

# Organic Solvent Nanofiltration Membranes to Separate and Purify Fatty Acids

Chad M. Gilmer and Ned B. Bowden

University of Iowa  
Department of Chemistry  
Iowa City, IA 52327  
Ned-bowden@uiowa.edu

## ABSTRACT

We recently developed a new class of organic solvent nanofiltration (OSN) membranes that can separate small organic chemicals into streams that are enriched in selected chemicals. These membranes were based on highly cross-linked polyepoxies fabricated from a mixture of amines and epoxides. By varying the amines and epoxides used to fabricate a membrane, the selectivity of the membrane in a separation was controlled. A wide variety of membranes were fabricated from diamines, diepoxides, and triepoxides and investigated in the separation of organic chemicals with molecular weights from 100 to 300 grams per mole. The separation of fatty acids including EPA, DHA, and saturated fatty acids were investigated with these membranes. The membranes allowed EPA-ethyl ether to permeate 1.4x faster than DHA-ethyl ester, and they allowed a C4 fatty acid ester to permeate 60x faster than a C18 fatty acid ester.

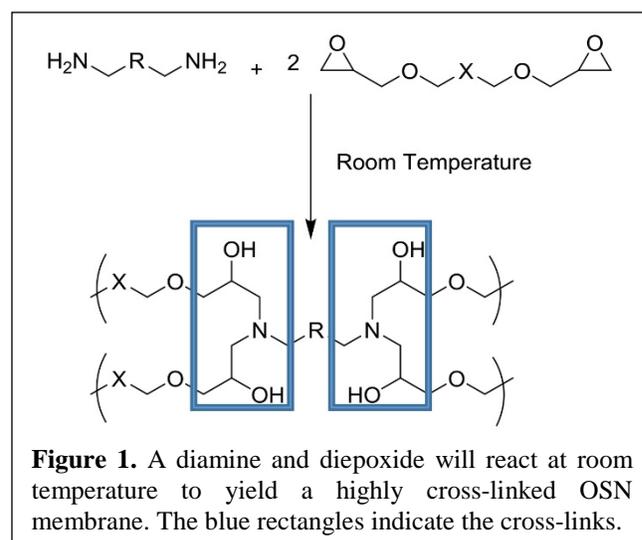
**Keywords:** membranes, fatty acids, vegetable oils, fish oil, separations

## 1 INTRODUCTION

Organic solvent nanofiltration (OSN) is the field of membrane science concerned with the membrane separation of organic chemicals with molecular weights between 100 and 2,000 grams per mole.<sup>(1-6)</sup> Chemicals in this molecular weight range have high boiling points that make their separation by distillation expensive, challenging, or even impossible. Furthermore, the purification of chemicals by column chromatography requires the use of solvents that must be removed and recycled and is not suited for many large scale separations. Membrane purification of organic chemicals has the potential to be inexpensive, require little to no heat, accessible to a wide range of chemicals that cannot currently be purified by distillation, and offer an alternative to established methods of purification. The challenge in this field is that few membranes exist that can separate organic chemicals with molecular weights above 100 grams per mole. Many of the examples of separations completed with OSN membranes require large differences of several hundred grams per mole between two chemicals for their separation to be successful.<sup>(1-6)</sup> New membranes are needed to advance this field.

Most examples of membranes in this field are composed of highly cross-linked polymers.<sup>(2, 5-9)</sup> To permeate through the membrane, chemicals must partition into the membrane and have a reasonable rate of diffusion within the polymer matrix. Because chemicals must be small enough to pass through the highly cross-linked polymeric membrane, the density of cross-links is an important parameter. A higher density of cross-links tends to slow the flux of chemicals through the membrane and alter the selectivity. The composition of the chemicals used to fabricate the membranes is also important although few systematic studies have been completed to vary the composition of the membranes.

