Title: Summer 2018 Research Report

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Intended for: Research report for my adviser, Dr. Andy Shreve, at UNM. This is to fulfill requirements to earn research credit hours for Summer 2018 for the NSME program.

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Summer 2018 Research Report

For UNM NSME PhD program research credits

As directed by Professor Andy Shreve

By Quinn McCulloch

07/26/18

Outline

- A switch of chemical systems and experimental design
- Liquid parameter modeling
- Countercurrent stage number and GC/MS detection limits
- Literature search
- Capillary pressure and flow resistance modeling
- Research on wish list items

A switch of chemical systems and experimental design

Out with the old…

- Previous solvent extraction system: water-triethylamine-decane
  - Ease of analysis w/ pH meter, but can’t readily automate analysis
  - Limited analytical precision via. pH, only ~ 1 ppm in best case
  - Large equilibrium k_d (~5). This limits the number of detectable countercurrent stages.
  - Enormous IFT at low TEA concentrations, which leads to ‘clogs’ in microfluidic assembly

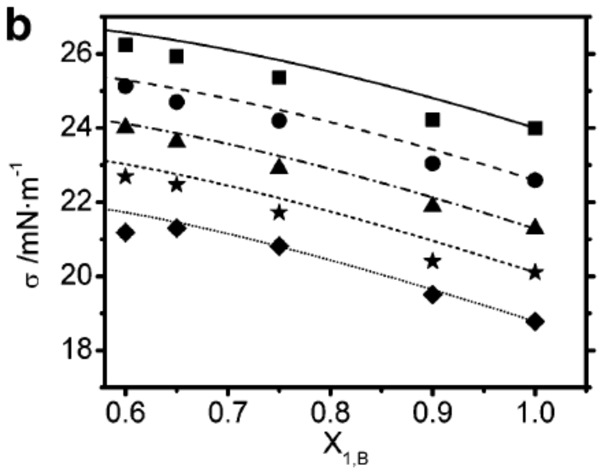
New system: water-acetone-toluene

- A well studied standard for demonstrating LLE
- Previously tested in our screen contactor: 75 μl/min in parallel flow and 25 μl/min in countercurrent flow were achieved.
- Directly usable in our graphene membrane-based contactor.

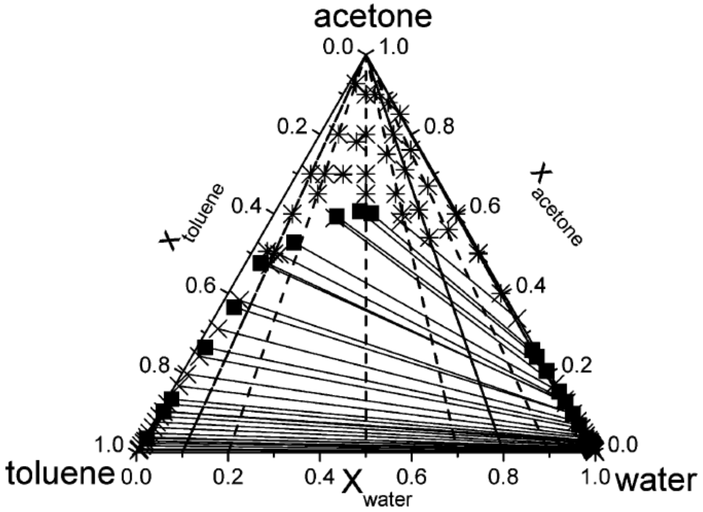
References:

Surface Tension of the Ternary System Water + Acetone + Toluene. Enders, S, et al. J. Chem. Eng. Data **2007**, 52, 1072-1079

Standard test systems for liquid extraction / European Federation of Chemical Engineering Working Party on Distillation, Absorption and Extraction. Misek, T., et al. 1985.



IFT as a function of acetone concentration in the water phase. The horizontal axis is the molar fraction, $[H_2O]/[C_3H_6O]$. The ratio of toluene to water was 3/5. The multiple lines are for different temperatures; circles are at ~ room temp. Lines are from Butler model (Enders, S, et al. 2007).



