

Microchannel Devices for Efficient Contacting of Liquids in Solvent Extraction

W.E. TeGrotenhuis, R.J. Cameron, M.G. Butcher,

P.M. Martin, R.S. Wegeng

Pacific Northwest National Laboratory

P.O. Box 999, MS P7-41

Richland, Washington

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Microchannel devices were designed and tested for efficient contacting of two liquids in solvent extraction and the results are presented. This study is part of an overall effort to produce and demonstrate efficient compact devices for chemical separations. Engineering these devices at the microscale offers many technical advantages. Achieving high contact area per unit system volume, thin film contacting, and establishing uniform flow distribution results in substantially higher throughput per total system volume over conventional technologies. This extended summary provides a general overview of background, theory, experimental procedures, results, and potential applications of microchannel devices for solvent extraction.

BACKGROUND

Developments in microfabrication techniques, based on techniques founded in the electronics industry, are facilitating development of novel hardware for performing traditional chemical processing at a miniaturized scale. Features can now be designed with resolutions approaching 1-10 μm or less in microchemical components. At this scale, the distances for heat and mass transfer can be uniformly minimized, giving extremely rapid transport rates that result in very short residence times and high throughput per unit hardware volume. In addition, process conditions can be more tightly controlled. Eventually, it may be possible to miniaturize entire chemical processes including most of the elements of traditional chemical processes, (e.g., heat exchangers, reactors, separators, and actuators).

The compact size enables distributed processing, which is particularly appealing for a number of applications. Although traditional economies of scale in scaling up chemical processes are not easily realized with microtechnology, potential exists for economies of mass production, analogous to the dramatic reductions in manufacturing costs experienced in the microelectronics industry. Progress in developing microchemical separators for solvent extraction applications is described here.

A novel approach for solvent extraction is under development based on microchannel devices. These devices resemble membrane contactors, but with much more versatility for substantially reducing mass transfer resistances, both in the flow streams and in the contactor plate. Film-contacting technologies offer advantages over more traditional mixer-settler technologies. One advantage is the ability to optimize the ratio of solvent flow to feed flow, which is generally minimized to reduce solvent recovery costs. Design of mixer-settlers becomes more difficult and mass transfer efficiency diminishes as the solvent-to-feed ratio becomes much less than one. Film contactors, on the other hand, can be designed and operated over a wide range of solvent ratios, which provides for optimal use of solvent, especially when the equilibrium distribution coefficient for the solute is large. Furthermore, the effectiveness of each stage of a mixer-settler or a film contactor with a mobile interface is limited by equilibrium, and multiple stages are required to achieve a more effective separation. However, if the interface is immobilized, the two liquid films can flow in counter-current directions, allowing for more effective separation in a single device.

Microchannel devices are engineered at the microscale to achieve much higher heat and mass transfer rates than are found in macroscale technologies. These devices, when applied to solvent extraction, allow intimate contacting of two immiscible fluids as they flow through very thin channels that are smaller than the normal mass transfer boundary layer. By reducing the mass transfer resistances in each phase, overall mass transfer rates can be significantly enhanced and the overall size of the equipment reduced. The approach here is to use a microengineered support for the interface to allow counter-current contacting while minimizing the mass transfer resistance in the support.

The architecture employed in this work consists of two micromachined channels separated by a contactor plate as shown in Figure 1. Devices can be operated co-currently or counter-currently. A micromachined contactor plate containing a matrix of uniform holes separates the channels. A micrograph of a hole matrix is shown in Figure 2.

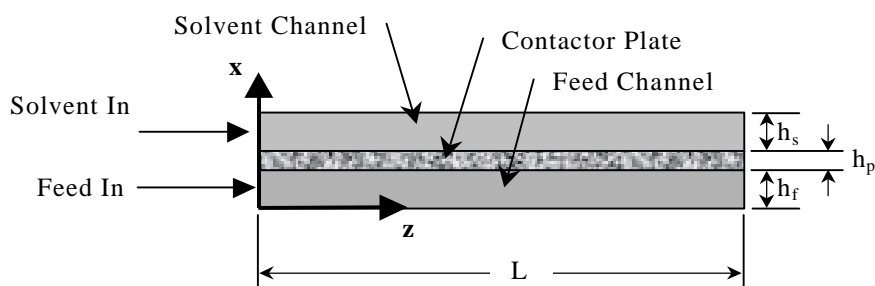


Figure 1. Microchannel contactor device geometry.

