

Diffusive and Convective Mass Transfer in Two-Phase Microchannel Flow: Non-Equilibrium Interfacial Tension

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Abstract. The kinetics of mass transfer from one phase to another is monitored in flow. The time-dependent interfacial tension between water and oil (determined from drop deformation dynamics in situ) serves as a measure of the butanol (diffusing species) concentration inside the drop. This concentration decreases from its initial value, as the butanol diffuses into the surrounding oil. This diffusive process is effectively two dimensional, i.e. only transverse to the flow.

Keywords: Microfluidics, multiphase flow, surfactant mass transfer, interfacial tension.

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INTRODUCTION

Drop-based microfluidic methods for incubation and analysis of cells, organelles and biochemicals are being developed.¹ These systems include a variety of chemical components, not all of which are exclusively partitioned to either phase. An investigation of the mechanisms and rates of interphase mass transfer is therefore of interest to evaluate the local concentration of a species. Here, we investigate the transfer of a surface active component, and the interfacial tension between phases serves as a measure of its local concentration inside the drop. The tension is determined in situ by analyzing the drop motion and shape.^{2,3} This method is advantageous, as it is implemented in microchannel flow, where both convective and complex-flow effects are present, and drop sizes are easily tailored.

EXPERIMENTAL SECTION

The following fluids and additives were used in this study: canola oil (procured from the local grocer, and used as received directly after opening the sealed bottle), n-butanol (Mallinckrodt⁴; also used as received), sodium dodecyl sulfate (sds, Fluka), and distilled and deionized water (resistivity = $18.0 \times 10^6 \Omega\text{-cm}$). Aqueous solutions of butanol (1 %, 2 % and 5 % mass fraction) and an aqueous solution of sds (0.05% mass fraction) were prepared. While the use of canola oil is certainly reasonable from a practical point of view, it may contain surface active impurities that can alter the interfacial tension. However, added surfactant (butanol or sds) has a much more significant effect.

Fabrication of the microfluidic device from polydimethylsiloxane (PDMS, Dow Sylgard) gel has been described in detail previously.³ A master channel mold was fabricated first from SU-8, 2075 (MicroChem), and then replicated with PDMS. The PDMS device was exposed briefly to O₂ plasma, sealed onto a clean glass slide, fitted with tubing and connected to micro-stepping syringe pumps (New Era Pump Systems). The syringe diameters are known, so that the pumps deliver fluid volumes with accuracy better than 0.1 %. Aqueous drops are produced at a T-junction and three inputs for the continuous fluid are provided in order to easily tune the drop size and spacing.³ The main channel of the device contains five constrictions, where drops may stretch, if viscous forces are strong enough. Detailed geometry of the constrictions is reported in Fig. 1.

Pumping and data acquisition are computer controlled (LabVIEW). 8-bit grayscale images (241 pixels x 992 pixels) were acquired with an Adimec 1000-M CCD camera at 100 Hz. Real-time image analyses (LabVIEW) of

instantaneous drop center of mass, major and minor axes, and orientation were recorded in time. The temperature was also recorded and used to compute the fluid viscosities.⁵ The dynamics of deformation and retraction of an isolated drop with uniform interfacial tension subject to an unbounded flow field are well established^{6, 7} and form a basis of interfacial tensiometry.^{2, 3} As noted previously,³ the transient response of a drop may be plotted thus to yield the apparent tension σ from the slope

$$\alpha \eta_c (5(\dot{\epsilon}_1 - \dot{\epsilon}_2)/(4\hat{\eta} + 6) - dD/dt) = \sigma D/a_0 \quad (1)$$

The parameter α is a weak function of viscosity ratio $\hat{\eta}$ ($=\eta_d/\eta_c$), and η_c is the continuous oil phase viscosity. $\dot{\epsilon}_i$ are the principal extension rates, D is deformation (normalized difference of principal drop radii), dD/dt is its material derivative, and a_0 is the drop radius. Numerical simulations of drop response to a strain rate impulse indicates that the apparent tension is accurate to 1% if $D < 0.02$.⁸ Marangoni effects, when present, can cause more significant deviations.⁸ The flow field in the channel was further explored by three-dimensional finite-element steady-state Navier-Stokes calculations (using approximately 10^4 tetrahedral elements, Comsol Multiphysics 3.2).

RESULTS AND DISCUSSION

Droplet motion and shape is tracked, as a drop flows along the microchannel and through a constriction (sample data in Fig. 1, drops are aqueous sds, 0.05% mass fraction). Since the drops are small compared to the height and width of the channel, and the relative viscosity of the drop is near zero, the drop velocity is expected to be nearly equal to the fluid velocity on the same streamline.⁹ Here the data is comparable to the centerline velocity, indicating that the drop is very close to that position. This data is taken from a constriction that is near to the end of the 5 cm long channel. When the drop velocity was recorded at upstream locations, variations up to several percent less than the calculated centerline velocity were observed, suggesting that the drop is introduced at a height that differs from the mid-plane of the channel (by as much as 15%) and subsequently migrates.¹⁰ Migration times (drop size dependent) are comparable to the passage times (several seconds). The passage time from the moment of drop formation to that of measurement of interfacial tension was determined using drop velocity measurements.