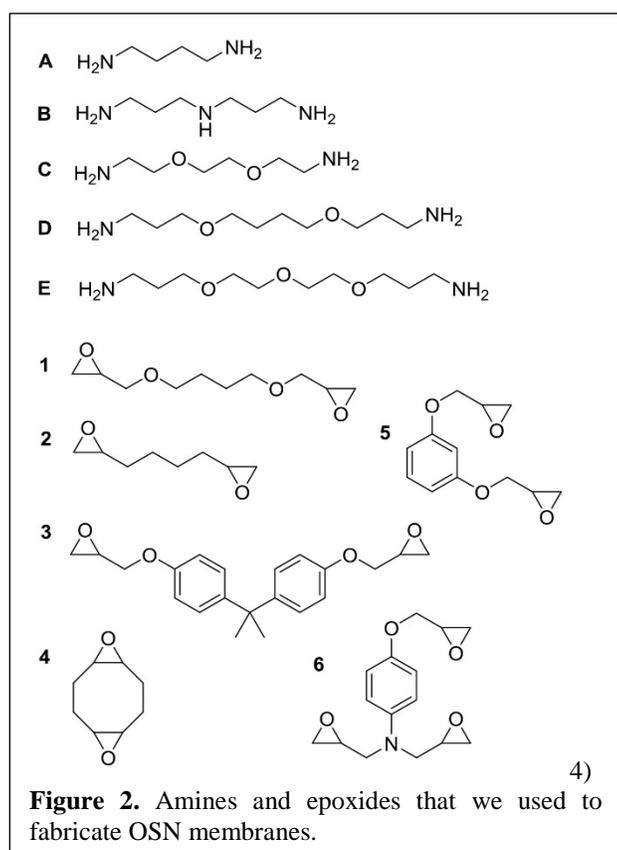
In this paper we report the fabrication of a wide range of membranes from mixtures of diamines, diepoxides, and triepoxides (Figure 1). The membranes were easily fabricated by mixing amines and epoxides and casting them on solid supports. The reaction between amines and epoxides was completed within 48 to 72 hours at room temperature. This paper reports, for the first time, how the density of cross-links was varied independently of the identity of the monomers used in the fabrication of the membranes. This study investigated which monomers lead to the most selective membranes and how altering the density of cross-links affected flux and selectivities.



**Figure 1.** A diamine and diepoxide will react at room temperature to yield a highly cross-linked OSN membrane. The blue rectangles indicate the cross-links.

## 2 RESULTS AND DISCUSSION

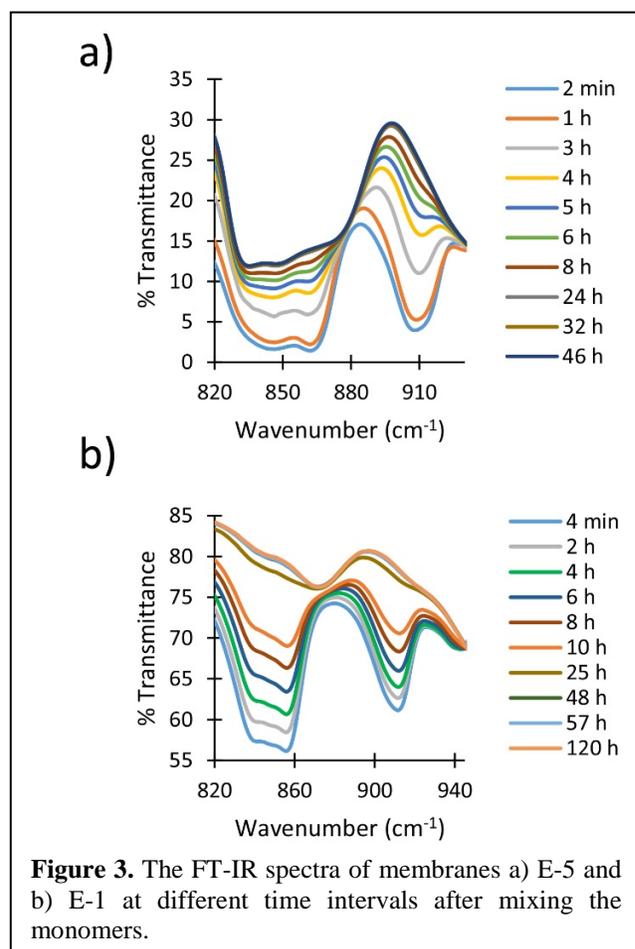
**2.1 Selection of membranes.** Membranes were initially fabricated from the amines and epoxides shown in Figure 2. These molecules were all commercially available and provided a range of different compositions for the membranes. The fabrication of each membrane had a 1/1 molar ratio of N-H bonds to epoxide because primary amines will react with two epoxides. At conversions of 100% this molar ratio yielded a known density of cross-links in the membranes and the membranes did not have residual NH bonds or epoxides.



