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Transfer of surfactants to an expanding oil water interface during membrane emulsification

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Introduction

There has been an increasing interest in a new technique for making emulsions known as Membrane Emulsification which uses a microporous membrane operated in cross-flow. The continuous phase is pumped along the membrane and sweeps away dispersed phase droplets forming from pore openings as shown in Figure 1. The key feature of the membrane emulsification process, which sets it apart from conventional emulsification technologies, is that the size distribution of the resulting droplets is primarily governed by the choice of membrane and not by the development of turbulent drop break up [1]. The main advantages of membrane emulsification are the possibility to produce droplets of a defined size with a narrow size distribution, low shear stress, the potential for lower energy consumption, and simplicity of design [2].

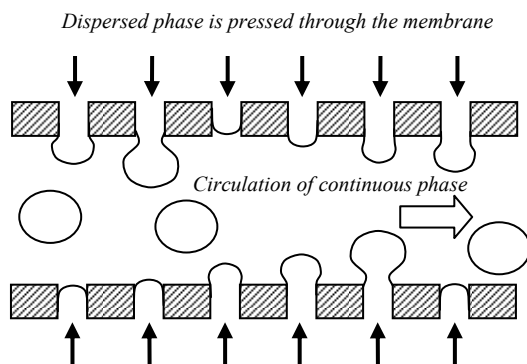


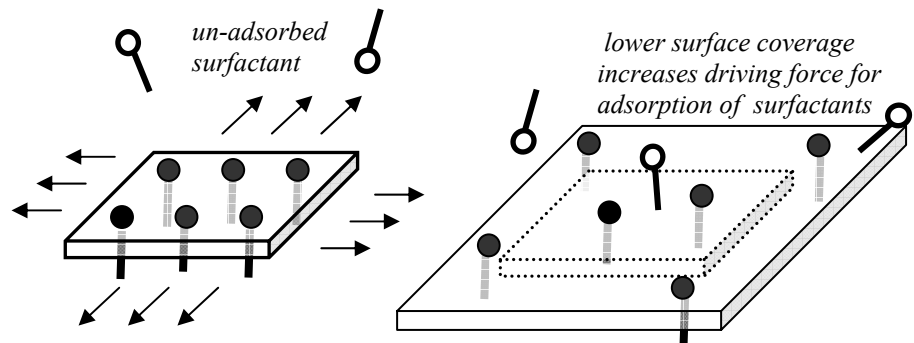
Figure 1: Principle of membrane emulsification

The interfacial tension and applied dispersed phase pressure determine the flow rate through the microporous membrane. As a droplet is pressed into the continuous phase, a new interface is created and surfactant molecules act at this surface to reduce the tension over time. Membrane emulsification differs from conventional emulsification processes in that the droplet formation time is of the same order of magnitude as the dynamic interfacial tension of common food emulsifiers [3]. The effect of emulsifiers is further complicated by the fact that droplet deformation and adsorption at the interface are coupled, thus both the rate at which deformation and detachment forces act, as well as how fast surfactants adsorb to the growing interfacial area become relevant over the time scales involved.

The objectives of this work were to describe the diffusion controlled adsorption of surfactants at the oil water interface, and secondly to model the flow of the dispersed phase through a pore and subsequent surface expansion rate as the drop grows into the continuous phase.

Tension and relaxation of the expanding interface

The interfacial tension force is the key retaining force during droplet formation and its dynamic effect will have a much greater impact on droplet formation than the equilibrium value. The rate of surfactant action determines the rate of the decrease in interfacial tension and thus the magnitude of the retaining force. The smaller the retaining force, the smaller the resulting droplets. When a new drop begins to grow from a pore, there is some surfactant already at the interface. However, because the area is increasing the mean surfactant surface coverage decreases, and is initially non-uniform. The Gibbs-Marangoni effect then quickly establishes a uniform surfactant film around the drop as it grows [4]. Figure 2.



1. Small area segment under expansion with surface coverage Γ , and surface tension γ .

2. Area has increased by ΔA after time Δt . As surface coverage decreases, interfacial tension increases. Diffusion of surfactant from bulk phase.