Water-acetone-toluene ternary diagram (Enders, S, et al. 2007)

Chemical source

Fisher Scientific:

- Toluene, 99.85%, Extra Dry over Molecular Sieve, AcroSeal™, ACROS Organics (~$40/L)
- Acetone, 99.9%, for residue analysis, ECD tested halocarbons free grade, ACROS Organics (~$40/L)
- In-house Millipore DI water

Proposed analytical method

GC/MS is readily available in LANL’s MPA-11 group, however there is a problem…

- Collected sample volume is only 50 μl from microfluidic chips because of low flow-rates.
- Traditional external and internal standard methods for quantitation are difficult with small volumes
  - Spiking the sample with a reference introduces uncertainty due to limited injection volume precision.
  - External standard introduces volumetric uncertainty at the point of auto-sampling due to the back-and-forth nature of referencing.
- The latter may be the best option, but there is another method that may work…

Solution: early internal standard introduction

The idea is to replace a small amount of toluene with an equal mole amount of a different organic. This new organic would act as a reference and would just ‘go along for the ride’ during the microfluidic experiments. Preferably, the organic would:

- Be immiscible with water
- Have very close to the same activity as toluene
- Not appreciably change the distribution ratio of acetone in the system

Potential organic standards:

Chemical	Deuterated toluene	Alkane or similar MW organic
Pros	• Same activity and characteristics as toluene. • k_d not expected to change with addition of toluene d_8. • Copious themodynamics are available from literature for toluene.	• Peaks will be clearly separate via GC/MS. • Immiscible with water.
Cons	• GC peaks may not fully separate, especially given the large contribution of the toluene matrix. • MS can be damaged if it is operated during toluene elution while ‘looking’ for toluene d8.	• May change k_d. • Thermodynamic measurements needed from scratch.

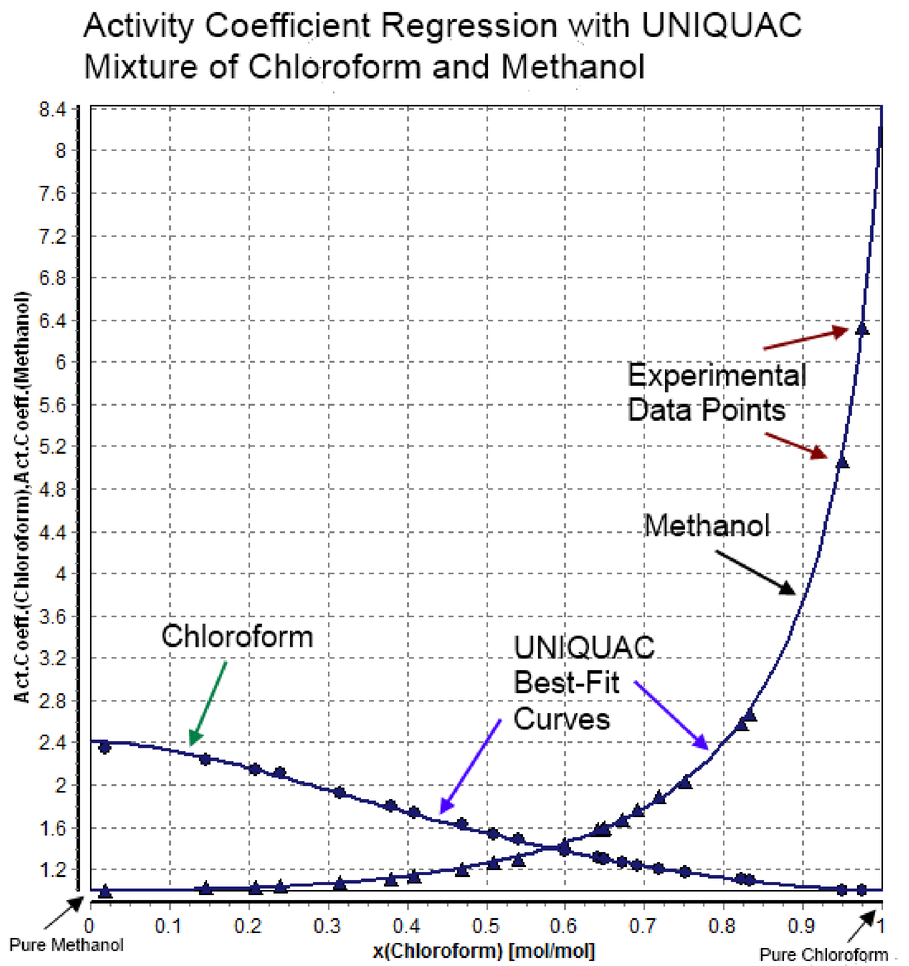
Liquid parameter modeling

Which standard to use? Modeling Log P and activity coefficients

In literature I happened upon UNIQUAC, UNIFAC, COSMOSPACE, and GEQUAC approaches to calculating Log P.