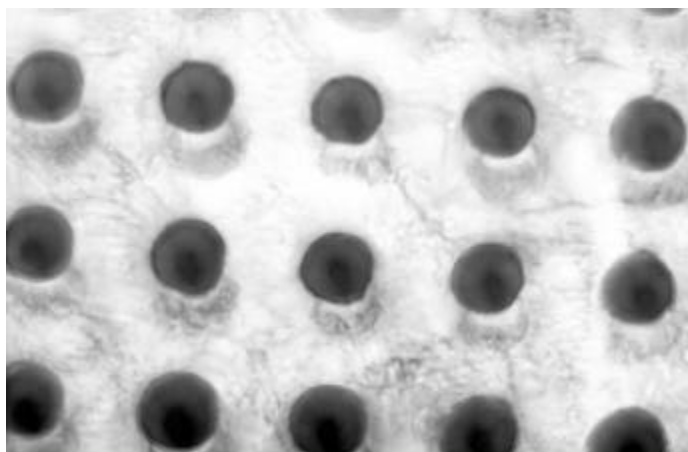


Figure 2. Micrograph of micromachined contactor plate fabricated from 1-mil (25- μm) Kapton substrate;

The mass transfer resistance of the device has contributions from each flow stream, from the contactor plate, and from the interface. Interfacial mass transfer resistance can dominate, particularly if the extraction involves an interfacial reaction, such as in the exchange of ions in the extraction of dissolved metals. If interfacial mass transfer resistance dominates, device performance is largely governed by the total interfacial surface area. The contactor plate mass transfer resistance is a function of several parameters, including the thickness of the contactor plate, porosity, tortuosity, and the solute diffusion coefficient in the wetting liquid filling the pores. The objectives in this work are to reduce the overall size of the equipment and improve operating efficiency by 1) improving mass transfer efficiency in the flow channels by reducing the thicknesses of the films, and 2) improving mass transfer efficiency in the contactor plate. Here, the relative importance of mass transfer resistance in the flow channels versus the contactor plate is explored theoretically and experimentally, using both micromachined contactor plates and commercial polymeric membranes.

THEORY

Theoretical performance of a microchannel contactor having two immiscible fluids flowing through rectangular channels separated by a porous rigid plate requires solution of the convective-diffusion equation. Because the width of each channel is much larger than the height of each channels, the side wall effects are neglected and the problem is reduced to two dimensions. The geometry is divided into three sections—the feed flow channel, the solvent flow channel, and the contactor plate—with equations written for each section. Boundary conditions allow the equations to be combined into a single

mathematical model of the overall device. Dispersion in the flow direction is neglected in all three sections, while convection is neglected in the transverse direction, which is valid at low concentrations.

Six boundary conditions exist for the case of the solvent wetting and filling the contactor plate, which are

$$\frac{\partial c_f}{\partial x} = 0 \quad \text{at } x = 0 \quad (1)$$

$$D_f \frac{\partial c_f}{\partial x} = k \left(c_f \Big|_{x=h_f} - m_s c_p \Big|_{x=h_f} \right) \quad \text{at } x = h_f \quad (2)$$

$$D_e \frac{\partial c_p}{\partial x} = D_f \frac{\partial c_f}{\partial x} \quad \text{at } x = h_f \quad (3)$$

$$c_p = c_s \quad \text{at } x = h_f + h_p \quad (4)$$

$$D_s \frac{\partial c_s}{\partial x} = D_e \frac{\partial c_p}{\partial x} \quad \text{at } x = h_f + h_p \quad (5)$$

$$\frac{\partial c_s}{\partial x} = 0 \quad \text{at } x = h_f + h_p + h_s \quad (6)$$

where: c_f represents the feed flow concentration; c_p represents the solute concentration in the holes in the plate; c_s represents the solute flow concentration; D_e represents an effective diffusion coefficient for the contactor plate that captures effects such as porosity and tortuosity; D_f is the solute diffusivity in the feed flow; D_s is the solute diffusivity in the solvent flow; h_f is the height of the feed flow channel; h_p is the thickness of the contactor plate; h_s is the height of the solvent flow channel; k is a mass transfer coefficient representing the mass transfer resistance across the interface; m_s is the equilibrium distribution coefficient, which is the ratio of feed concentration to solvent concentration at equilibrium, assumed to be constant over the concentration range in the device.

Equations 1 and 6 provide for zero flux through the solid channel walls. Equation 2 represents constant flux across the interface based on an interfacial mass transfer model. Equation 3 assumes continuity of flux on both sides of the liquid-liquid interface and Equations 5 and 6 represent continuity and constant flux at the contactor plate on the solvent side.

