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# Water in oil emulsions from hydrophobized metal membranes and characterization of dynamic interfacial tension in membrane emulsification

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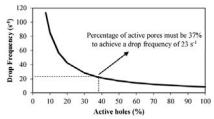
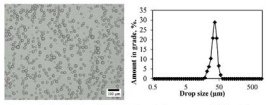
## GRAPHICAL ABSTRACT

Representation of the vertical oscillating membrane emulsification device used with an inset showing the regular pore pattern of the membrane (triangular array) and the shape of the tubular membrane used.




Drop frequency against fraction of active pores for a PVA drop size of 35.8 μm




Droplets formed during injection of 13.5% PVA solution at 1 mL min$^{-1}$ in to kerosene with 40 mM Span® 80 surfactant concentration using a surface shear of 7.3 Pa

## ARTICLE INFO

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## ABSTRACT

Hydrophobization of metal surfaces is reported based on silanization reactions. The aim was its application to metal porous membranes for the production of water in oil emulsions using a process known as membrane emulsification. A vertical oscillating membrane system was used to carry out drop formation experiments. It is shown that drop size can be tuned between 35 and 85 μm by changing just the surfactant concentration in the continuous phase. In addition, a method to determine the percentage of active pores during the membrane emulsification process is demonstrated. This method links knowledge acquired in the surfactant adsorption dynamics and drop expansion rate. Using this approach, pore velocity can be determined, which will help in determining the boundary between dripping and jetting from a pore. This study reinforces the importance of dynamic interfacial tension which must be considered in process design, and modelling purposes, particularly in two liquid phase systems using membranes such as membrane emulsification.

## 1. Introduction

Emulsification using a microporous membrane to produce droplets of a desired size distribution has become an accepted technology. Most academic studies use membranes made from ceramics [1–3], silicon or glass [4,5], surfaces that are naturally hydrophilic, but can be rendered hydrophobic by various treatments [6,7]. However, the adoption of membrane emulsification for commercial processes has been limited,

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due in part to their low mechanical resistance, or pore channel structure that tends to foul with deposited material during use in long-term production [6]. The metal membranes used in this study have a well-defined pore size, a narrow pore size distribution and are equidistantly spaced. The pore channel length of these membranes is the membrane thickness which was 100 μm. These types of metal membranes can be made from nickel, or stainless steel, possess good chemical resistance and fulfil the mechanical resistance requirement commonly found in industry. In a former study [8], a tubular stainless steel microporous hydrophilic membrane was used in a small-scale laboratory azimuthally oscillating membrane emulsification device with throughput of 1 L $h^{-1}$ (of injected phase) providing a uniform droplet size (CV < 10%) of an oil in water emulsion. For some processes, such as controlled release particles for certain pharma application, or some analytical chromatography supports, this continuous process throughput may be equal to full-scale production. For lower value systems productivity could be raised by increasing the porosity of the tubular membrane, changing the geometry of the system, or simply injecting at a higher rate accepting a likely loss of uniformity. In the membrane manufacturing process, porosity of these membranes can be controlled and increases with bigger pore sizes and lower distances between pores. The latter should provide higher productivity, as the total number of pores present can be increased.

However, a significant and highly practical unknown factor whenever modelling, or designing, a membrane emulsification processes is the number of 'active' pores. It is often reported that the number of pores present that participate in a membrane emulsification is very significantly less than the total number of pores present on the membrane. There is no accepted way to be able to predict the number of active pores and limited methods to estimate the value from operating data [3,9–11].

The natural forms of stainless steel and nickel surfaces are mildly hydrophilic which is appropriate for the production of oil in water (o/w) emulsions. However, in order to produce uniform water in oil emulsions (w/o), a hydrophobic membrane is normally desired [9,12,13]. To produce water in oil emulsions the surface properties of the membrane are normally changed, lowering the surface free energy and achieving a hydrophobic surface. The superficial velocity, or approach velocity of the dispersed phase liquid, during membrane emulsification can be easily determined from a knowledge of the disperse phase flow rate, and the membrane surface area. However, determining the velocity in a pore is far more complicated because many variables (porosity, wetting, dynamic interfacial tension, shear, etc.) of the system may influence this velocity. Pore velocity is an important parameter in membrane emulsification as it will determine whether working conditions are within the dripping regime (drops sheared off tangentially to the membrane surface) rather than jetting regime (drops formed by micro-jet break-up). Usually, to provide greater control over the drop size and distribution in ME, the dripping regime is preferred: formation of drops on the membrane surface, contact angle continuous phase to solid surface < 90°, where drops are sheared off [14]. However, if pore velocity is increased above a certain threshold, a change occurs from the dripping to the jetting regime. In the jetting regime, a micro-jet of dispersed phase is discharged from the pore and the continuous-membrane contact angle approaches 90°.