I since have attained a license through LANL's Center for Non-linear Studies (CNLS) to use SCM's ADF software. It contains a package called COSMO-RS, which uses DFT and quantum mechanics to calculate thermodynamic properties and can handle ions, ionic liquids, and acids and bases.

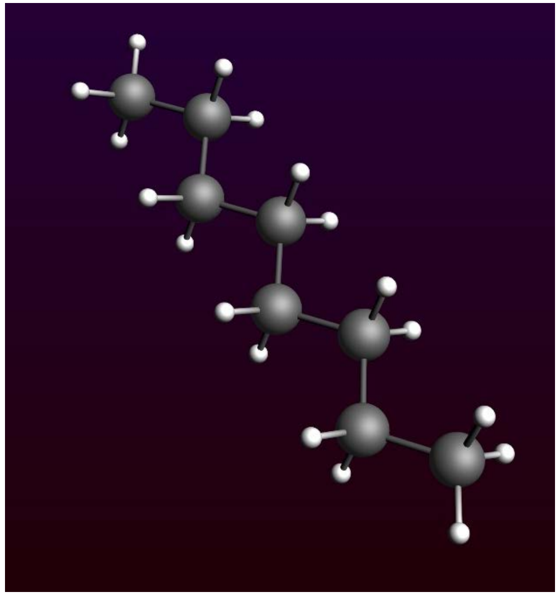
Some COSMO-RS results are on the following slides.


Activity Coefficient Regression with UNIQUAC
Mixture of Chloroform and Methanol

Experimental Data Points from Dortmund Data Bank
Original Source: Hiaki T., Kurihara K., Kojima K., J.Chem.Eng.Data, 39(4), 714-719, 1994

COSMO-RS results

- Over 20 molecular models built
- Geometrical optimization performed using PM7 Hamiltonian
- Solvation method: COSMO-CRS



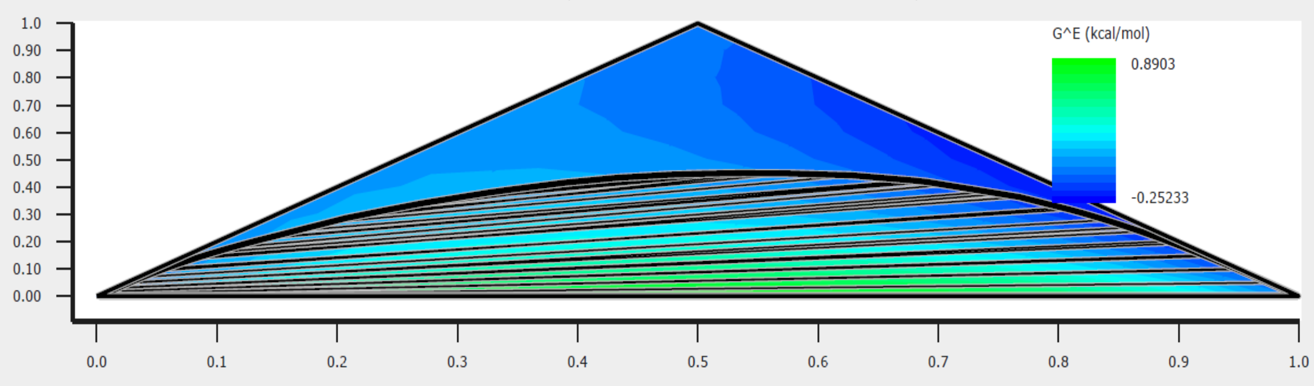
Example: octane model using COSMO-RS

Selected, consolidated data: partition coefficients and activity coefficients			
		Activity	
Solvent	**Log P**	**Coefficient**	
water	-5.2504	5.5016	
touene	3.3994	3.6702	Criteria
Solutes (infinite dilute)			
toluene d8	3.3996	3.6700	Best match
acetone	-2.0087	0.0068	
decane	7.1097	16.8748	
ethylbenzine	4.0390	4.5532	
isopropylbenzine	5.1230	6.6875	
hexane	4.4172	6.5658	
heptane	5.1636	8.7315	
octane	5.8246	10.9632	
pentane	3.8681	5.5182	
benzene	2.8797	3.1479	Best alternative
butane	3.2313	4.3721	
dimethylbenzine	3.8466	4.1424	
dimethylbenzine	3.9439	4.2733	
phenylsilane	4.1440	4.8888	
aniline	0.7873	1.2290	
cyclohexane	3.8311	5.8589	
cycloheptane	4.2761	6.7826	

