

# Separation of Water and Isopropyl Alcohol Mixtures with Graphene Oxide Membranes

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**Abstract-** Hydrophilic, water selective, Graphene Oxide (G.O.) membranes were prepared by coating aqueous G.O. solution on a hydrophilic PVDF (polyvinylidene fluoride) polymeric support. G.O. membranes were found to provide competitive permeate flux and purity when compared to other state-of-the-art and commercial membranes. Membranes were tested by pervaporation using water/isopropyl alcohol (IPA) mixtures at 50 to 70 °C. We observed water fluxes ranging from 0.1 to 2 kg/m<sup>2</sup>/hr, with the water flux increasing linearly with water vapour pressure and decreasing linearly with the thickness of the GO layer. The permeate consisted of 97.0 – 99.3 wt% water, with no discernable trend line in the investigated temperature and membrane thickness region.

## Nomenclature

$J$	Permeability, kg/h/m <sup>2</sup>
$km.p$	Mass transfer coefficient, kg $\mu$ m/h/m <sup>2</sup> /bar
$\delta_{GO}$	Membrane thickness, $\mu$ m
$P_L$	Water partial pressure on the liquid side, bar
$P_P$	Water partial pressure on the permeate side
$x$	Water mole fraction, dimensionless
$T$	Temperature, K
$\gamma(T)$	Water activity coefficient at temperature $T$ , dimensionless
$\Delta W$	Weight difference, mg
$V_{GO}$	Volume of the G.O. solution, L
$C_{GO}$	Concentration of the G.O. solution, mg/L

## 1. Introduction

Concentration driven separation using membranes with ultra – fast water permeation rates and high selectivities are highly sought after in the chemical industry. Currently, polymeric membranes exhibit high selectivities and economically feasible transport rates (White, 2006). However, they are prone to rapid degradation during the membrane surface cleaning operation and swelling if exposed to organic solvents at elevated temperatures (Van der Bruggen et al., 2008, Ulbricht, 2006). Porous inorganic membranes (ceramic, zeolite) have circumvented these issues. They tend to have good chemical compatibility with organic materials across a wide range of temperatures and a strong rigid structure able to withstand harsh environments.(van Veen et al., 2011). However, their manufacturing process is time consuming and complex resulting in a high cost, which limits their economic feasibility in the chemical industry.(Choi et al., 2006, van Veen et al., 2011, Verweij, 2012) In 2012 ,(Nair et al., 2012) reported a submicron thick G.O. membrane capable of facilitating highly selective water transport. Since then, highly selective and cheap G.O. has caught researcher attention as a potential hydrophilic membrane material (Huang et al., 2014a).(Yeh et al., 2013, Liu et al., 2014, Huang et al., 2014b).

The main aim of our research is to investigate water flux and permeate purity *via* pervaporation through G.O. – PVDF membranes and evaluate the competitiveness of GO membranes with commercial membranes.

## 2. Theory

Typically, G.O. is obtained by an oxidation of graphite using Hummers method or Improved Hummers method (Hummers and Offeman, 1958, Chen et al., 2013, Marcano et al., 2010) The method uses Sulphuric acid, H<sub>2</sub>SO<sub>4</sub>, Sodium Nitrate, NaNO<sub>3</sub>, and Potassium Permanganate, KMnO<sub>4</sub> all of which are mass produced chemicals and can be purchased at a low price. The oxidised graphite is then exfoliated to yield G.O. suspension containing predominantly single layer sheets. This, in turn, can be used to produce a semipermeable hydrophilic membrane with an extraordinary affinity for water.(Nair et al., 2012). The permeability has been attributed to the formation of nanoscale wrinkles and structural defects in the basal plane of the G.O. material which is a result of the amorphous oxygenated regions.(Huang et al., 2013) Interestingly, no gas molecules like helium can pass through the membrane.(Nair et al., 2012)

