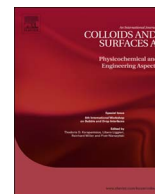




Contents lists available at ScienceDirect

Colloids and Surfaces A

journal homepage: www.elsevier.com/locate/colsurfa

Membrane emulsification: Formation of water in oil emulsions using a hydrophilic membrane

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ARTICLE INFO

Keywords:

Membrane surface
Hydrophilic
Water in oil emulsion
Polyvinyl alcohol (PVA)
Droplets and contact angle

ABSTRACT

It is shown that formation of water based droplets in an immiscible (i.e. oil) continuous phase can be achieved using a hydrophilic porous metal membrane without prior hydrophobic treatment of the membrane surface. This avoids the need for “health and safety approval” of typical hydrophobic treatments for the membrane, which often use chemicals incompatible with pharma or food applications. To investigate this, wetting experiments were carried out: sessile droplets were used to determine static contact angles and a rotating drum system was used to determine contact angles under dynamic conditions. In the latter case the three-phase contact line was observed between the rotating drum, water and the continuous phase used in the emulsification process; a surfactant was present in the continuous phase which, in this process, has a double function: to assist the wetting of the membrane by the continuous phase, and not the disperse phase, and to stabilize the droplets formed at the surface of the porous membrane during membrane emulsification.

1. Introduction

Currently several industries rely on conventional emulsification processes using high shear rotor-stator devices and high-pressure valve homogenizers, which are not suitable when dealing with shear sensitive substances and when a controlled droplet size is required. Therefore, other emulsification techniques are often explored. Regarding low shear handling and uniform droplet size there are two systems that stand out: microfluidic devices and membrane emulsification. They both offer control over the droplet formation and operate under mild shear stress conditions. In both cases formulation and process parameters are key factors i.e., combination of parameters such as (dynamic) interfacial tension, type of surfactant, wetting characteristics of material used and viscosity of both liquids can be very important. Therefore, an erroneous choice of these parameters might make the difference between highly uniform, or very polydisperse, drop size. Comparing the two techniques they can be characterised as (i) the higher uniformity drops that microfluidics can produce and (ii) higher throughputs that membrane emulsification can achieve. Therefore, if the process to be optimised requires high throughputs then membrane emulsification is the best choice. Previously in [1] a novel membrane emulsification device was presented which operates continuously. In [1] a throughput of 1 L h^{-1} was tested using a $5 \mu\text{m}$ pore size membrane with an interpore distance of $200 \mu\text{m}$. Droplets generated at some conditions were below $50 \mu\text{m}$ which suggests decreasing the

interpore distance by at least three times will still avoid the contact of drops during their growth and detachment. In addition, certain applications could require the use of a bigger pore size, which combined with smaller interpore distance, gives the possibility to increase substantially the porosity of the membrane allowing much higher throughput. Thus, membrane emulsification is a technique to consider for industrial process development especially when “made to measure” drop size, low shear application and reasonable throughputs are required. However, other challenges might need to be overcome to implement this technique at an industrial scale, such as chemical compatibility and use of safe approved materials. Over the years users of membrane emulsification tend to use a hydrophilic porous membrane for production of oil in water (o/w) emulsions, or a hydrophobic porous membrane for production of water in oil (w/o) emulsions [2]. The most common materials used to manufacture these porous membranes have a hydrophilic nature such as metals (stainless steel [1,3,4] and nickel [5–8]), Shirasu porous glass [9,10] or ceramic (e.g. alumina oxide [11–13]). Therefore, hydrophobic treatment of these hydrophilic membranes, or coating of their surfaces, is used when the aim is production of a w/o emulsion. Frequently, these treatments/coatings applied have problems with longevity and stability which are crucial at an industrial scale. The materials used for surface modification are subject to regulatory approval when the production of formulations for food or medical grade products are required, and this possibly becomes an obstacle to adoption of membrane emulsification. In this paper, the

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<http://dx.doi.org/10.1016/j.colsurfa.2017.04.077>

Received 26 February 2017; Received in revised form 28 April 2017; Accepted 29 April 2017
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use of (clean) metal hydrophilic porous membranes without any extra surface modification in order to produce uniform w/o emulsions, contrary to the usually adopted procedure is explored. A solution of 13.5% wt polyvinyl alcohol (PVA) as disperse phase and kerosene as the continuous phase with the presence of surfactant: Span[®] 80 was used as a model system. This system was chosen because it is appropriate as an example of a possible formulation used at industrial scale for productions of uniform PVA beads, or encapsulation, via the entrapment method, of a desired ingredient.

Earlier studies [1,5,14] have showed a good agreement between equation 1 and drop size obtained for low injection rates using membrane emulsification. That modelling is the result of a force balance between drag force and capillary force assuming complete wetting of the continuous phase ($\theta = 0^\circ$) of the pores by the continuous phase.

$$x = \frac{\sqrt{18\tau^2 r_p^2 + 2\sqrt{81r_p^4 \tau^4 + 4\gamma^2 r_p^2 \tau^2}}}{3\tau}, \quad (1)$$

where r_p is the pore radius, τ is the shear stress applied, γ is the interfacial tension and x is the droplet diameter. It can be expected that the contact angle will play a considerable role in the droplet formation mechanism and consequently on the resultant droplet size (Fig. 1). Therefore, in the case of partial wetting of the continuous phase ($0^\circ > \theta > 90^\circ$) resultant equation is as follows:

$$x = \frac{\sqrt{18\tau^2 r_p^2 + 2\sqrt{81r_p^4 \tau^4 + 4\gamma^2 r_p^2 \tau^2 \cos^2(\theta)}}}{3\tau}, \quad (2)$$

Nonetheless, the force balance model (Eq. (1) and (2)) doesn't take into account the influence of the flux of the injecting material through the membrane. Earlier many investigations empirically found that higher flux leads to bigger droplet sizes in the dripping regime [1,4,5,15,16]. Transition from dripping to jetting regime occurs above a certain critical capillary number, which is independent of the contact angle [2], but still depends on the formulation used. Experimental observation of the influence of contact angle of drops in a membrane emulsification device is not very straightforward and therefore different approaches were adopted below.