The two convective-diffusion equations for the flow channels are solved numerically using the Crank-Nicholson implicit method of finite differences, iterating from the feed end to the discharge end in sequential steps. The x-direction is non-dimensionalized by the feed channel height, h_f , and concentrations are non-dimensionalized by the feed initial concentration, c_p . The z-direction is analogous to time and is non-dimensionalized. A Sherwood number is defined for the interfacial mass transfer using feed side diffusivity and feed channel height for consistency. The other two diffusivities, D_e and D_s , are scaled by the feed diffusivity, D_f . The interfacial boundary condition, Equation 2, becomes

$$Sh \frac{\partial \tilde{c}_f}{\partial \tilde{x}} = \tilde{c}_f \Big|_{\tilde{x}=1} - m_s \tilde{c}_p \Big|_{\tilde{x}=1} \quad \text{at } \tilde{x} = 1 \quad (7)$$

For most calculations reported here, the Sherwood number is assumed to be very small, representing very fast kinetics across the liquid-liquid interface. The other boundary conditions are similarly non-dimensionalized.

EXPERIMENTAL PROCEDURES

Three types of experiments have been performed in support of this investigation. In the first, equilibrium concentration ratios were measured over a range of total solute concentrations to quantify the equilibrium partitioning coefficients for theoretical comparison. In the second, water and cyclohexane were run co-currently through the microcontactor device and the water effluent was measured for cyclohexane concentration. The flow channel mass transfer resistance is measured by itself in these experiments, because the cyclohexane wets the contactor plates. This allowed validation of the theoretical model for the flow channel mass transfer resistance. In the third set of experiments, cyclohexanol was added to the water stream and cyclohexane was used as the extractant. Although this is not necessarily a useful solvent extraction system, it serves the purpose of a model test system to evaluate and compare device performance. Results are included in this summary only for the equilibrium partition experiments and for the extraction of cyclohexanol from water into cyclohexane.

Equilibrium Partitioning of Water, Cyclohexanol, and Cyclohexane

Equilibrium partitioning coefficient data were collected by mixing a stock solution of 1000 mg/L cyclohexanol in water with cyclohexane in various volume ratios. The mixtures were allowed to equilibrate over several days. Samples were then taken from the water phase and analyzed by gas chromatography.

Micromachined Contactor Plates and Microporous Teflon Membranes

Two thicknesses of micromachined contactor plates were used in the microchannel device. Micromachined contactor plates were fabricated by laser drilling a matrix of holes through Kapton polymeric 1-mil and 2-mil film (25- μm and 50- μm) covering an area 1-cm wide by 8-cm long. The holes are conical, averaging 25 μm in diameter on one side and 35 μm in diameter on the other side of the 25- μm -thickness films. Porosity was estimated at 26%. The micromachined contactors were coated with Teflon to make them more non-wetting to water, giving higher breakthrough pressures.

For comparison to the performance of the micromachined contactor plates, experiments were performed with a Gelman 3- μm Zefluor PTFE (Teflon) microporous membrane. This membrane has a microporous Teflon layer approximately 15- μm thick mounted onto a 165- μm thick Teflon macroporous substrate, for a total thickness of 180 μm . The porosity of the 15- μm microporous layer is calculated to be 44%, based on void volume information obtained from Gelman. The contactor device was consistently configured with the Teflon layer located toward the organic liquid side for all experiments.

Microchannel Device

The experiments were performed using a microchannel device to distribute flow across the micromachined contactor plate or the microporous Teflon membrane at varying channel heights and flow rates. The channels of the device are 10-cm long, 1-cm wide, and can be configured with various channel heights that can be different for the feed and solvent sides. In all experiments reported here, the same channel heights were used on both sides and at equal flow rates. Channel heights used were 200 μm , 300 μm , 400 μm , and 500 μm . The micromachined contactor plates have 8 cm of active porous area, while the full 10 cm of channel length is utilized with the microporous Teflon membrane. A Harvard Apparatus, Model #22, syringe infusion pump was used to pump the liquids at constant flow rate through the contactor. Pressure differential between the two liquid streams was measured in the tubing immediately downstream of the discharge ports of the microcontactor device using a water manometer. The water stream discharge pressure was kept slightly higher than the cyclohexane stream discharge pressure, though the pressure differential was generally less than an inch of water column.

RESULTS AND DISCUSSION

Results were obtained for equilibrium partitioning and microchannel device solvent extraction performance using the micromachined contactor plates and microporous Teflon membrane at varying channel heights and flow rates.

