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Author(s): Mcculloch, Quinn

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Summer 2017 Microfluidics Research Report

Quinn McCulloch

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Background

Liquid-liquid Extraction (LLE), also known as solvent extraction, represents a large subset of chemistry where one or more solutes are transferred across an interface between two immiscible liquids. This type of chemistry is used in industrial scale processes to purify solvents, refine ore, process petroleum, treat wastewater, and much more. Although LLE has been successfully employed at the macroscale, where many liters/kgs of species are processed at large flow rates, LLE stands to benefit from lab-on-a-chip technology, where reactions take place quickly and efficiently at the microscale. A device, called a screen contactor, has been invented at Los Alamos National Laboratory (LANL) to perform solvent extraction at the microscale. This invention has been submitted to LANL's Feynman Center for Innovation, and has been filed for provisional patent under U.S. Patent Application No. 62/483,107 [1].

The screen contactor consists of a housing that contains two different screen materials, flame-treated stainless steel and polyether ether ketone (PEEK) thermoplastic, that are uniquely wetted by either an aqueous or an organic liquid phase, respectively. Liquids in this device flow longitudinally through the screens. The fine pore size of the screens (tens of microns) provide large capillary/adhesional forces while maintaining small hydraulic pressure drops. These physical characteristics are paramount to efficient microscale liquid phase separation.

To demonstrate mass transfer using the screen contactor, a well-known chemical system [2] consisting of water and n-decane as solvents and trimethylamine (TEA) as a solute was selected. TEA is basic in water so its concentration can easily be quantified using a digital pH meter and an experimentally determined base dissociation constant. Characterization of this solvent system and its behavior in the screen contactor have been the focus of my research activities this summer. In the following sections, I have detailed experimental results that have been gathered.

Liquid property measurements

Interfacial tension (IFT) is an important predictor of phase separation in our device. The native IFT between water and purified n-decane is extremely large at ~ 52 mN/m, but the addition of TEA causes a reduction in IFT [2]. To both verify published numbers and to establish an appropriate concentration to begin contactor experiments, we measured IFT as a function of mean TEA concentration. Fig. 1 depicts the results of this experiment. Mean TEA concentration refers to the molarity of TEA in the total volume of water + n-decane. For these experiments, the volume ratio between the organic and aqueous phase was always 1:1.

In addition to the above IFT experiments, equilibrium pH values for various mean TEA concentrations were gathered in order to establish the base dissociation constant. Figs. 2a and 2b show plots of pH and IFT of the various mean concentrations tested.

The base dissociation constant for this system was determined to be:
Kb TEA @ ~22C = 1.49 x 10^{-3}.