"Wetting and interface interaction" knowledge was acquired for the system, which includes two liquid phases and a solid phase prior to emulsification experiments. Liquid-surface interactions often have been underestimated and considered insufficiently compared with other physical parameter of membranes, such as, pore size distribution and pore distance. The latter parameters become irrelevant when the surface chemistry is not adequately adjusted [17]. The importance of interactions between liquid-liquid and liquid-solid can be seen in other two phase systems processes such as emulsion separation using membranes [2].

Wetting properties of a system: two immiscible liquids and a solid surface, is the *contact angle*. The sessile drop method is frequently used for measuring static contact angles between three different phases, i.e. solid, liquid and vapour, but the principle is equally applicable to the interface of two liquids and a solid. Drops deposited on the surface were

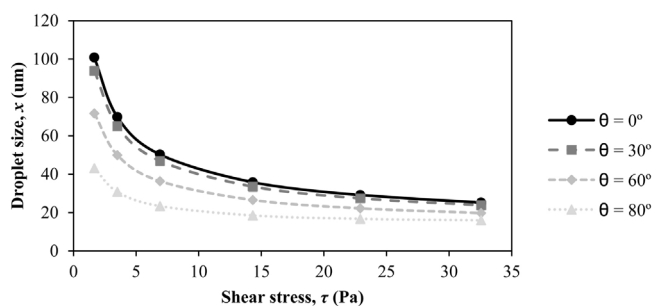


Fig. 1. Influence of the contact angle on the final drop size.

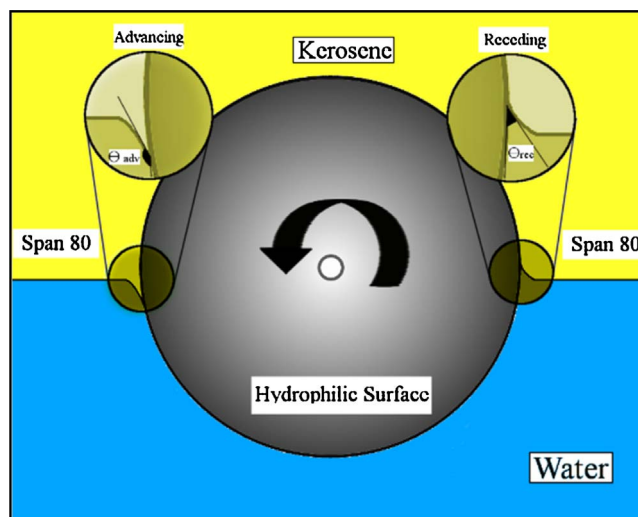


Fig. 2. Schematic diagram of a side view of a drum half immersed in aqueous phase and half immersed in an organic phase sometimes with surfactant (Span[®] 80).

surrounded by an immiscible liquid with, or without, the presence of surfactant [18,19]. The presence of amphiphilic molecules in a solution affects the wettability of a surface in contact with the solution [20].

G. K. Auernhammer and his co-workers are currently using a rotating drum setup for studying velocity-dependent wetting/dewetting processes of complex (surfactant) solutions between a solid-gas-liquid interface [21–24]. Below a similar setup is adopted, however, the vapour phase is replaced by an organic phase to allow the investigation of wetting properties between two liquids and a solid phase. Two immiscible liquids were in contact with the surface (316 Stainless steel) of the drum which is the surface that was treated similarly to the porous membranes used in membrane emulsification experiments. In Fig. 2, a schematic diagram of the side view of the drum is presented. Fig. 2 shows that this homemade setup provides observation of both sides of the drum (advancing and receding contact angles) when half immersed in two immiscible liquids. The influence of surfactant in the organic phase was characterised for different rotation speeds and different surfactant concentrations.

Several authors observed that contact angle depends on both surface properties and on the surfactant used [19,25,26]. Different concentrations of the same surfactant influence on the contact angle, using an identical surface to membrane emulsification tests, was investigated.

2. Material and methods

In the emulsification experiments, a solution of 13.5% (w/w) Poly (vinyl alcohol (PVA, M_w 13,000–23,000 87–89% hydrolysed Sigma Aldrich, UK) was used as the disperse phase, while the continuous phase was kerosene (reagent grade, low odour, Sigma Aldrich, UK) containing an (oil soluble) surfactant – Span 80[®] (Sigma Aldrich, UK), which was used at various concentrations between 5 and 100 mM. The membrane emulsification device used was a Dispersion Cell (see Fig. 3) supplied by Micropore Technologies Ltd. This device uses a 24 V DC motor to drive a paddle stirrer, which provides shear at the membrane surface (Fig. 3a and b). A paddle stirring speed of 800 RPM (8 V) was used for all the experiments providing a maximum shear at the membrane surface of 5.8 Pa. The method used to determine the maximum shear is described in [5] using a density value of 780 kg/m³ and a viscosity of 1.64×10^{-3} Pa s). A syringe pump (World Precision Instruments, Florida, USA) was used to provide pulseless flow. Two different injection rates were tested: 0.2 and 0.5 mL/min. The continuous phase volume was 100 mL, and 5 mL of disperse phase was injected through the membrane for each experiment. A flat disc membrane containing uniform cylindrical pores of 10 μm pore size and

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