The second stage of the process leading to a relaxed state of the drop is the transport of the surfactant to the subsurface. The subsurface is not fixed but rather

Figure 2. Surface expansion and tension relaxation due to transport of surfactants

defined as the position from where surfactant molecules can adsorb without further transport. The driving force of the transport is generated by the concentration gradient created as the bulk solution is depleted of surfactant molecules near the subsurface as they are transferred from the soluted to the adsorbed state [5].

Once transported to the interface adsorption takes place and can be described by diffusion-controlled adsorption models. The classical being that derived by Ward and Tordai (1946). It is based on the assumption that the surface coverage, Γ , is limited by the diffusion of the surfactant from the bulk continuous phase [6].

$$\Gamma(t_a) = 2\sqrt{\frac{D}{\pi}} \left(C_{bulk} \sqrt{t_a} - \int_0^{\sqrt{t_a}} C(0, t_a - \lambda) d\sqrt{\lambda} \right) \quad (1)$$

Where D is the diffusion coefficient, t_a is the time available for adsorption, C_{bulk} and C is the concentration in the bulk and subsurface respectively, and λ is a dummy variable. Equation 1 is simplified by considering the limiting cases of “short time” and “long time” approximations. The short time approximation provides a description of the beginning of the adsorption process, and is given by:

$$\Gamma(t) = 2C \sqrt{\frac{Dt_a}{\pi}} \quad (2)$$

Equation 2 can also be expressed in terms of interfacial tension, by applying the Gibb's isotherm equation [6].

$$\gamma(t) = \gamma_o - 2RTC \cdot \sqrt{\frac{Dt_a}{\pi}} \quad (3)$$

Whereas the long time approximation considers an adsorption process near equilibrium, γ_e is the equilibrium interfacial tension, and Γ_e the equilibrium surface coverage:

$$\gamma(t) = \gamma_e + RT \frac{\Gamma_e}{C} \cdot \sqrt{\frac{\pi}{4Dt_a}} \quad (4)$$

To determine whether a short or long time model is valid, it is useful to compare the time available for adsorption, t_a , to the characteristic diffusion time for the surfactant of interest τ_D [7]. By considering the characteristics of a given system an appropriate model is chosen and then used in the development of the overall transport equation. During drop formation in membrane emulsification the surface is far from obtaining and equilibrium surface tension, thus the short time approximation applies.

Estimation of the Diffusion Coefficient

It is possible to obtain values for the surfactant diffusion coefficient from dynamic interfacial tension measurements. By using the data at short surface ages, and plotting $(\gamma_o - \gamma(t)) / C_{bulk}$ by $t^{0.5}$ the slope of the linear portion of the curve yields the apparent diffusion coefficient for the system by solving for D in equation 3. A sample calculation is shown in Figure 3 with data from [3] and [8].

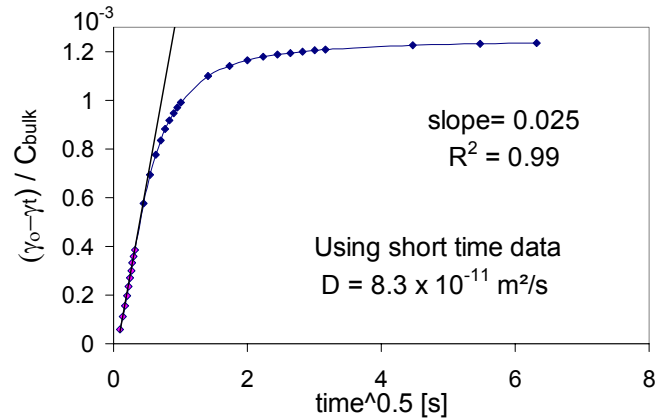


Figure 3. Calculated apparent diffusion coefficients of Tween 20 using data for 2% w/w at 20°C

Defining and solving the transport equation

Since the surfactant is not soluble in the oil phase a balance for the surfactant species in the continuous phase $C(z, t)$ is a function of both position from the interface, z , and time, given by:

$$\left(\frac{\partial C}{\partial t} \right)_z + U_z \frac{\partial C}{\partial z} = D \frac{\partial^2 C}{\partial z^2} \quad (5)$$

The U_z term is the velocity of convection in the bulk continuous phase. Typical flow conditions used during membrane emulsification were analysed, and it was found not necessary to include U_z for droplets smaller than 100 μm forming in a cross flow system because the droplets grow within the laminar sub layer of the continuous phase and we assume a long uniform membrane. The radial velocity of the moving interface (or speed at which the drop front moves) can also be neglected since it has a relative motion and a velocity gradient of less than 50 s^{-1} . In comparison, the velocity gradient at the membrane wall (generated by the continuous phase flow) has been estimated to be over the range of 10 000 to 50 000 s^{-1} [9].