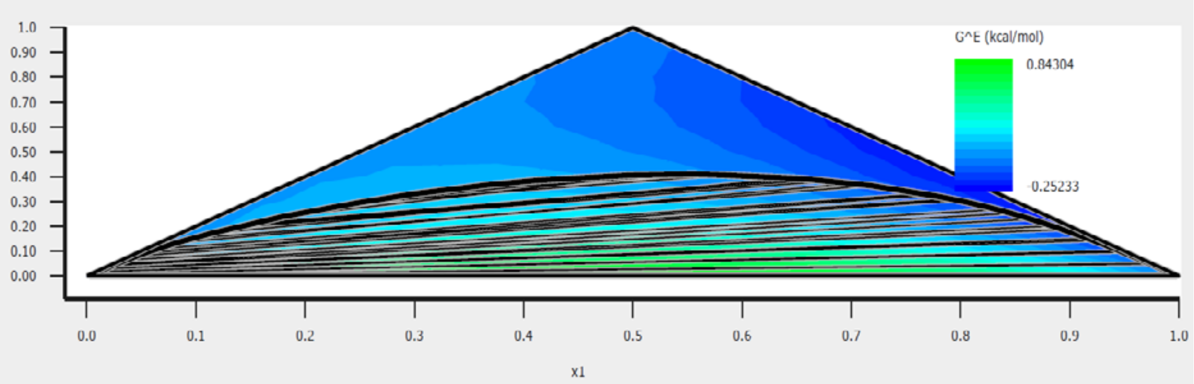
Ternary diagrams via COSMO-RS

The purpose of this exercise was to qualitatively match the miscibility envelope of the pure water-acetone-toluene system.

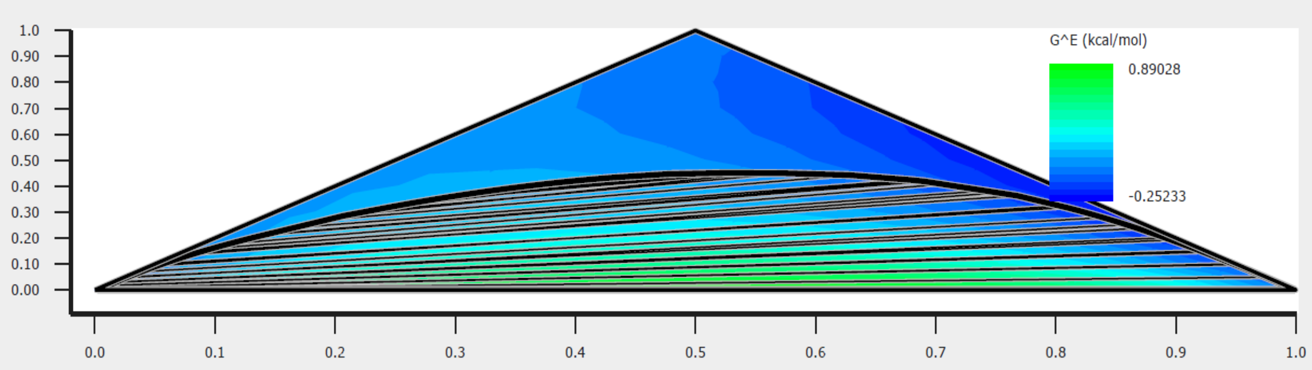
Water-acetone-toluene (benchmark: ideal)