Figure 1

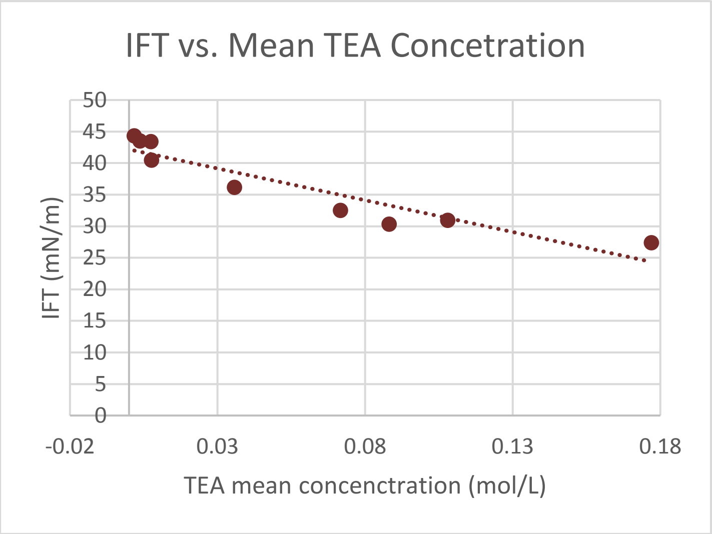


Figure 2a

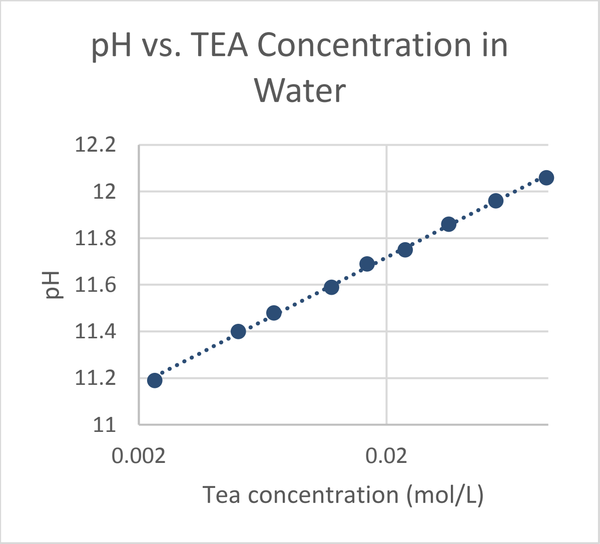
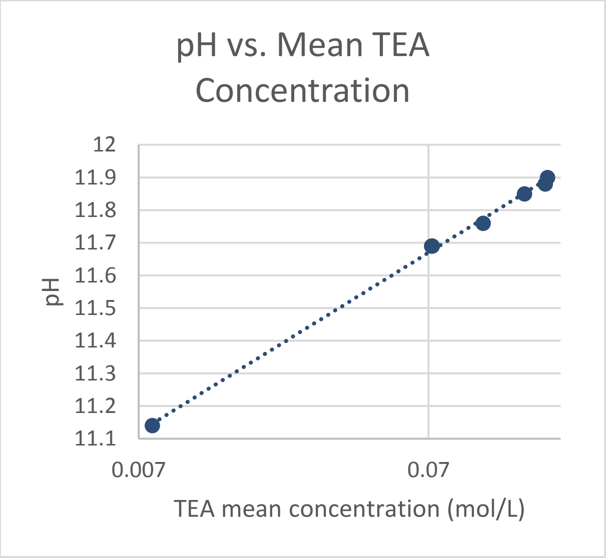


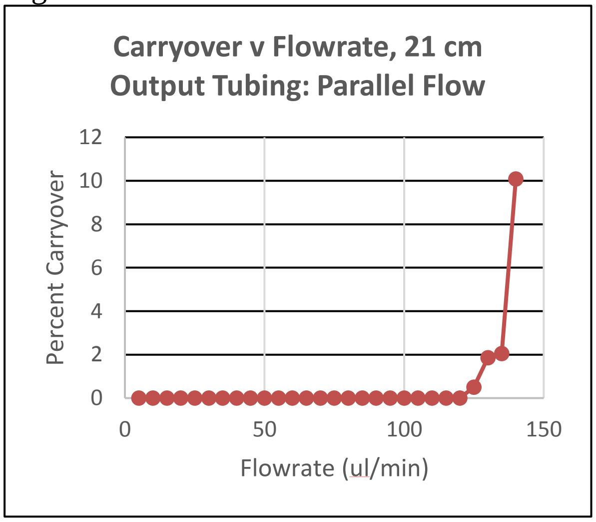
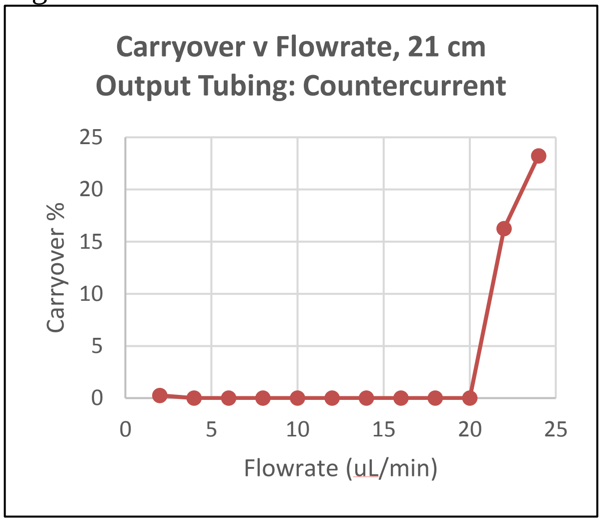
Figure 2b



Screen contactor test flowing

To establish which flow regimes will be stable in the contactor, a single-layer device was assembled. This device was tested incrementally at increasing flow rates until phase carryover was detected in the incorrect outlet tubing. To perform these tests, TEA was combined with equal parts water and n-decane to create a 0.18 mol/l mean concentration solution. This solvent system was shaken for 24 hours and allowed to separate for 24 hours in a separatory funnel. This mixing/separating procedure was carried out in order to establish equilibrium between the phases. The separatory funnel was then used to separate the two liquids for loading into our KD Scientific syringe pump.

