Reactive Epoxy Nanofiltration Membranes with Disulfide Bonds for the Separation of Multicomponent Chemical Mixtures

Supporting Information
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Fabrication of epoxy membranes.

Fabrication of membrane B\(^3\)C\(^1\)-2.
4-Aminophenyldisulfide (0.20 g, 0.80 mmol) and 4,4-ethylenediamine (0.057 g, 0.27 mmol) were dissolved in DMF (0.33 mL) in a scintillation vial. After fully dissolving, purified 1,4-butanediol diglycidyl ether (0.4 mL, 2.1 mmol) was added to the reaction mixture and the vial was placed in an oil bath at 60°C for 9 h. The vial was then removed and 0.05 mL of the reaction mixture was cast on a polyacrylonitrile solid support. The casted membrane was placed in an oven at 60°C and allowed to cure for 7 d.

Fabrication of membrane B\(^1\)C\(^1\)-2.
4-Aminophenyldisulfide (0.14 g, 0.56 mmol) and 4,4-ethylenediamine (0.120 g, 0.56 mmol) were dissolved in DMF (0.34 mL) in a scintillation vial. After fully dissolving, purified 1,4-butanediol diglycidyl ether (0.42 mL, 2.2 mmol) was added to the reaction mixture and the vial was placed in an oil bath at 60°C for 7 h. The vial was then removed and 0.05 mL of the reaction mixture was cast on to a polyacrylonitrile solid support. The casted membrane was placed in an oven at 60°C and allowed to cure for 7 d.

Fabrication of membrane B\(^1\)C\(^3\)-2.
4-Aminophenyldisulfide (0.70 g, 0.28 mmol) and 4,4-ethylenediamine (0.179 g, 0.84 mmol) were dissolved in DMF (0.33 mL) in a scintillation vial. After fully dissolving, purified 1,4-butanediol diglycidyl ether (0.41 mL, 2.2 mmol) was added to the reaction mixture and the vial was placed in an oil bath at 60°C for 4.5 h. The vial was then removed and 0.05 mL of the reaction mixture was cast on to a polyacrylonitrile solid support. The casted membrane was placed in an oven at 60°C and allowed to cure for 7 d.

Fabrication of membrane C-2.
4,4-Ethylenediamine (0.25 g, 1.1 mmol) was dissolved in DMF (0.33 mL) in a scintillation vial. After fully dissolving, purified 1,4-butanediol diglycidyl ether (0.43 mL, 2.3 mmol) was added to the reaction mixture and the vial was placed in an oil bath at 60°C for 3 h. The vial was then removed and 0.05 mL of the reaction mixture was cast on to a polyacrylonitrile solid support. The casted membrane was placed in an oven at 60°C and allowed to cure for 5 d.

Stability of 4-aminophenyldisulfide in the presence of a primary amine.

In an NMR tube 4-aminophenyldisulfide (0.1 g, 0.4 mmol), allylamine (0.1 mL, 1.3 mmol), and dimethylsulfoxide-d\(_6\) (0.5 mL) were combined and mixed thoroughly. \(^1\)H NMR spectra were collected at various time points. After 36 days there was no noticeable degradation of 4-aminophenyldisulfide in the presence of allylamine.
Figure S1. $^1$H NMR spectrum of 4-aminophenyldisulfide and allylamine after 36 days showing no degradation.

Permeation of chemicals through initial membranes tested.

The [permeate]/[retentate] describes the ratio of concentration of chemicals in the permeate stream to the concentration of chemicals in the retentate stream. This ratio determines the amount of chemicals that have permeated the membrane, and is used to determine the flux of the chemicals through the membrane. Further details of this method are explained in a prior publication\(^1\). In reference to Table S1 below, n/a refers to a concentration of chemicals in the permeate stream that was too low to be measured.

Table S1. Permeation of chemicals through membrane B-1.

| Chemical          | [permeate]/[retentate] |
|-------------------|------------------------|
|                   | 1 day | 2 days | 3 days | 10 days |
| $p$-Nitrobenzaldehyde | n/a   | 0.003  | 0.006  | 0.011   |
| Triethylamine      | n/a   | n/a    | n/a    | n/a     |
| Tripropylamine     | n/a   | n/a    | n/a    | n/a     |

Table S2. Permeation of chemicals through membrane B-2.