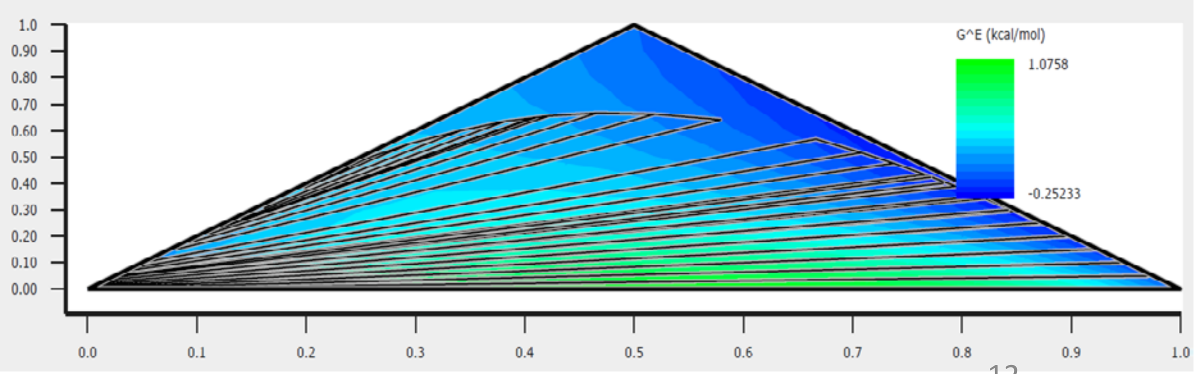
Water-acetone-benzene (very similar: good)



Water-acetone-toluene d8 (almost perfect match: best)



Water-acetone-heptane (very dissimilar: poor)



Decisions on standard

- Toluene d_8 is preferred because it is not anticipated to effect k_d. This organic has been purchased (Sigma-Aldrich, 99.96% isotopic purity, > 99% chemical purity, $318/10 ml) and will arrive in ~ 1 week. It will be implemented/attempted first.
- Benzene (already on-hand) will be used if toluene d_8 fails GC/MS criteria.
- An external standard method will be used as a last resort.

Any way we look at it, there will be a period of GC/MS method and chemical system development.

Countercurrent stage number and GC/MS detection limits

Equation for estimating countercurrent stages

$$\mathrm{Conc}_{\mathrm{Raff.}} = \left(\frac{\mathrm{V}_{\mathrm{aq}}}{(\mathrm{V}_{\mathrm{org}} * k_d) + \mathrm{V}_{\mathrm{aq}}}\right)^{\mathrm{n}} * \mathrm{Conc}_{\mathrm{Feed}}$$

When $\mathrm{V}_{\mathrm{aq}} = \mathrm{V}_{\mathrm{org}}$

$$\mathrm{Conc}_{\mathrm{Raff.}} = \left(\frac{1}{k_d + 1}\right)^{\mathrm{n}} * \mathrm{Conc}_{\mathrm{Feed}}$$

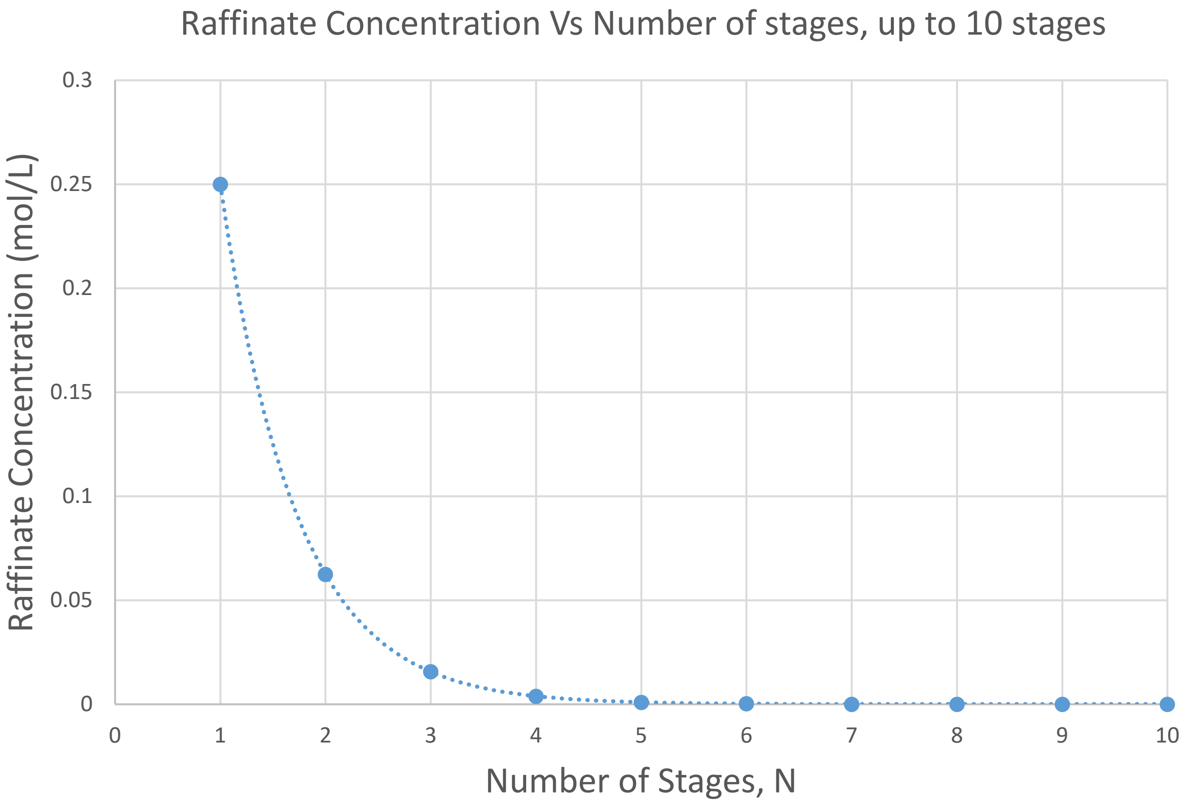
GC detection limits needed as a function of stage number