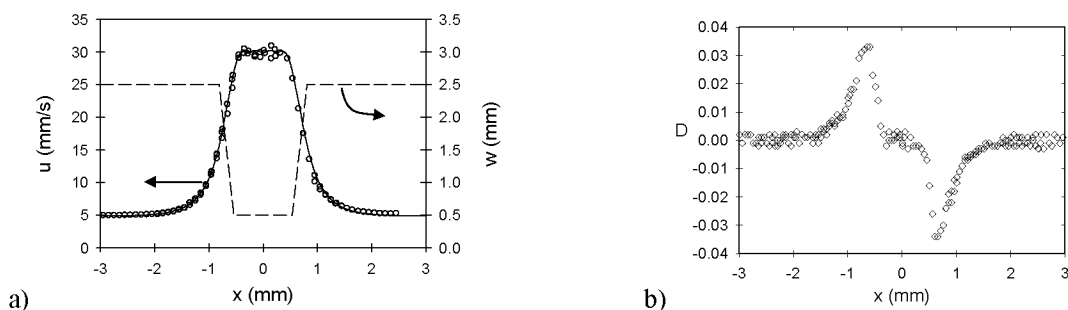


FIGURE 1. Drop velocity (a) and deformation (b) as drops pass through a constriction in the channel. The channel width profile w is plotted in (a) with dashed lines, and the channel height is 496 μm . Data points signify measurements (whose statistical uncertainty is illustrated by their scatter) and the solid curve (in a) is a finite element calculation of the centerline velocity. Total volumetric flow rates in (a) and (b) are 12.82 mL/h and 10.82 mL/h, respectively, while the drop radius is $54 \mu\text{m} \pm 2 \mu\text{m}$.

The drop shape is nearly spherical. The largest distortions occur at the entrance and exit of the constriction (Fig. 1 b), where the acceleration is of greatest magnitude (Fig. 1a). This perturbation is minor and short lived, and its effect on mass transfer from the drop is not expected to be significant. Inertia too is of little significance, since the maximum value of Re is 0.1. The apparent interfacial tension is obtained according to equation 1 from analysis of the entrance region (i.e. $x: [-2, -1]$, as shown in Fig. 1).

Based on such data, restricted to the entrance and $D < 0.02$,⁸ the apparent σ is measured as a function of a_0 , interface age (drop residence time) and input butanol concentration $c(0)$ (Fig. 2). When $c = 0$ (pure water/oil), σ is independent of a_0 , drop spacing and total flow rate (interface age). However, when $c(0) > 0$, σ became a function of a_0 , $c(0)$ and interface age. As the interface ages, σ increases. However, Fig. 2 a does not show the minimum in interfacial tension that is expected in such systems where there is surfactant mass transport across the liquid/liquid interface.^{11, 12} This minimum is not observed here, since short interface age (< 1 s) are not accessible in this device.

A convection-diffusion model was applied to estimate the concentration of butanol inside the drop as a function of interface age. Since the solute is convected in the oil from the neighborhood of one drop to that of the subsequent one more quickly than it diffuses from the drop, the phenomenon is effectively two-dimensional; diffusion is only

relevant transverse to the streamlines. We also assume that convection homogenizes the concentration inside the drop. Diffusion from a finite uniform cylindrical source gives the following time dependent source concentration.¹³

$$c(t)/c(0) = \left(1 + 2\sqrt{Dt}/a + 3Dt/a^2\right)^{-1} \quad (2)$$

The characteristic timescale of this mass transfer process is a^2/D (of the order of a few seconds), where D here denotes diffusivity. By varying a_0 and interface age, the adsorption isotherm can be constructed (Fig. 2b).

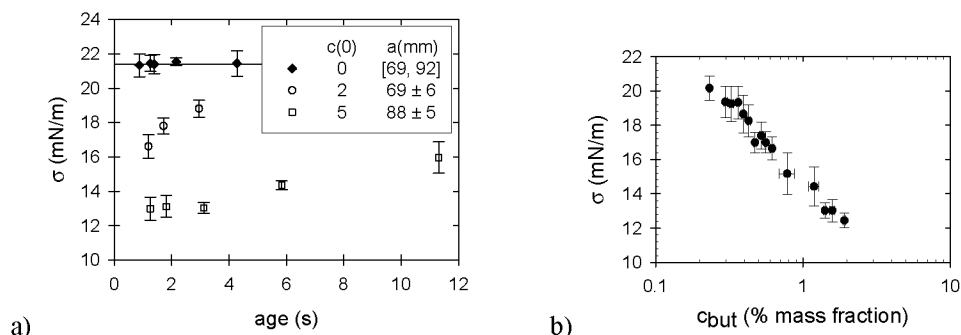


FIGURE 2. a.) Measured interfacial tension σ vs. interface age. Initial n-butanol concentration $c(0)$ and average drop radii a are listed in the legend. Standard uncertainties are reported. b.) Measured interfacial tension σ vs. estimated n-butanol concentration.

CONCLUSIONS

These measurements, analysis and modeling of decaying interfacial pressure demonstrate quantitative detection of the kinetics of release of a surface-active solute diffusing from a drop in two-phase flow, accounting for convection inside and outside the drop. The ability to adjust drop size here provides access to a range of dimensionless interface age. This ability to tune drop size and that of scaling the device channel and drop dimensions is valuable for future studies of interfacial kinetics of surfactants during flow.

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