A LANL-built optical system consisting of a light emitting diode and a photodetector was used to monitor the liquid phases in the outlet tubing and to quantify carryover. By quantifying this phase carryover, we were able to establish precise flowrate thresholds at which these devices fail. These tests were first performed in a parallel flow configuration, and then the inlet and outlet tubing of the aqueous phase were swapped and the measurements were repeated for the countercurrent configuration. Below in Figs. 3a and 3b are plots of flowrate vs. carryover % for the organic outlet in parallel and countercurrent configurations.

Figure 3a	Figure 3b
	

A set of four Elveflow microfluidic pressure sensors were implemented to monitor pressures at the inlets and outlets of the contactor at different flowrates. Information provided by the sensors helps to characterize the flow resistance throughout the system, and to provide feedback for efforts to model contactor performance and failure. Figs. 4 and 5 depict pressure readings for the aqueous and organic inlets and outlets at multiple flow rates.

Figure 4

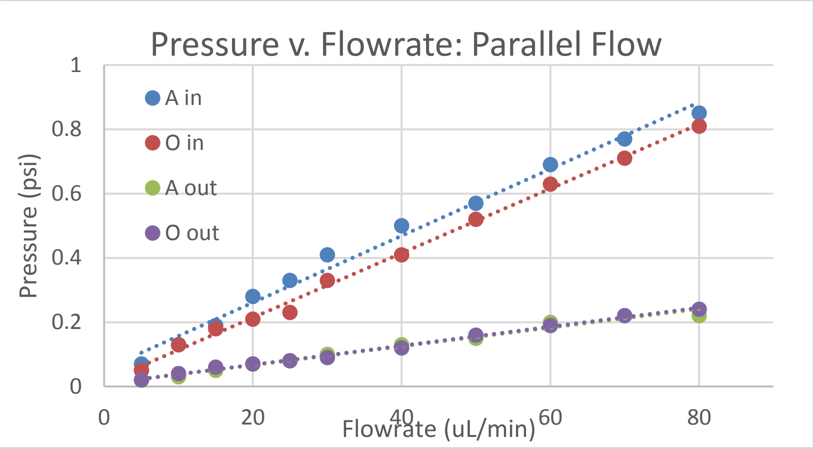
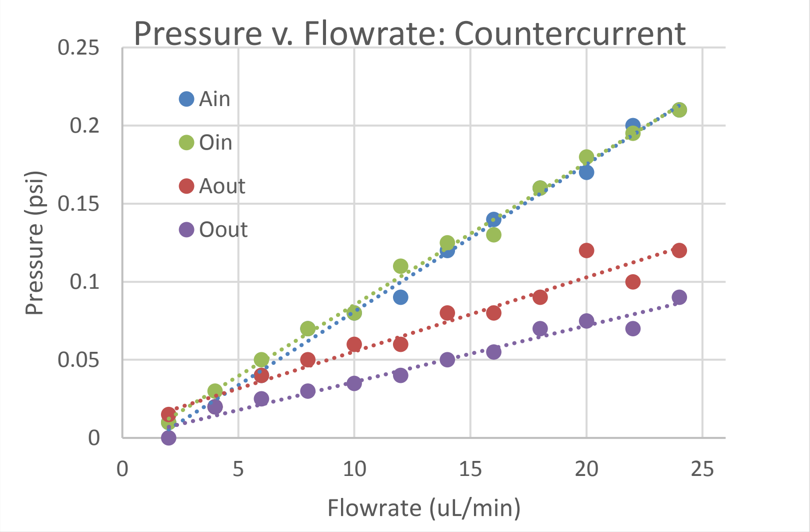