The reaction between the amine E and epoxides 5 and 1 were monitored by Fourier transform-infrared (FT-IR) spectroscopy.<sup>(10-12)</sup> The monomers were mixed at a molar ratio of 1/1 for N-H bond to epoxide and cast between two salt plates. The peaks for the disappearance of the N-H bonds and the appearance of the O-H bonds were monitored from 3200-3600  $\text{cm}^{-1}$ , but these peaks overlapped and the extent of the reaction could not be determined. The epoxide peaks at 910 and 860  $\text{cm}^{-1}$  were monitored as a function of time after the monomers were mixed (Figure 3). These epoxide peaks disappeared over a period of 48 to 72 hours which demonstrated that these reactions proceeded to high yields at room temperature. All of the membranes were

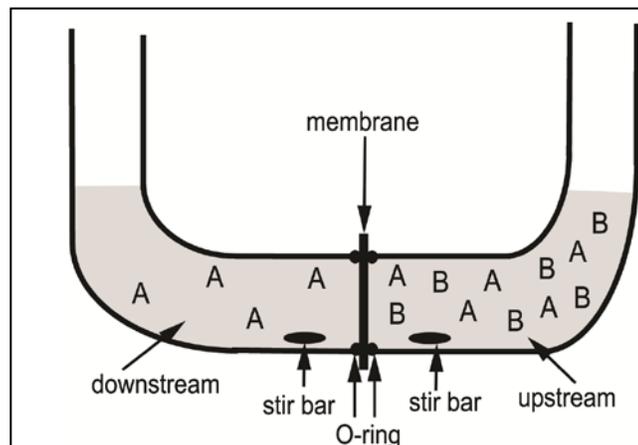
allowed to cure for at least 48-72 hours to ensure that the reactions between amines and epoxides were complete.

**2.2 Selection of separation conditions.** To investigate the selectivities of the membranes they were initially placed vertically between two glass reservoirs (Figure 4). Next, solvent was added to both glass reservoirs and chemicals to be separated were added to solvent on one side of the membrane. The solvent with the chemicals was labelled the upstream side and solvent without the chemicals was labelled the downstream side. The chemicals diffused from the upstream to the downstream sides of the membranes, and this was monitored by  $^1\text{H}$  NMR spectroscopy as a function of time.