| Chemical          | [permeate]/[retentate] |
|-------------------|------------------------|
|                   | 1 day | 2 days | 3 days | 4 days  |
| $p$-Nitrobenzaldehyde | 0.04  | 0.082  | 0.135  | 0.158   |
| Triethylamine      | 0.02  | 0.038  | 0.078  | 0.08    |
| Tripropylamine     | 0.005 | 0.009  | 0.018  | 0.02    |
Table S3. Flux of chemicals through a C-2 epoxy membrane.

| Chemical              | Absolute Flux (mol/cm²*h) | Relative Flux |
|-----------------------|----------------------------|---------------|
| p-Nitrobenzaldehyde   | $1.56 \times 10^{-6}$      | 2.68          |
| Triethylamine         | $1.20 \times 10^{-6}$      | 2.07          |
| Tripropylamine        | $5.80 \times 10^{-7}$      | 1.00          |

FT-IR spectra of epoxy membranes.

Figure S2. FT-IR spectra of membrane B-2.
Figure S3. FT-IR spectra of membrane B3C1-2.

Figure S4. FT-IR spectra of membrane B1C1-2.
Figure S5. FT-IR spectra of membrane B1C3-2.

The conversion of the epoxide functional group was determined by examining the area of the parabola for the peak at 910 cm\(^{-1}\) using OMNIC software. For the first spectrum collected, this area calculated is assumed to be equivalent to 100% of the epoxide functional group present. For subsequent spectra the area was measured again and compared to first spectrum to determine the percentage of epoxide functional groups that have reacted. For example in Figure S5 the spectrum collected at 3 min has an area that was equivalent to 100% of the epoxide functional group present. The area of the parabola for the spectrum collected at 166 h has lost 92% of the original area from the spectrum at 3 min, so 92% of the epoxide functional groups have reacted, thus the membrane has reached 92% conversion.

Table S4. Conversion of the epoxide functional group for each membrane after the reaction has reached completion.

| Membrane   | Conversion (%) |
|------------|---------------|
| C-2        | 82            |
| B1C3-2     | 89            |
| B1C1-2     | 91            |
| B2C1-2     | 92            |
| B-2        | 94            |
Raman spectra of epoxy membranes before and after treatment with cysteamine.

Figure S6. Raman spectrum of membrane C-2 before treatment with cysteamine.

Figure S7. Raman spectrum of membrane C-2 after treatment with cysteamine.
Figure S8. Raman spectrum of membrane B1C3-2 before treatment with cysteamine.

Figure S9. Raman spectrum of membrane B1C3-2 after treatment with cysteamine.
**Figure S10.** Raman spectrum of membrane B3C1-2 before treatment with cysteamine.

**Figure S11.** Raman spectrum of membrane B3C1-2 after treatment with cysteamine.
Figure S12. Raman spectrum of membrane B-2 before treatment with cysteamine.

Figure S13. Raman spectrum of membrane B-2 after treatment with cysteamine.
Diffusion apparatus used for the separation of chemicals.

Figure S14. Picture of a diffusion apparatus used to monitor the separation of chemicals.

Permeation of chemicals through the stimulus-responsive epoxy membrane before and after breaking the crosslinks.

Table S5. Permeation of chemicals though membrane C-2.

|                  | Before Treatment with Cysteamine | After Treatment with Cysteamine |
|------------------|---------------------------------|---------------------------------|
|                  | Relative Flux | Normalized Flux | Relative Flux | Normalized Flux |
|                  |               | (mol/cm²*h)² |               | (mol/cm²*h)² |
| \( p \)-Nitrobenzaldehyde | 5.71          | 1.37 x 10⁻⁶ | 5.26          | 1.41 x 10⁻⁶ |
| Triethylamine    | 4.41          | 1.06 x 10⁻⁶ | 3.95          | 1.06 x 10⁻⁶ |
| Tripropylamine   | 2.13          | 5.11 x 10⁻⁷ | 1.89          | 5.09 x 10⁻⁷ |
| Triphenylmethane | 1.00          | 2.40 x 10⁻⁷ | 1.00          | 2.69 x 10⁻⁷ |

\( ^a \) All flux values carry a ± 4.24% relative error.
### Table S6. Permeation of chemicals though membrane B1C3-2.

|                     | Before Treatment with Cysteamine | After Treatment with Cysteamine |
|---------------------|----------------------------------|---------------------------------|
|                     | Relative Flux | Normalized Flux (mol/cm²*h) \(^a\) | Relative Flux | Normalized Flux (mol/cm²*h) \(^a\) |
| **p-Nitrobenzaldehyde** | 12.4 | \(1.56 \times 10^{-6}\) | 9.23 | \(1.70 \times 10^{-6}\) |
| Triethylamine       | 8.81 | \(1.10 \times 10^{-6}\) | 6.38 | \(1.17 \times 10^{-6}\) |
| Tripropylamine      | 3.27 | \(4.10 \times 10^{-7}\) | 2.77 | \(5.09 \times 10^{-7}\) |
| Triphenylmethane    | 1.00 | \(1.25 \times 10^{-7}\) | 1.00 | \(1.84 \times 10^{-7}\) |

\(^a\) All flux values carry a ± 4.24% relative error.