The key membrane performance characteristics are permeation flux and permeate purity which are affected by: i) mass transport through the liquid boundary layer, ii) preferential sorption of the permeating species into a membrane matrix, iii) diffusion through the GO layer, iv) desorption from the GO layer, v) vapour transport through a porous PVDF support, vi) mass transport through a vapour boundary layer.(Baker, 2004) All of these steps can be mathematically combined (Wijmans and Baker, 1995) to yield the solution diffusion model, which stems its roots from the Fick's law. An alternative version of the solution – diffusion model is shown in equation (1).

$$J = k_{M.P}/\delta_{GO} * (P_L - P_P) \quad (1)$$

$$J = k_{M.P}/\delta_{GO} \left( x_{water} * \gamma_{water}(T) 10^{5.40221 - \frac{1838.675}{-31.737+T}} \right) \quad (2)$$

In this equation (1),  $J$  is the permeation flux (kg/h/m<sup>2</sup>),  $k_{M.P}$  is the permeation coefficient, which is the product of all aforementioned parameters involved in the membrane permeation flux and permeate purity (kg μm/h/m<sup>2</sup>/bar) and  $\delta_{GO}$  is the membrane thickness (μm).  $P_L - P_P$  is the permeation driving force expressed as the difference of the partial pressure of water on the liquid and vacuum sides respectively (bar). The absolute pressure on the permeate side is significantly smaller than the water vapour pressure on the process side, and can thus ignored as a contributing factor. Further in equation (2),  $x$  is the water mole fraction in the fluid,  $T$  is the temperature of the liquid on the process side (K), and  $\gamma(T)$  is water activity coefficient (dimensionless).  $\gamma(T)$  is computed from the NRTL model using Aspen Plus.

## 3. Experimental

### 3. 1. Membrane Coating

A circular hydrophilic polyvinylidene fluoride (PVDF) membrane (GVWP04700 Durapore, purchased from Millipore). was placed in the middle of a three piece Whatman filter funnel (70mm diameter, 210 mL reservoir volume). The funnel was filled with 20 ± 1 mL of DI water to pre-wet the PVDF membrane. A vacuum was applied to initiate filtration. Once the water passed through the filter the vacuum was switched off and the funnel was filled with a desired amount of G.O. suspension (±1 mL) obtained from Graphene Supermarket (3 – 25 mg/L diluted with deionised water) . To filter the G.O. suspension the vacuum was applied either by water vacuum tap (460 mbar) or by vacuum pump (10 mbar); the vacuum was measured using manometer (FB57057 Fisher Scientific). As the liquid passed through the PVDF a graphene oxide film was deposited on the surface. On completion of the filtration, the three piece filter funnel was disassembled and the membrane was carefully removed and placed in an oven (STATUS) at 76 °C for at least 2 h. This produced golden - brown graphene oxide coating on a

PVDF polymeric support. The thickness of the membrane was varied by changing the amount of the G.O. used to produce the film.

The concentration of the G.O. suspension was determined by measuring the weight gain of a support membrane after G.O. coating with a known volume of GO suspension. A fresh PVDF membrane was weighted using a Mettler Toledo AB 304 S microbalance with an accuracy of  $\pm 0.1$  mg before and after the coating process described in section 3.1. The concentration of the GO solution can be calculated using equation (3):

$$C_{GO} = \frac{\Delta W}{V_{GO}} \quad (3)$$

Where  $\Delta W$  is the weight difference (mg),  $V_{GO}$  is the suspension volume used to produce a membrane (L), and  $C_{GO}$  is the concentration of the G.O. solution (mg/L). Thereafter, thickness of the films were calculated by dividing the mass placed on the support polymer by the surface area coated and the G.O. density.

