following the “scratch” method described by (Anariba, DuVall and McCreery 2003). The polyamide was isolated on a glass slide and scratched with a sharp needle tip. The topography of the membrane obtained by the AFM in tapping mode reveals the depth of the scratch, which corresponds to the thickness of the active layer.

#### Water vapour sorptions:

The sorption of of water vapour by the membranes were conducted on a Gravimetric Sorption Analyzer (GHP-FS, with a Cahn D-200 balance, VTI Scientific Instruments, Florida) in flow mode. Figure 2 is a schematic of the instrument. Membrane samples were placed in a sample holder that is suspended inside a temperature controlled chamber. The relative humidity inside the chamber is controlled by varying the flow of saturated and dry helium gas. For a given relative humidity, the system is allowed to equilibrate until a constant mass was recorded.



**Figure 2: Water sorption measurement instrument (Gravimetric Sorption Analyzer).**

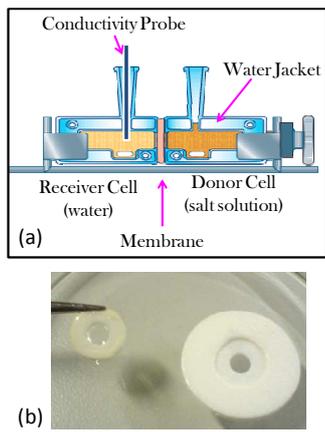
#### Salt diffusion experiments:

The membranes were stripped of their paper backing support, so it was not practical to run reverse osmosis experiments on the membranes. Therefore, direct osmosis technique was employed to examine the salt diffusion through various layers of a thin film composite membrane.

A diffusion cell from Permgear was used to perform direct osmosis experiments. The set up is depicted in Figure 3 (a). It consisted of a two compartment cell design. The membrane was sandwiched between two teflon gaskets and clamped between the two compartments. One compartment (receiver cell) was filled with Milli-Q water whereas the other compartment (donor cell) was filled with electrolyte solution. The solutions were stirred to reduce external concentration polarization. Cooling water was used to maintain the temperature of the solutions at 20 °C. The concentration of electrolyte in the receiver cell was recorded as a function of time using a conductivity probe, and the conductivity converted to salt concentration via a calibration curve.

Figure 3 (b) is an image of the gasket used to sandwich the membranes between the diffusion cells. The smaller gasket on the left shows a single layer of polyamide from an SW30 membrane laid over the orifice. This was then placed in the gasket and between the cells as indicated in Figure 3 (a).

For all experiments, the membranes were examined without the paper backing. The different layers investigated and the abbreviation used are as follows: 1) SW30 polysulfone with polyamide - SW30 (PS+PA), 2) SW30 polyamide - SW30PA, 3) GE polysulfone - GEPS and 5) GE polysulfone with insitu polyamide - GEPS+PA.



**Figure 3: (a) Diffusion cell and (b) image of the active polyamide layer and gasket to be sandwiched between the diffusion cell.**

The mass transfer coefficient or permeability constant was calculated using Equation 1 (Jost 1960):

$$-\frac{V}{2A} \ln \left( 1 - \frac{2C_R(t)}{C_D(0)} \right) = k_{ov}t \quad [1]$$

$$k_{ov} = \frac{1}{\frac{1}{k_{PS}} + \frac{1}{k_{PA}}} \quad [2]$$

Where  $C_w(t)$  is the salt concentration in the receiver cell at time  $t$ ,  $C_s(0)$  is the initial salt concentration in the donor cell,  $V$  is the volume of solution in each cell,  $A$  is the membrane area and  $K_{ov}$  is the overall mass transfer coefficient. For membranes with two layers, the overall mass transfer coefficient measured can be related to the mass transfer coefficients in polysulfone (PS) and polyamide (PA) described by Equation 2.