At $k_d = 3$ and $\text{Conc}_{\text{feed}} = 1$ M

# of stages	Raff conc. (mol/L)
1	0.25
2	0.0625
3	0.015625
4	0.00390625
5	0.000976563
6	0.000244141
7	6.10352E-05
8	1.52588E-05
9*	3.8147E-06
10	9.53674E-07
11	2.38419E-07
12	5.96046E-08
13	1.49012E-08
14**	3.72529E-09

* 9 stages requires ppm scale resolution

* 14 stages requires ppb scale resolution



Literature search

The better portion of three weeks was dedicated to a broad literature search, aimed at getting a feel for contemporary techniques for micro-scale solvent extraction. Ultimately, this information is to be used for writing the introductory section of the first screen contactor system paper. This review included 47 publications, six of them being review articles. General findings include:

- Prevalent use of dimensionless numbers to predict biphasic flow regimes
- A variety of mass transfer models for different flow regimes.
- Predominantly, literature was focused on slug flow, dispersed flow, and membrane-partitioned liquid-liquid flow. There were also numerous papers on membrane-less parallel microflow.
- I only found two papers that demonstrated *countercurrent*, laminar biphasic flow without the use of a partitioning membrane. These examples were finicky, in the sense that critical flow rates had to be maintained.

Our screen contactor uses ribbon-like porous materials to establish scalable, countercurrent, liquid-liquid microflow; this indeed seems like a novel technology worth publishing.

Capillary pressure and flow resistance modeling

Screen contactor principle of operation

The microfluidic screen contactor separates liquids by assuring that biphasic capillary pressure, P_c, is larger than the hydraulic pressure drops, P_h, that is, $P_c >> P_h$. As such, some of this Summer’s literature searching was aimed at finding better models for these two parameters.

P_c

Although liquid-liquid capillary pressure can be derived using a simple force diagram of the three phase point of a solid-liquid-liquid interface, this approach falls apart when 1) enough attention is paid to molecular-scale phenomena, and 2) when the geometry of the wetted materials become complicated, i.e. not circular.

I used a thermodynamic approach based on the work of Norman R. Morrow (Morrow, N. R., 1969) on flow through porous media, and Gibbs, J. W. (!) in his collection of scientific papers (1961 reprint).

The derivation begins with Helholtz free energy, and links PV work to changes in surface area (surface energy) work. The resulting equation for oil (o), water (w), and a solid (s) is:

$$P_c = \frac{\Delta A_{sw}}{\Delta V_w} \sigma_{wo} \cos\theta$$

where A_{sw}, V_w, σ_{wo}, and θ are surface area of the solid-water interface, volume of water, IFT of between the oil and water, and the contact angle, respectively.

This surface-volume ratio approach leads to easy modeling and can be corroborated by BET measurements in the future. Not that this equation can also be used for the oil phase by simply changing subscripts.