### 3. 2. Pervaporation

The pervaporation setup used in all experiments is shown in Fig. 1. It comprises of: i) a conical flask (250 mL) which was used as a feed tank (T1) ii) a pump P1, (Knauer Smartline two piston pump) to circulate the fluid through the cell, iii) a back pressure regulator BPR (2.8 bar) was used to keep the system from boiling. (iv) In - house developed agitated stainless steel pervaporation cell PERVAP (74 mL, 9.08 cm<sup>2</sup> active membrane surface area). Agitation in the cell was provided by a magnetic stirrer bar rotating at 900 rpm. and iv) the permeate side is connected to two cold traps TRAP1 and TRAP2 which were set - up in parallel to ensure continuous operation. Liquid nitrogen was used as a cooling liquid for the permeate condensation (-195 °C). The vacuum side pressure was set at <5 mbar at all times using vacuum pump P2, (EDWARDS RV3).

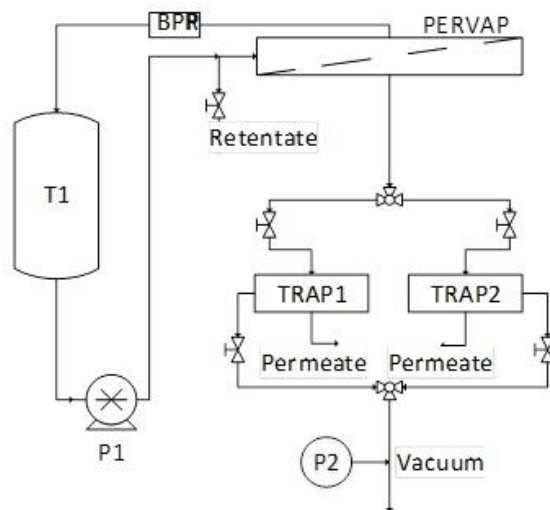


Fig. 1. – Pervaporation setup

A conical flask, T1, was filled with  $65 \pm 1$  mL of deionised water and  $150 \pm 1$  mL IPA, analytical grade purchased from VWR International, resulting in a 30 wt% water/IPA solution. A vacuum on a pervaporation cell vacuum side was then applied by EDWARDS RV3 vacuum pump, P2. Once < 5 mbar pressure was reached on the vacuum side of the pervaporation cell the process fluid pump P1 was used to fill the process side with the water/IPA solution.

The full pervaporation cell was then placed in a hot oil or water bath set at 50 – 70 °C. This was followed by approximately 1 hour of pre – equilibrium stage allowing pervaporation cell to reach process temperature and pervaporation flux gain steady state. Thereafter, samples were taken every 1 – 3 hours and analysed by Karl Fischer (Metler Toledo DL38) and GC (HP 6890Series coupled with HP5 30m length, 0.25  $\mu$ m film thickness, reversed – phase column).

## 4. Results and Discussion

### 4. 1. Effect of Liquid Side Water Vapour Pressure on Water Flux And Permeate Purity

To gain an insight into the G.O. – PVDF membrane permeation performance in a presence of 30 wt% water/IPA mixture pervaporation tests were performed in a temperature range of 50 – 70 °C. To test if the GO membrane behaviour is consistent with equation (1), the pervaporation flux through a

membrane with a 2.1  $\mu\text{m}$  GO layer is plotted first against the driving force  $P_L$  (Figure 2, a). The permeate flux increases linearly with the driving force  $P_L$  whilst maintaining the purity of the water on the permeate side at unprecedented levels between 97.9 to 99.5 wt%. In all experiments the observed permeate quality was considered to be very pure and is comparable purity with other research or commercial membranes. (Han et al., 2014, Qiao et al., 2005) The variations in water purity do not follow any observed trend, and are most likely caused by a variation in the membrane quality.