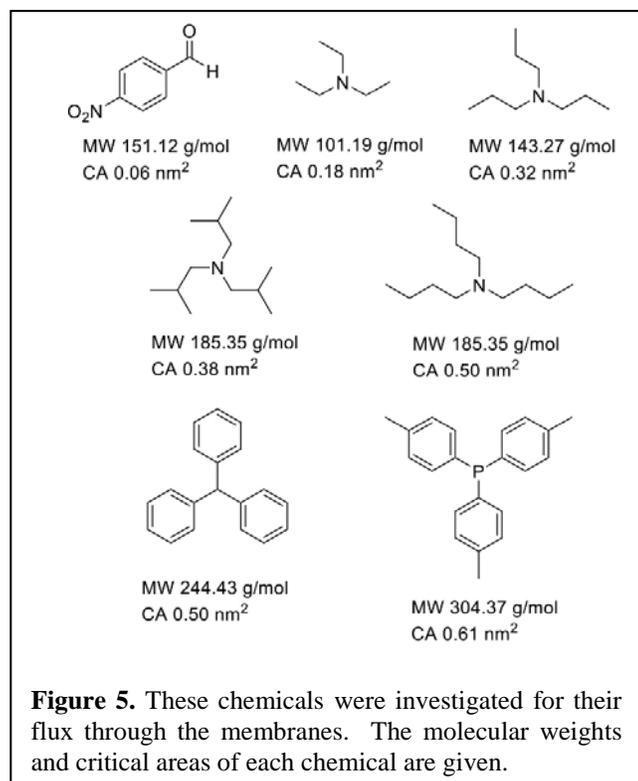


Membranes were fabricated from each of the amines and epoxide 5. Membranes fabricated from amines A and B did not allow chemicals to permeate, but membranes fabricated from amines C, D, and E allowed chemicals to permeate the membranes. The chemicals that were investigated included *p*-nitrobenzaldehyde and triphenylmethane as shown in Figure 5. These two chemicals had modest differences in molecular weights, but they possessed large differences in critical areas (CA). The critical area was the smallest rectangular cross-sectional area of the chemicals as measured using a computer

modeling program. The values for CA provide an estimate for the smallest size of pores that the molecules can diffuse through and provide a better reference for their relative size than molecular weight. The membrane fabricated from amine E had the fastest flux and the highest difference for permeation of *p*-nitrobenzaldehyde compared to triphenylmethane.



**Figure 4.** A membrane was placed between two reservoirs of solvent. In the upstream solvent a mixture of chemicals (indicated as A and B) were added. The chemicals were allowed to diffuse through the membrane and their concentrations in the upstream and downstream solvents were periodically measured.



**Figure 5.** These chemicals were investigated for their flux through the membranes. The molecular weights and critical areas of each chemical are given.

Membranes fabricated from amine E and epoxides 1, 5, and 6 had fast flux and illustrated how changing the molecular weight between cross-links ( $M_c$ ) and choice of monomers affected the separations (Table 1). The value for  $M_c$  was calculated based on the composition of the monomers used in the fabrication of the membranes; it represented the average molecular weight between two adjacent cross-links in the membrane. The values for  $M_c$  are useful for providing a measure of the density of cross-links for membranes and the relative size of the “pores”. Amine E yielded two cross-links when reacted with epoxides 1 and 5, but the addition of triepoxide 6 yielded an additional cross-link. Thus, by increasing the amounts of epoxide 6 the values for  $M_c$  were lowered.

**Table 1.** The values for MWCO and  $M_c$  for six membranes.

	Membrane					
	E-6	E-5 <sup>1</sup> 6 <sup>1</sup>	E-5 <sup>3</sup> 6 <sup>1</sup>	E-5	E-5 <sup>1</sup> 6 <sup>1</sup>	E-1
$M_c$ (g/mol)	164	187	202	221	195	211

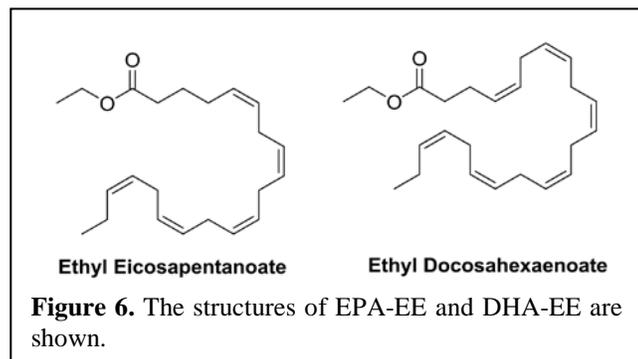
**Table 2.** Relative flux for chemicals through a series of membranes.