P_h

- A version of the Carman-Kozeny equation for flow through porous media was derived. Results are as follows.

$$D = \frac{4\varepsilon V_s}{A_s(1-\varepsilon)}, \qquad \frac{dP}{dx} = \frac{8\mu Q}{\pi\left(D/2\right)^4}$$

- Above, the conventions from the previous slide are maintained. Additionally, D, Q, and ε are theoretical pore diameter, average flow rate, and void fraction, respectively. The equation for D possesses a surface-volume ratio, but now it is the volume of the solid, not the liquid.
- Combining the equations yields:

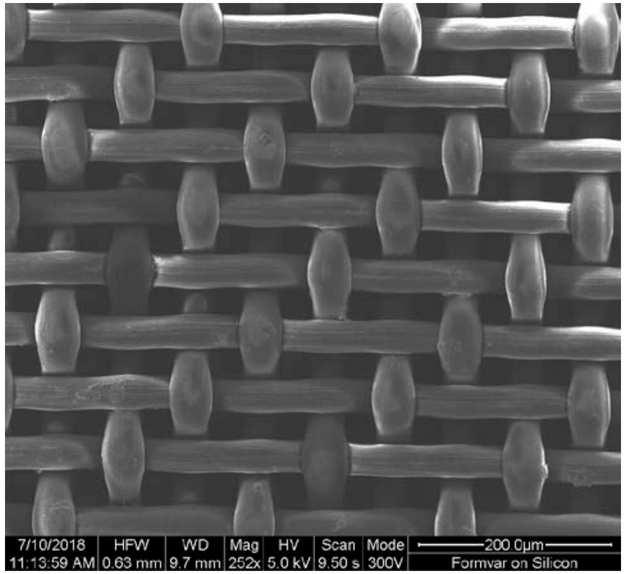
$$\frac{dP}{dx} = \frac{2\mu A_s\left(1-\varepsilon\right)}{\varepsilon V_s}$$

Modeling surface-volume ratios for screen meshes

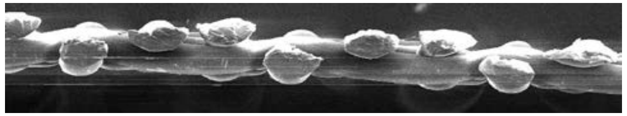
SEM images of the two different screens, PEEK polymer and 304 stainless, were captured and dimensionally analyzed.

Top images of the screens are provided along with side views to depict the variability in the weft and warp geometries of the weave.