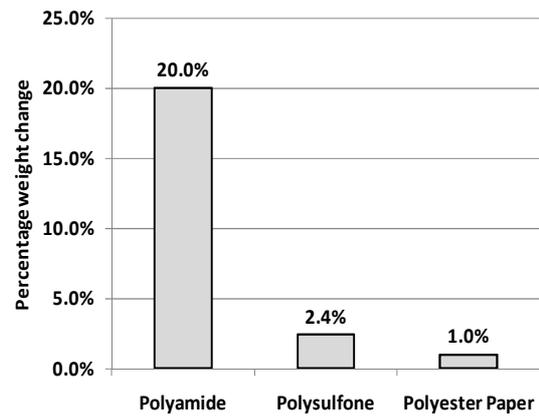
## RESULTS AND DISCUSSION

### Thickness:

The thickness of the individual layers of membrane studied are tabulated in Table 1. The thickness of the commercial polyamide is comparable to the thickness given by the manufacturer. The polyamide made in the lab was thinner compare to SW30PA. For SW30PS+PA, the contribution from the polyamide will be negligible.

**Table 1: Thickness of the individual layers of membrane studied.**

Membrane layer	Thickness [ $\mu\text{m}$ ]
SW30 PA	$0.232 \pm 0.003$
SW30 PS+PA	$67 \pm 3$
PA	$0.138 \pm 0.009$
GEPS	$56 \pm 4$



**Figure 4: The percentage of weight change of the individual layers at 95 % relative humidity. Water vapour sorptions:**

The data for the water vapour sorption by the individual layers of SW30 membrane is presented in Figure 4 as the percentage weight change at a relative humidity of 95 %. The polysulfone used has the polyamide layer. However, because the polyamide is so thin it only constitutes 0.3 % of the total weight of the membrane. It is thus assumed that the percentage weight change recorded is predominately due to the polysulfone layer only.

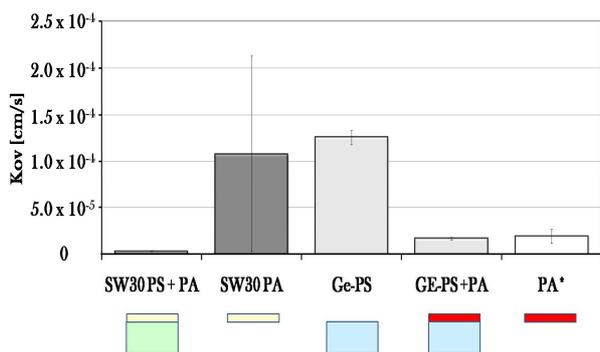
Figure 4 shows that the percentage weight change is greatest for the aromatic polyamide at 20 %, follow by the polysulfone at 2.4 % and the lowest weight change of 1.0 % by the polyester paper backing. These suggests that the polyamide is more hydrophilic compare to the polysulfone and polyester paper. The hydrophilic properties of the polyamide are well known and can be related to the amide (-NH) and carbonyl (-CO) groups (Arthur 1989, Puffr and Sebenda 1967)

### Salt diffusion experiments:

The mass transfer coefficient of NaCl for various membrane layers is shown in Figure 5. For the two layers of SW30 PS+PA, a  $k_{ov}$  of  $3.2 \times 10^{-6}$  cm/s was measured. However, for SW30PA, the  $k_{ov}$  measured was high ( $1.08 \times 10^{-4}$  cm/s) and there was a large error bar associated with it. This suggests that the unsupported polyamide is too thin to be self-supporting and is damaged when clamped between the diffusion cells.

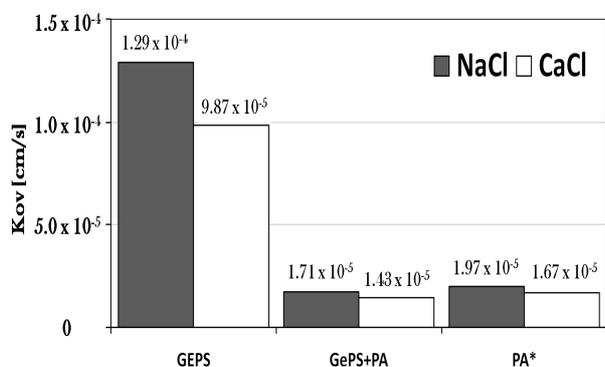
In order to use Equation 2 to calculate the  $k_{PA}$ , we need to determine  $k_{ov}$  for the two layers and then  $k_{PS}$ . For GEPS, a  $k_{PS}$  of  $1.26 \times 10^{-4}$  cm/s was measured. When a layer of polyamide was interfacially polymerized on GEPS, the  $k_{ov}$  was  $1.66 \times 10^{-5}$  cm/s. This is slightly greater than the SW30PS+PA, which can be attributed to a thinner active layer shown in Table 1. In addition to this, SW30 may have an extra coating, which would give the membrane extra resistance to the diffusion of salt. Using Equation 2,  $k_{PA}$  was calculated to be  $1.91 \times 10^{-5}$  cm/s. This indicates that for the two