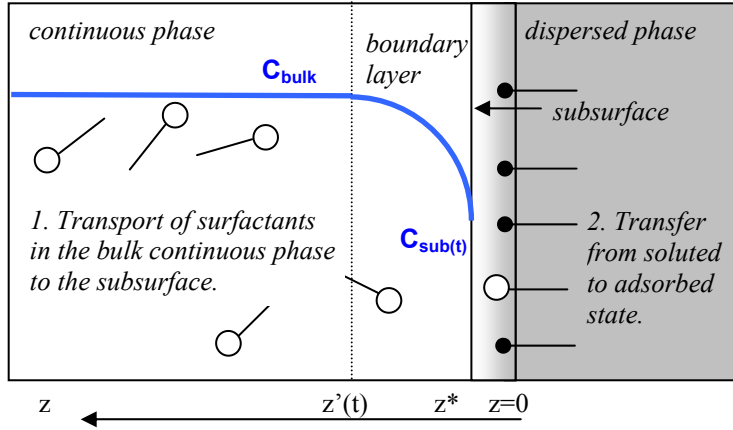


Figure 4. Physical model of transport with adsorption of surfactants

where M_{wt} is the molecular weight of the surfactant. The subsurface for Tween 20 was estimated to be 71 nm. Equation 6 can be solved for the subsurface concentration over time.

$$C_{(z,t)} = C_{bulk} \cdot \text{erf}\left(\frac{z}{\sqrt{4D \cdot t}}\right) \quad (6)$$

Coupled Effects

Knowing the sub-surface concentration of surfactant is not enough in the case of an expanding drop because the expansion rate is dependent on the interfacial tension set by the surface coverage of surfactants. This is a coupled process governed by the diffusion of the surfactant from the bulk continuous phase to the subsurface where adsorption can occur, as well as the depletion due to the isotropic expansion of the interface. The rate of surface expansion is important in defining this problem as it represents a depletion in terms of surface coverage of the surfactant in the transfer process. Therefore, a MATLAB program was written to track the geometry of growing drops, yielding information such as the radius of curvature average surface age, surface area, S , and expansion rate, $\dot{\epsilon}$. This expansion information is used to calculate the current interfacial tension at each time step in the MATLAB program by considering the change in surface coverage due to both diffusion to, and expansion of the surface using Equation 7.

$$\frac{d\Gamma}{dt} = \dot{\Gamma}_{diff} - \dot{\Gamma}_{expansion} \quad \text{where, } \dot{\Gamma}_{diff} = \frac{C_{sub(t)} \sqrt{\frac{D}{\pi}}}{\sqrt{t}} \quad \text{and} \quad \dot{\Gamma}_{expansion} = 2C_{sub(t)} \sqrt{\frac{Dt}{\pi}} \times \frac{\dot{\epsilon}}{S} \quad (7)$$

The flow model and calculation of surface expansion rates

The model of dispersed phase flow was implemented in MATLAB and uses a potential flow approach in the form of an electrical circuit analogy, Figure 4. According to Ohm's law, the voltage drop over a resistor is equal to current through it times its resistance, $V = IR_{ohm}$. Similarly the pressure drop through a flow section is equal to the flow rate times the hydraulic resistance $P = QR_{flow}$ [11]. In this case three resistances to flow were considered, resistance from the membrane causing a pressure loss along the pore, ΔP_{hyd} , the resistance caused by the disjoining pressure across the oil water interface due to capillarity, ΔP_{cap} and the pressure in the continuous phase, P_{cts} . The interesting aspect to this approach is that it does not assume a constant flow through the pore over the drop formation time, but rather takes into account how the change in radius of curvature of the drop and surface relaxation, decreases the capillary pressure, thus allowing the flow to increase. The algorithm of the program is shown schematically in Figure 5. The data from the simulation calculations was processed and plots of the pressure losses from flow and capillarity, integrated shear rate, and flow velocity were produced. In addition, a production time estimation was added to give a sense of the length of time it would take to produce a 20% internal phase ratio emulsion for a given membrane area.