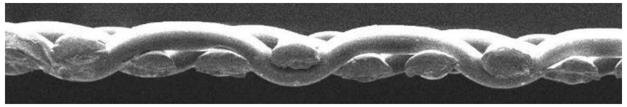
PEEK



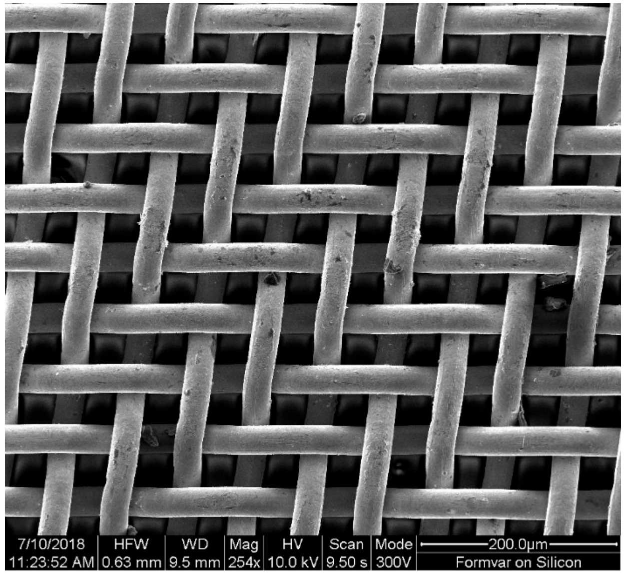
Warp ↔



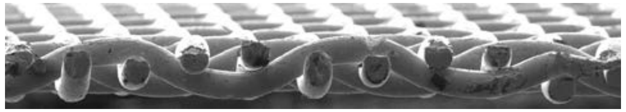
Weft ↔



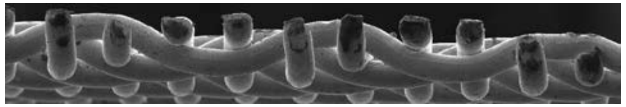
Stainless



Warp ↔

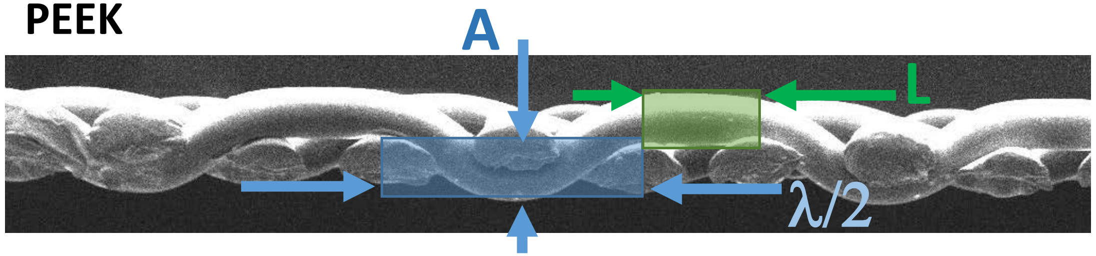


Weft ↔

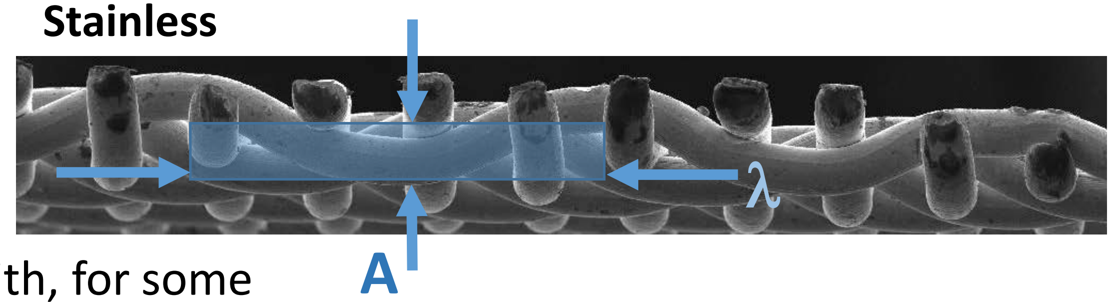


Modeling area and volume

PEEK



Stainless



- A woven wire roughly follows a sinusoidal function with, for some geometries, an additional linear section of wire (see green box above). The general form of this wave function is:

$$y(x) = A\sin(\mathrm{kx})$$

- Path integral was derived, but computed numerically for each given set of constants.

$$ds = \int_0^\lambda \sqrt{dx^2 + dy^2} = \int_0^\lambda \sqrt{1 + (dy/dx)^2}\,dx = \int_0^\lambda \sqrt{1 + \left(Ak\cos(kx)\right)^2}\,dx$$

- Because the stainless screen had a square 2/2 weave, this sinusoidal path integral was sufficient. The PEEK screen, however, possessed a square 2/1 pattern (over 2, under 1). As such, a piecewise integral was used, where one segment was sinusoidal, and another was linear (green and blue boxes, respectively).
- Once the path lengths were computed, Pappus's Centroid theorem was then employed, where the length is multiplied by the circumference or cross-sectional area of the wire, to give its total surface area and volume.
- Lastly, the number of wires were accounted for to represent a unit area of woven mesh– 3+3 wires for PEEK, and 4+4 wires for stainless

Results

Material	Aws/Vw	Aws/Vs	ε
PEEK	0.19	0.37	0.22
Stainless	0.24	0.36	0.34

Note: propagation of errors will be used to estimate uncertainties in these calculations. I haven't had time to do this yet.

Dimensionless numbers for screen contactor

- **Capilary number (Ca) –** Ratio of viscous force to IFT. Ca << 10^{-5} indicates that flow is dominated by capillary forces.
- **Weber number (We) –** Ratio of inertial force to IFT. Typically for We > 1, flow is laminar/parallel. We circumvent this limitation by using porous materials.
- **Reynolds number (Re) –** Ratio of We/Ca. Used to predict turbulent behavior. Flow is expected to be laminar if Re < 2100, and turbulent if Re > 4000.
- **Bond number (Bo) –** Ratio of gravitation force to interfacial force. Bo << 1 indicates that interfacial forces dominate.
- **Kelvin-Helmholtz instability (KHI) –** Ratio of the difference in the fluid velocities squared to the Kelvin-Helmholtz function value. No instabilities are expected for KHI <<1.

Dimensionless numbers (order of magnitude)	
Ca	10^-5
We	10^-5
Re	10^-1
Bo	10
(DV)^2/KH	10^-3

Results – We have an entry level capillary number– our system is functioning well, however it would benefit from decreasing this number. The Bond number could also stand to be decreased in the future. Based on Re, we are clearly in a non-turbulent flow regime. No Kelvin-Helmholtz instabilities are expected.

Selected references

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