### Table S7. Permeation of chemicals though membrane B1C1-2.

|                     | Before Treatment with Cysteamine | After Treatment with Cysteamine |
|---------------------|----------------------------------|---------------------------------|
|                     | Relative Flux | Normalized Flux (mol/cm²*h) \(^a\) | Relative Flux | Normalized Flux (mol/cm²*h) \(^a\) |
| **p-Nitrobenzaldehyde** | 14.0 | \(1.02 \times 10^{-6}\) | 6.67 | \(2.26 \times 10^{-6}\) |
| Triethylamine       | 10.1 | \(7.36 \times 10^{-7}\) | 4.97 | \(1.69 \times 10^{-6}\) |
| Tripropylamine      | 4.47 | \(3.25 \times 10^{-7}\) | 2.36 | \(8.01 \times 10^{-7}\) |
| Triphenylmethane    | 1.00 | \(7.27 \times 10^{-8}\) | 1.00 | \(3.39 \times 10^{-7}\) |

\(^a\) All flux values carry a 4.24% relative error.

### Table S8. Permeation of chemicals though membrane B3C1-2.

|                     | Before Treatment with Cysteamine | After Treatment with Cysteamine |
|---------------------|----------------------------------|---------------------------------|
|                     | Relative Flux | Normalized Flux (mol/cm²*h) \(^a\) | Relative Flux | Normalized Flux (mol/cm²*h) \(^a\) |
| **p-Nitrobenzaldehyde** | 15.9 | \(5.09 \times 10^{-7}\) | 4.87 | \(2.69 \times 10^{-6}\) |
| Triethylamine       | 11.0 | \(3.54 \times 10^{-7}\) | 3.57 | \(1.97 \times 10^{-6}\) |
| Tripropylamine      | 2.78 | \(8.91 \times 10^{-8}\) | 1.85 | \(1.02 \times 10^{-6}\) |
| Triphenylmethane    | 1.00 | \(3.21 \times 10^{-8}\) | 1.00 | \(5.52 \times 10^{-7}\) |

\(^a\) All flux values carry a 4.24% relative error.

### Table S9. Permeation of chemicals though membrane B-2.

|                     | Before Treatment with Cysteamine | After Treatment with Cysteamine |
|---------------------|----------------------------------|---------------------------------|
|                     | Relative Flux | Normalized Flux (mol/cm²*h) \(^a\) | Relative Flux | Normalized Flux (mol/cm²*h) \(^a\) |
| **p-Nitrobenzaldehyde** | 6.34 | \(8.49 \times 10^{-7}\) | 2.07 | \(4.10 \times 10^{-6}\) |
| Triethylamine       | 3.91 | \(5.23 \times 10^{-7}\) | 1.76 | \(3.49 \times 10^{-6}\) |
| Tripropylamine      | 1.69 | \(2.26 \times 10^{-7}\) | 1.15 | \(2.28 \times 10^{-6}\) |
| Triphenylmethane    | 1.00 | \(1.34 \times 10^{-7}\) | 1.00 | \(1.98 \times 10^{-6}\) |

\(^a\) All flux values carry a 4.24% relative error.
Table S10. Flux of chemicals through PZ solid support.

|                 | Relative Flux | Normalized Flux (mol/cm²*h)\(^a\) |
|-----------------|---------------|------------------------------------|
| p-Nitrobenzaldehyde | 1.38          | 8.20 x 10^-6                      |
| Triethylamine    | 1.38          | 8.18 x 10^-6                      |
| Tripropylamine   | 1.22          | 7.26 x 10^-6                      |
| Triphenylmethane | 1.00          | 5.94 x 10^-6                      |

\(^a\) All flux values carry a 4.24% relative error.

References

1) C. M. Gilmer and N. B. Bowden, *ACS Appl. Mater. Interfaces*. 2016, 8, 24104-24111.