layers, 13 % resistance is due to the polysulfone support and 87 % is due to the active layer.



**Figure 5: Mass transfer coefficient of NaCl for various layers of membrane. The \* indicates that the coefficient was calculated using equation 2. 50 g/L (0.87 M) of NaCl was used.**

The mass transfer coefficient for  $\text{CaCl}_2$  through the different membrane layers are depicted in Figure 6. Compared to NaCl, the mass transfer coefficient for  $\text{CaCl}_2$  is lower. This is as expected as calcium is sterically larger and has a higher charge (Hall, Lloyd and Starov 1997) and as a result, there is a lower concentration of  $\text{CaCl}_2$  in the membrane than for NaCl. In addition, the diffusion coefficient for  $\text{CaCl}_2$  is slower compare to NaCl. This is reflected in the lower  $k_{ov}$  in the GEPS for  $\text{CaCl}_2$  compare to NaCl.



**Figure 6: Mass transfer coefficient of  $\text{CaCl}_2$  through a GePS, GEPS+PA and PA\*. The \* indicates that the coefficient was calculated using equation 2. A salt concentration of 0.034 M was used.**

## CONCLUSION

In this work, it has been demonstrated that the active layer of a thin film composite membrane (thickness  $\approx 232 \pm 3$  nm) can be isolated free from any support.

Water sorption measurements showed that at 95 % humidity the active layer had a water vapour sorption of 20 % by weight compare to 2.4 % by the polysulfone and 1.0 % by the polyester paper backing.

The active layer was proven to be too thin to be investigated by the diffusion cell for salt transport properties. However, assuming that the resistance in the two layer membrane are in series, we were able to calculate the salt transport through the active layer. It was found that 87 % of the total resistance is from the active layer and 13 % from the polysulfone support. The mass transfer coefficient of NaCl and  $\text{CaCl}_2$  through the active layer was calculated. It was found that  $\text{CaCl}_2$  had a lower mass transfer coefficient compare to NaCl. This is because calcium is sterically larger, has a higher charge and lower diffusion coefficient.

We intend to extend the work to study a variety of salts as well as both boric acid and endocrine disruptors. The aim is to build a database of data for the development of an improved model of solute permeation through RO and NF membrane materials.

## ACKNOWLEDGMENTS

The authors would like to thank the support of Particular Fluids Processing Centre, a Special Research Centre of the Australian Research Council for access to equipment.

## REFERENCES

- Freger, V. *Environ. Sci. Technol.* **2004**, Environ. Sci. Technol., 38, 3168.
- Cadotte, J. E., Interfacially synthesized reverse osmosis membrane, US Patent, 4,277,344, Feb. 22, 1978
- Anariba, F.; DuVall, S. H.; McCreery, R. *Anal. Chem.* **2003**, Anal. Chem., 75, 3837.
- Jost, W. *Diffusion in solids, liquids and gases*; Academic Press: New York, 1960.
- Arthur, S. D. *J. Membr. Sci.* **1989**, J. Membr. Sci., 46, 243.
- Puffr, R.; Sebenda, J. *J. polym. Sci. Part C* **1967**, J. polym. Sci. Part C, 16, 79.
- Hall, M. S.; Lloyd, D. R.; Starov, V. M. *J. Membr. Sci.* **1997**, J. Membr. Sci., 128, 39.