Molecules	Membrane					
	E-1	E-1 <sup>3</sup> 6 <sup>1</sup>	E-5	E-5 <sup>3</sup> 6 <sup>1</sup>	E-5 <sup>1</sup> 6 <sup>1</sup>	E-6
<i>p</i> -Nitrobenzaldehyde	10	20	167	250	100	90
Triethylamine	10	18	111	167	50	39
Tripropylamine	6	8	44	50	15	9
Triisobutylamine	4	3	27	25	7	1
Tributylamine	3	3	27	25	7	3
Triphenylmethane	3	3	7	3	4	0 <sup>a</sup>
Tri( <i>p</i> -tolyl)phosphine	1	1	1	1	1	0 <sup>a</sup>

<sup>a</sup>These molecules did not permeate the membrane at a measurable rate.

**2.3 Separation of organic chemicals.** Six membranes with values for  $M_c$  ranging from 164 to 221 g mol<sup>-1</sup> were investigated for their selectivities to separate the chemicals shown in Figure 5 (Table 2). For each separation the flux of tri(*p*-tolyl)phosphine was the slowest and the flux of *p*-nitrobenzaldehyde was the fastest. The difference in flux for these two chemicals was strongly dependent on the choice of monomers used to fabricate the membranes. Membranes fabricated from diepoxide 1 had a modest difference in flux of 10/1 for *p*-nitrobenzaldehyde to tri(*p*-tolyl)phosphine, but membranes fabricated from diepoxide 5 had a difference of flux of 167/1 for these chemicals. Furthermore, the difference in flux was changed when membranes were fabricated with triepoxide 6. The triepoxide increased the value for  $M_c$  and a membrane fabricated from a 3/1 molar ratio of diepoxide 5 to triepoxide 6 had a difference in flux of 250/1 for *p*-nitrobenzaldehyde to tri(*p*-tolyl)phosphine. This result is remarkable because these chemicals only possess a difference of 2x in molecular weight but a 250x difference in flux.

We applied these membranes towards the separation of eicosapentaenoic acid-ethyl ester (EPA-EE) and docosahexaenoic acid-ethyl ester (DHA-EE). These are two of the key fatty acids found in fish oil and are typically found at concentrations of 18% for EPA and 12% for DHA. To concentrate these omega-three fatty acids, fish oil is converted into ethyl esters and then separated and purified. The separation and purification of EPA-EE and DHA-EE are challenging because these fatty acids are highly unsaturated with five and six carbon-carbon double bonds that make them prone to oxidation at elevated temperatures (Figure 6). Methods to separate and purify these chemicals using a membrane separation at room temperature are important. We investigated the separation of these chemicals using two different membranes fabricated from a mixture of amine E and epoxides 1 and 6 (Table 3). Both membranes had a difference of flux of 1.4x and the EPA-EE permeated faster than DHA-EE. This result is important because it demonstrates that these fatty acid esters can be separated and purified using membranes.



**Table 3.** Relative flux of EPA-EE and DHA-EE through membranes E-1 and E-1<sup>36</sup><sup>1</sup>.

Molecule	Membrane	
	E-1	E-1 <sup>36</sup> <sup>1</sup>
EPA-EE	4.2	1.4
DHA-EE	3	1 <sup>a</sup>

<sup>a</sup>The flux value of DHA-EE through membrane E-1<sup>36</sup><sup>1</sup> was set to one and other flux values were compared relative to this value.

### 3 CONCLUSIONS

We developed a simple method to synthesize a wide range of highly cross-linked membranes that separated chemicals with molecular weights below 300 g mol<sup>-1</sup>. The composition of the membranes was varied by the choice of amines and epoxides, the composition of the membranes had a large impact on how they separated chemicals. Membranes fabricated from diepoxide 5 were more selective than those fabricated by diepoxide 1, and the selectivities could be altered by adding triepoxide 6 to the

membranes. We applied these membranes to the separation of EPA-EE and DHA-EE and observed a difference in flux of 1.4x.

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