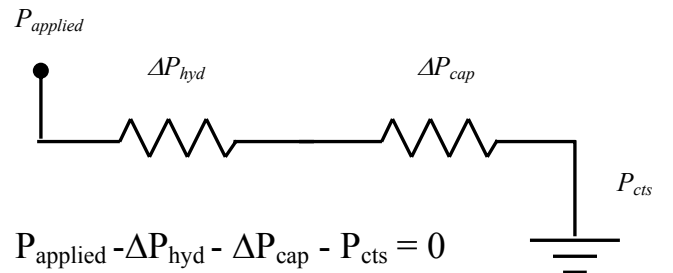


Figure 4. Circuit analogy showing sources of pressure loss

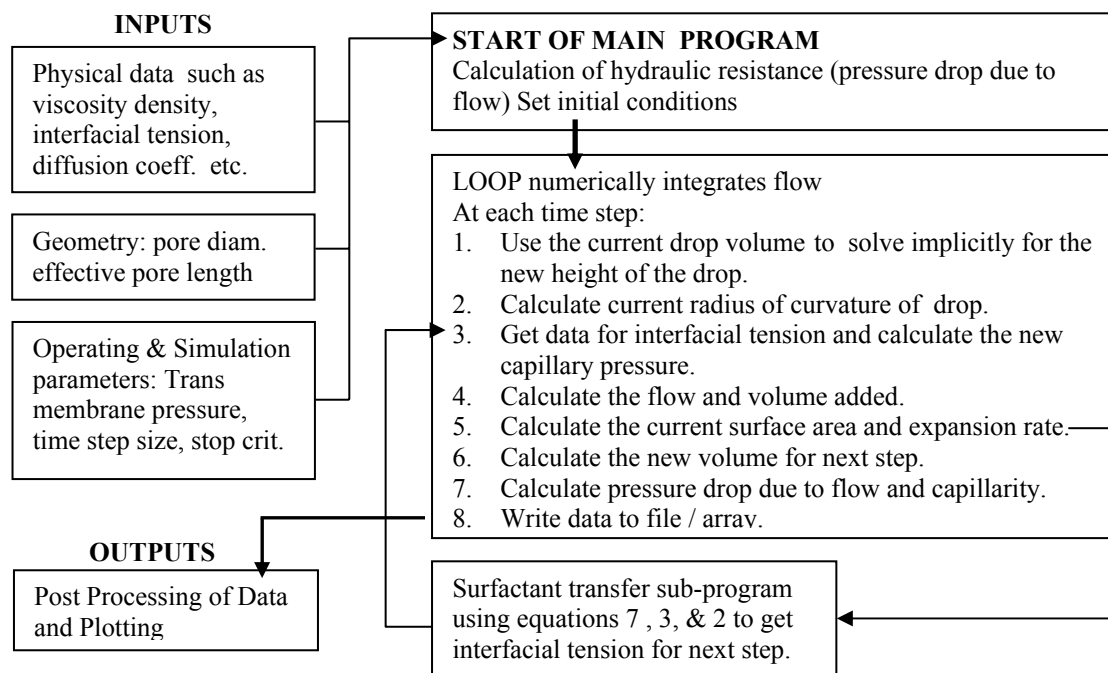


Figure 5. Overview of the Program

From analysing the results of the simulations using a range of geometries and applied pressures some general conclusions could be drawn: 1. Under all conditions studied, the Reynolds number describing the dispersed phase flow was less than 10^{-5} , meaning that the flow was laminar and creeping. 2. The lower the applied pressure, the higher the effect of the capillary pressure in regulating the flow. This means that interfacial effects have a greater impact than that predicted by models which assume a constant dispersed phase flow. 3. At higher drop formation rates (5 to 10 s^{-1}) there is significantly less time for surface relaxation. This, however, may not be as important since in order to achieve these rates the pressure losses are dominated by flow in the membrane and the capillary pressure plays a smaller role.

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