Equilibrium Partitioning of Water, Cyclohexanol, and Cyclohexane—The equilibrium partitioning data show that, within the accuracy of the measurements, the partition coefficient is fairly constant over the range of total concentrations examined. An equilibrium partitioning coefficient of 1.3 ± 0.2 was used in subsequent theoretical calculations.

Microchannel Device Solvent Extraction Performance—Solvent extraction data were acquired with cyclohexanol as the extractant using three channel heights in the experiments with the microporous Teflon membrane and one channel height with the micromachined contactor plate. Data for each membrane or contactor plate and channel height were acquired from a single run by varying the flow rate with several purge volumes between conditions to allow the system to equilibrate.

The microporous Teflon membrane tests showed a significant improvement in performance when the flow channel heights were decreased from 400 μm to 300 μm , indicating appreciable mass transfer resistance in the flow channels at 400- μm channels. However, no discernible improvement is seen in decreasing the channel heights further to 200 μm , indicating the mass transfer resistance in the membrane dominates at this smaller channel height. The micromachined contactor plate performed at least as well as the microporous Teflon membrane.

The 300- μm channel height data are compared to theoretical calculations in Figure 3. The equilibrium partitioning coefficient is set to the average measured value of 1.3, and the interface mass transfer resistance is neglected by setting the Sherwood number to a low value (0.0003). Different theoretical curves are shown for values of the plate effective diffusion coefficient. None of the curves fit the data well over the full range of residence times. The relatively poor fit suggests that the equilibrium partitioning coefficient is too low and a value approaching two would fit the data better. However, this would also require the effective diffusion coefficient through the contactor plate to be close to the bulk phase diffusion

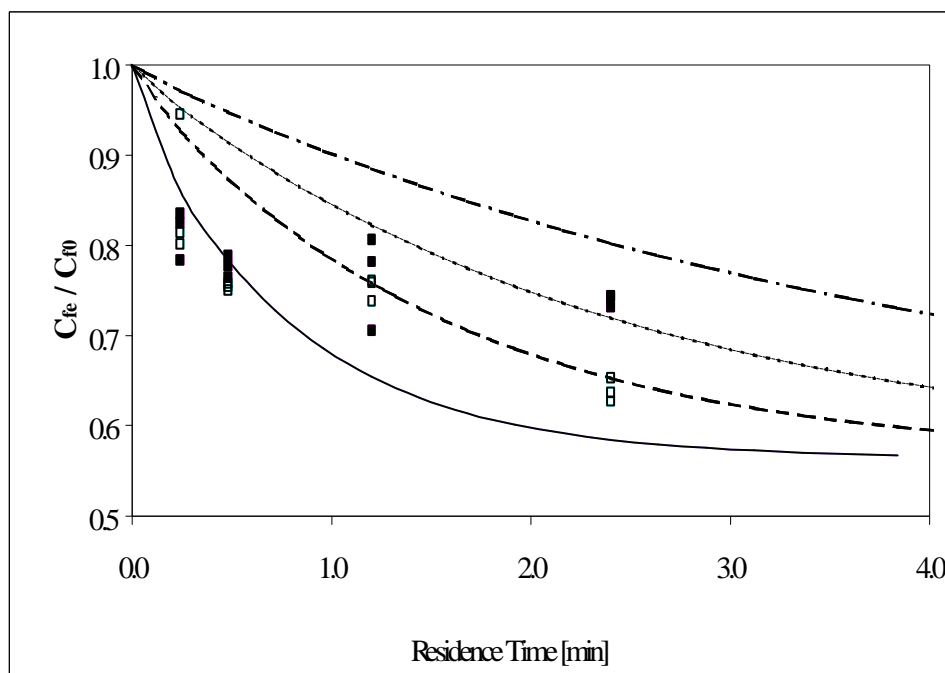


Figure 3. Comparison of solvent extraction data for 300- μm channels to theoretical prediction, presented as effluent cyclohexanol concentration normalized by feed concentration; 300- μm channel heights with Teflon membrane (\square) and 300- μm channel heights with micromachined plate (\blacksquare) compared to predictions for $D_e/D_f = 1.0$ (—), $D_e/D_f = 0.1$ (---), $D_e/D_f = 0.05$ (- - -), and $D_e/D_f = 0.025$ (— - —), using 1-cm by 8-cm channel dimensions, $m_s = 1.3$, $h_f = 25 \mu\text{m}$, $D_f = D_s = 0.84 \times 10^{-5} \text{ cm}^2/\text{s}$, and neglecting mass transfer resistance at the interface.

coefficient, which is not indicated by the comparisons between various channel heights as discussed above. Another possible cause for this discrepancy is the concentration dependence of the equilibrium partitioning coefficient, which so far has not been elucidated by the partitioning data. Another concern is nonuniformities in the flow distribution due to variations in channel height caused by flexing of the contactor plates and membranes, which can not be captured in the two-dimensional theoretical model. Variations in channel heights effectively allow bypass of the device because a disproportionate fraction of the flow will follow the thicker paths that have more mass transfer resistance, thereby giving poorer overall mass transfer.