It is normally postulated that a membrane should not be wetted by the disperse phase, and ideally fully wetted by the continuous phase. Surfactants, used to stabilise the drop formed by the membrane, are complex molecules that may also act as wetting agents for the membrane and, therefore, change the surface properties of that membrane in a way that could be unwanted for the purpose of membrane emulsification. Due to their amphiphilicity, surfactants will diffuse and adsorb to interfaces where they orientate hydrophilic groups towards hydrophilic sites, while hydrophobic groups will be attracted towards hydrophobic sites. Surfactant molecules with multiple hydrophilic and hydrophobic sites can rearrange their molecule structure, influenced by concentration [15,16]. So, these molecules can adsorb to liquid-gas, liquid-liquid interfaces and liquid-solid interfaces. Therefore, a good knowledge of the interaction of the dissolved components that may help the disperse phase wet the membrane, and a careful control to prevent this is important. In a practical sense this may lead to a situation where the surfactant concentration should be kept low, to minimise adsorption onto the membrane, but the concentration should be sufficient to be able to stabilise the emerging drops at the desired size. Under these conditions drops emerging from the membrane may not necessarily experience the equilibrium interfacial tension of the dispersed phase-continuous phase (with surfactant) mixture, as the rate of drop growth can be greater than the rate of surfactant adsorption at the emerging interface. This has led to the term dynamic interfacial tension. Van der Graaf et al. [17] studied in detail the influence of dynamic interfacial tension during drop formation in membrane emulsification for o/w emulsions. It was observed that higher throughputs of the disperse phase through the membrane, or higher surfactant concentrations, led to smaller drop formation times.

From the Young equation, it follows that the wall contact angle is a function of the properties of the solid (metal membrane) and the two immiscible liquids:

$$\cos\ \theta = \frac{\gamma_{CS} - \gamma_{DS}}{\gamma_{CD}}, \tag{1}$$

where $\gamma_{DS}$ and $\gamma_{CS}$ are the interfacial tensions of the boundary solid/disperse phase and the boundary solid/continuous phase respectively; $\gamma_{CD}$ is the interfacial tension between the two immiscible liquids. A lower interfacial tension between the two fluids will, therefore, lead to a smaller wall contact angle.

Throughput of the disperse phase in membrane emulsification is key to the implementation of this process at commercial scale. The throughput is primarily dependent on the transmembrane pressure, pore size, membrane porosity and the viscosity of the fluids. The amount of active pores is also important to achieve high throughputs, as well as for design and modelling purposes. However, this is a parameter difficult to determine. There is evidence that activation of pores occurs randomly, some pores might become active while others may stop [18,19]. In the study reported here, it is shown that the percentage of active pores can be estimated indirectly based on the dynamic interfacial tension. A larger flow rate of dispersed phase will lead to a faster expansion rate of drop formation which will increase the dynamic interfacial tension for a given surfactant concentration. However, a larger concentration of the surfactant should reduce the dynamic interfacial tension for a given drop formation rate.

In this work, the surfactant selected to stabilize the emulsion was sorbitan monooleate (Span® 80) which is a low molecular weight surfactant, soluble in the oil phase. It was dissolved in the continuous phase and was responsible for stabilizing the aqueous polymer drops formed at the membrane surface and avoiding coalescence. The polymer dissolved in the aqueous phase was poly(vinyl alcohol). This is a surface-active polymer commonly used as the stabilizer in oil in water (o/w) emulsions [20–22]. Thus, using this formulation, there will be two surface agents adsorbing to the surface resulting in a rapid decrease of the interfacial tension while drops are being formed. Using this approach, PVA drops will be obtained and, if desired, they can be polymerised, forming solid particles. Production of uniform PVA particles can be very interesting when used in certain medical applications [13].

### 1.1. Disperse phase drop size modelling

There are several published models for the prediction of the drop size formed during membrane emulsification as a function of detachment force (shear stress), interfacial tension and pore size of the membrane. Previous work with the type of membrane used in this study was based on the following [8,13,23,24]:

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