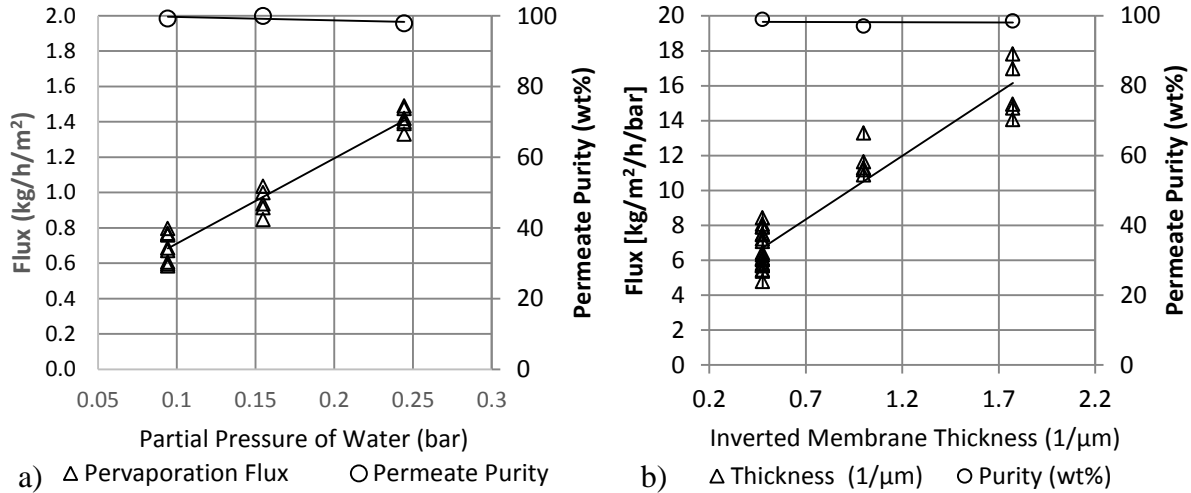


Fig. 2. a) Pervaporation Flux vs Partial Pressure (2.1  $\mu\text{m}$ ), b) Pervaporation Flux vs Thickness

#### 4. 2. Effect Of Membrane Thickness On Water Flux And Permeate Purity

To test pervaporation flux change with respect to the membrane thickness the pervaporation flux in equation (2) was divided by the partial pressure of water over the solution to yield equation (4):

$$\frac{J}{P_L} = k_{M,P} \frac{1}{\delta_{GO}} \quad (4)$$

To test the impact of GO layer thickness, we evaluated the flux at different temperatures for a range of 3 different membranes (

Fig. 2, b). The pervaporation flux linearly increased with a decrease in the selective membrane layer which was anticipated and is in agreement with well established membrane research. (Wijmans and Baker, 1995) Pervaporation flux was extremely high with a pervaporation constant  $k_{M,P}$  having a value of  $12.4 \text{ kg } \mu\text{m}/\text{h}/\text{m}^2/\text{bar} \pm 24\%$ . It was estimated that a  $1.2 \mu\text{m}$  membrane at one bar pressure and 30 wt% water in IPA would result in a  $10 \text{ kg}/\text{h}/\text{m}^2$  water flux.

The purity of the permeate remained high in the entire region studied and was in a range of 97 – 99 wt%; There was, again, no observable trend for the permeate purity in the studied thickness range.

#### 5. Conclusions

Hydrophilic water selective G.O. membranes were successfully coated on a hydrophilic PVDF support layer. The GO layer was stable in a temperature range of 50 – 70  $^{\circ}\text{C}$ . Pervaporation tests with the membranes demonstrated excellent, and consistently high (>97%) water purity of the permeate and high water transport fluxes. The highest pervaporation flux was found to be  $1.87 \text{ kg}/\text{h}/\text{m}^2$  and a permeate purity of 97.04 wt%. using  $1 \mu\text{m}$  G.O. membrane at 60  $^{\circ}\text{C}$ . The water flux was modelled as function of water vapour pressure and GO layer thickness. The model indicates GO membranes can potentially reach a water flux greater than  $10 \text{ kg}/\text{h}/\text{m}^2$  at submicron thick GO layers, making them comparable to the commercial and the state-of-the-art membranes. (Qiao et al., 2005)