Assuming the theoretical curves are indicative of mass transfer resistance through the contactor plate and considering the longer residence time data, the micromachined contactor plate has an effective diffusion coefficient that is approximately one-tenth of the bulk phase diffusion coefficient. A factor of four can be attributed to the 26% porosity. Tortuosity is not expected to be important because the holes are straight and close to vertical. The additional 2.5 factor may be attributed, for example, to poor flow distribution or to inactive pores if bubbles are trapped in the pores.

The microporous Teflon membrane is approximately seven times thicker than the micromachined contactor plate, so the effective diffusion coefficient must be scaled accordingly. Therefore, the effective diffusion coefficient displayed by the long residence time microporous Teflon membrane data would be closer to 0.33, which is considerably larger than the micromachined contactor plate. This illustrates that there are multiple avenues to improving mass transfer through the micromachined contactor plate, including increasing the porosity and manufacturing a thinner plate.

POTENTIAL APPLICATIONS

Based on the testing performed to date using microchannel devices for contacting liquids, an estimate was made of the annual processing capability of a scaled-up system that would fit into a volume of 1.8 ft^3 , about the size of a file cabinet drawer. For residence times varying from 10 to 100 s, such a device could process 3.3 to 33 M gal/yr. This operating efficiency, coupled with substantial size reduction, suggests that microchannel devices and systems may create a significantly different approach to the way physio-chemical processing systems are utilized, integrated, and applied as compared to conventional technologies.

A wide diversity of potential applications for microchannel devices is envisioned, though such conceptualizing is in the early stages. The high productivity per unit volume of microchannel devices affords opportunities for remote and highly constrained applications such as down well treatment of contaminated groundwater; treatment of high-level nuclear waste inside of storage tanks; or for production of oxygen, fuel, or other resources on board spacecraft or on the surface of planetary bodies. Work is beginning on incorporating microchannel technology into NASA's In Situ Resource Utilization projects. Because microchannel devices are light, compact, and efficient, military commandos may be able to carry them into the field to make products that are too heavy or bulky to transport (such as water purification units) or products that are dangerous to store and transport (such as chemical agents). Additional applications that may benefit from the extreme compactness of microchannel hardware are anticipated.

Microchannel technology may also shift the economies of mass production toward more distributive processing. Instead of producing bulk chemicals that must be stored and distributed, many chemicals can be manufactured at their point of use in the future. This is particularly advantageous with acutely toxic or hazardous chemicals that have high storage and transportation risks. Another example is placing microchannel chemical systems on board ships, allowing processing during shipment and adjusting the makeup of the products to match the needs when the ship reaches port.

CONCLUSIONS

Microchannel devices offer a novel approach to chemical processing where very rapid heat and mass transfer are achieved, thereby realizing high throughput per unit system volume, better process control, and better efficiencies. Furthermore, fabrication techniques adapted from the microelectronics industry can provide economies of mass production to support process scale-up, instead of relying on traditional economies of scale.

Performance of a microchannel device has been demonstrated using both micromachined contactor plates and commercial microporous membranes over a range of flow rates and channel heights. Results indicate that first generation micromachined contactor plates perform at least as well as the commercial membranes tested, with significant potential for improving performance. Future efforts in developing micromachined contactor plates will be directed toward reducing mass transfer resistance by reducing contactor plate thickness, increasing porosity, and using more rigid materials to give uniform flow thickness.

Overall mass transfer in microchannel devices can be limited by diffusion in the flow channels, diffusion through the contactor plate, or by the interface. Theoretical predictions and comparison of data for varying channel heights indicate that contactor plate mass transfer resistance becomes significant as the channel height decreases below 300 μm for current contactor plates. However, as the contactor plates become more efficient, the need is anticipated for operating with substantially smaller channel heights. Therefore, continued advancements in this technology will require efforts in reducing mass transfer resistance of both the contactor plates and of the flow channels.

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