Figure 5



Screen contactor modeling

The benefit of flowing longitudinally through wettable screens is that the screens provide large capillary forces while maintaining small hydraulic pressure drops. Precise modeling of the wettability and capillary forces of a mesh material are difficult because of the screen's complicated geometry. Rather than trying to do this exactly, my Mathematica model approximates the cross section of a screen to be linear array of n capillaries of radius r. As such, the flow performance and the onset of carryover can be predicted using just these two numbers, along with the various known physical parameters of our assembly and solvent system. Roughly speaking, n and r, can be estimated based on the geometry of the screen contactor assembly, but these numbers can only be calculated precisely via flow experiments. At present, I estimate n ~ 1000, and r to be 13 microns. These numbers will be calculated more precisely over the next month as I continue to analyze data collected over the summer.

Upcoming work

During the Fall 2017 semester I plan make progress on the following fronts.

- We have already begun to perform mass transfer experiments using the TEA system. For these experiments, I am loading the n-decane phase with TEA and then measuring the pH of the aqueous phase after the liquids have passed through the screen contactor. These tests are being performed in parallel and countercurrent configurations.
- My initial model for these devices calculates hydraulic pressure drops as a function of geometry, much in the same way that I am calculating capillary pressure. Rather than doing this, I will be using the aforementioned Elveflow pressure sensors to measure pressure drops through a known length of screen material, and then use this to empirically dictate flow resistances through an unknown length of mesh.
- A liquid manifold is being designed to allow one to purge air out of the screen contactor, and to switch from parallel to countercurrent flow configurations via the manipulation of valves. Currently, these tasks are performed by disconnecting and then reconnecting tubing, which inevitably introduces air bubbles. Adding a valve manifold to the system will alleviate this problem.
- A Drop Shape Analysis system, called the DSA25, purchased from KRUSS USA, has been used heavily to measure the interfacial tensions of our liquids and biphasic contact angles of our liquids on our wetted materials. There is an ongoing effort to measure contact angles of the TEA chemical system. These measurements will be completed in the upcoming weeks.
- We are beginning to experiment with a niobium oxide surface coating on the stainless steel screens to improve chemical resistance and to improve aqueous phase adhesion. Determining a Nb deposition procedure and the appropriate stoichiometric ratio needed to optimize biphasic contact angles will be ongoing work next semester.

Summary

During the Summer 2017 semester, I focused on testing a chemical system to demonstrate solvent extraction using our LANL-invented screen contactors. The chemical system chosen consists of immiscible water and n-decane phases and trimethylamine as a solute. A significant amount of time was dedicated to the characterization of this liquid-liquid system. Additionally, an equilibrated water/TEA/n-decane system was test flowed through our contactor to establish stable flow regimes and to gather data to feed into my Mathematica model.

Acknowledgements

I would like to take a moment to acknowledge my students and collaborators at LANL. I am currently mentoring two students, Quintessa Guengerich and Sebastian Litchfield, both of which are Chem E students from New Mexico Tech. They have proved to be extremely dedicated and thoughtful research assistants and have been an indispensable part of our microfluidic efforts. In addition, I am part of LANL's Milli and Microfluidic Purification and Recovery (MMPR) program. This program consists of over 20 people, and has been the ground upon which my research stands. I would, in particular, like to acknowledge the Principle Investigators Steve Yarbro and Becky Chamberlin. Also affiliated with MMPR, I would like to thank my LANL research and academic advisor, George Goff, as well as Garrison Stevens and Alison Root for their COMSOL and SPICE modeling support and continued support for my modeling efforts in Mathematica.

Bibliography

1 McCulloch, Q., Yarbro, S., Chamberlin, R. & Guengerich, Q. Microfluidic Liquid-Liquid Contactor Based on Wettable Screens. United States patent Application No. 62/483,107 (2017).

2 Fricke, M. & Sundmacher, K. Mass Transfer Model of Triethylamine across the n-Decane/Water Interface Derived from Dynamic Interfacial Tension Experiments. *Langmuir* **28**, 6803-6815, doi:10.1021/la204413f (2012).