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## Reference

- Baker R. 2004, *Membrane Technology And Applications*, 2nd Edition, John Wiley & Sons.
- Chen J., Yao B., Li C. & Shi, G. 2013, An Improved Hummers Method for Eco-Friendly Synthesis of Graphene Oxide, *Carbon*, 64, 225-229.
- Choi H., Stathatos E. & Dionysiou D. D. 2006, Sol-Gel Preparation of Mesoporous Photocatalytic TiO<sub>2</sub> Films and TiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> Composite Membranes for Environmental Applications, *Applied Catalysis B: Environmental*, 63, 60-67.
- Han Y-J., Wang K-H., Lai J-Y., and Liu Y-L. 2014, Hydrophilic Chitosan-Modified Polybenzimidazole Membranes For Pervaporation Dehydration Of Isopropanol Aqueous Solutions, *Journal Of Membrane Science*, 463, 17-23.
- Huang H., Song Z., Wei N., Shi L., Mao Y., Ying Y., Sun L., Xu Z. & Peng X. 2013, Ultrafast Viscous Water Flow Through Nanostrand-Channelled Graphene Oxide Membranes, *Nat Commun*, 4.
- Huang H., Ying Y. & Peng X. 2014a, Graphene Oxide Nanosheet: An Emerging Star Material for Novel Separation Membranes, *Journal Of Materials Chemistry A*, 2, 13772-13782.
- Huang K., Liu G., Lou Y., Dong Z., Shen J. & Jin W. 2014b, A Graphene Oxide Membrane with Highly Selective Molecular Separation of Aqueous Organic Solution, *Angewandte Chemie International Edition*, 53, 6929-6932.
- Hummers W. S. & Offeman R. E. 1958, Preparation of Graphitic Oxide, *Journal of the American Chemical Society*, 80, 1339-1339.
- Liu R., Arabale G., Kim J., Sun K., Lee Y., Ryu C. & Lee C. 2014, Graphene Oxide Membrane For Liquid Phase Organic Molecular Separation, *Carbon*, 77, 933-938.
- Marcano D. C., Kosynkin D. V., Berlin J. M., Sinitskii A., Sun Z., Slesarev A., Alemany L. B., Lu W. & Tour J. M. 2010, Improved Synthesis Of Graphene Oxide, *Acs Nano*, 4, 4806-4814.
- Nair R. R., Wu H. A., Jayaram P. N., Grigorieva I. V. & Geim A. K. 2012, Unimpeded Permeation of Water Through Helium-Leak-Tight Graphene-Based Membranes, *Science*, 335, 442-444.
- Qiao X., Chung T.-S., Guo W. F., Matsuura T. & Teoh M. M. 2005, Dehydration of Isopropanol and its Comparison with Dehydration of Butanol Isomers from Thermodynamic and Molecular Aspects, *Journal Of Membrane Science*, 252, 37-49.
- Ulbricht M. 2006, Advanced Functional Polymer Membranes, *Polymer*, 47, 2217-2262.
- Van Der Bruggen B., Mänttari M. & Nyström M. 2008, Drawbacks of Applying Nanofiltration and How to Avoid Them: A Review, *Separation And Purification Technology*, 63, 251-263.
- Van Veen H. M., Rietkerk M. D. A., Shanahan D. P., Van Tuel M. M. A., Kreiter R., Castricum H. L., Ten Elshof J. E. & Vente J. F. 2011, Pushing Membrane Stability Boundaries with Hybsi® Pervaporation Membranes, *Journal Of Membrane Science*, 380, 124-131.
- Verweij H. 2012, Inorganic Membranes, *Current Opinion In Chemical Engineering*, 1, 156-162.
- White L. S. 2006, Development of Large-Scale Applications in Organic Solvent Nanofiltration and Pervaporation for Chemical and Refining Processes, *Journal Of Membrane Science*, 286, 26-35.
- Wijmans J. G. & Baker R. W. 1995, The Solution-Diffusion Model: A Review, *J. Membr. Sci.*, 107, 1-21.
- Yeh T.-M., Wang Z., Mahajan D., Hsiao B. S. & Chu B. 2013, High Flux Ethanol Dehydration Using Nanofibrous Membranes Containing Graphene Oxide Barrier Layer, *Journal Of Materials Chemistry A*.