Preparation of Water-in-Oil Emulsions Using Microporous Polypropylene Hollow Fibres: Conditions for Producing Small Uniform Droplets*

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The preparation of water-in-oil emulsions was investigated in a Microdyn membrane module consisting of 40 hydrophobic polypropylene hollow fibres with a mean pore size of 0.4 μm. The experiments have been carried out using demineralized water as the disperse phase, mineral oil Velocite No. 3 as the continuous phase, and polyglycerol polyricinoleate as the emulsifier. The mean droplet diameter increased with increasing transmembrane pressure and with decreasing the emulsifier contentration. At the emulsifier content of 10 mass % and transmembrane pressure of 28 kPa the mean droplet diameter was only 0.27 μm, which is 33 % lower than the membrane pore size. One of the possible explanations is that water cannot completely displace oil from the interior of the pores due to high viscosity of oil compared with water. Therefore, some amount of oil phase was retained inside the pores reducing the effective pore diameter.

Emulsification is usually performed using high-pressure homogenizers and rotor/stator systems, such as stirring vessels, colloid mills or toothed disc dispersing machines [1]. In the dispersing zone of these machines high shear stresses are applied to deform and disrupt large droplets of a premix. Therefore, high energy inputs are required and shear-sensitive ingredients, such as proteins and starch, may lose functional properties resulting in poor system stability.

Membrane emulsification is a relatively new technique introduced by *Nakashima* and *Shimizu* [2] in the late 1980s. In this process, the disperse phase is pressed through the pores into the continuous phase where small droplets are directly formed. The application of a microporous membrane for the dispersion of phases holds several advantages over conventional emulsification devices: *1.* Membrane emulsification method enables to obtain very fine emulsions of controlled droplet sizes and narrow droplet size distributions. *2.* Successful emulsification can be carried out with much less consumption of emulsifier and energy than in conventional methods. *3.* Because of the low shear stress acting on a membrane surface, membrane emulsification allows the use of shear-sensitive ingredients, such as starch and proteins.

According to the DLVO theory [3], the monodispersity of emulsion droplets is necessary for forming a stable dispersion against aggregation. The production of monodispersed emulsions is especially important in the preparation of uniform metal oxide particles by the hydrolysis of alkoxide [4], in the preparation of a liquid crystal/polymer composite film which is the key material of any liquid crystal display device [5], in the hydrolysis of olive oil by lipase [6], in the preparation of liposomes [7] and other pharmaceutical products, in the synthesis of uniform polymeric microspheres by suspension polymerization [8, 9], *etc.* These uniform microspheres can be used as carriers for enzymes, cells or catalysts, packings for analytical or preparative columns [10], *etc.*

The microporous membrane used for emulsification must have a narrow pore size distribution with a mean pore diameter between 0.1 μm and 10 μm and the membrane surface must not be wetted with the disperse phase. Therefore, an O/W emulsion is produced using a hydrophilic membrane and a W/O emulsion

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is produced using either a hydrophobic membrane or a hydrophilic membrane previously treated with the oil phase to render it hydrophobic. In comparison to preparation of W/O emulsions using a hydrophobic membrane, the disperse phase flux can be increased from several tens to 100 times through the use of a hydrophilic membrane pretreated with the oil phase [11].

The Shirasu porous glass (SPG) membrane developed by *Nakashima* and *Shimizu* [12] is the most suitable membrane presently available for a membrane emulsification system. The pore size of SPG can be varied over a wide range and the wettability of membrane surface can be changed by surface modification with organic silanes. Also, the compressive strength and thermal resistance of SPG is very high. In addition to SPG, monodispersed O/W emulsions were successfully prepared using microporous ceramic membranes [13—15] and microporous polysulfone hollow fibres [16].

There is a very small number of papers dealing with the preparation of W/O emulsions by a membrane emulsification method. It can be explained by the fact that the preparation of W/O emulsions is difficult in comparison to O/W emulsions. It is because the water droplets are hard to stabilize by an electrical double-layer repulsion force in an oil phase with low dielectric constant [17]. All previous investigations dealing with the preparation of W/O emulsions by a membrane emulsification method were based on the use of porous glass membranes [17—19]. According to the authors knowledge, this study is the first attempt to obtain monodispersed W/O emulsions using polypropylene hollow fibres. Until now, these fibres have been used for microfiltration [20], membrane distillation [21], liquid pertraction [22], bubbleless gas absorption [23], and other nondispersive membrane-based phase contact processes.

EXPERIMENTAL

W/O emulsions containing demineralized water as the disperse phase and mineral oil Velocite No. 3 (Carl Herzog oG, Germany) as the continuous phase were stabilized using polyglycerol polyricinoleate (PGPR 90, Danisco, Denmark) as the oil-soluble emulsifier. The emulsions were prepared in a Microdyn membrane module (Wuppertal, Germany), type MD 020 CP 4N. It consists of 40 microporous hollow fibres made of polypropylene with an inner diameter of 1.7 mm and a mean pore size of 0.4 μm. The effective length of a fibre bundle is 468 mm and the effective membrane area is 0.1 m^2. The hollow fibres were potted at both ends with polyurethane resin inside a cylindrical polypropylene shell with an outer diameter of 25 mm and a length of 500 mm.

The experimental set-up used in this work is shown in Fig. 1. After each cleaning cycle all lines were filled with water. In order to remove residual water from the fibres, lines, and a gear pump, the oil phase was first

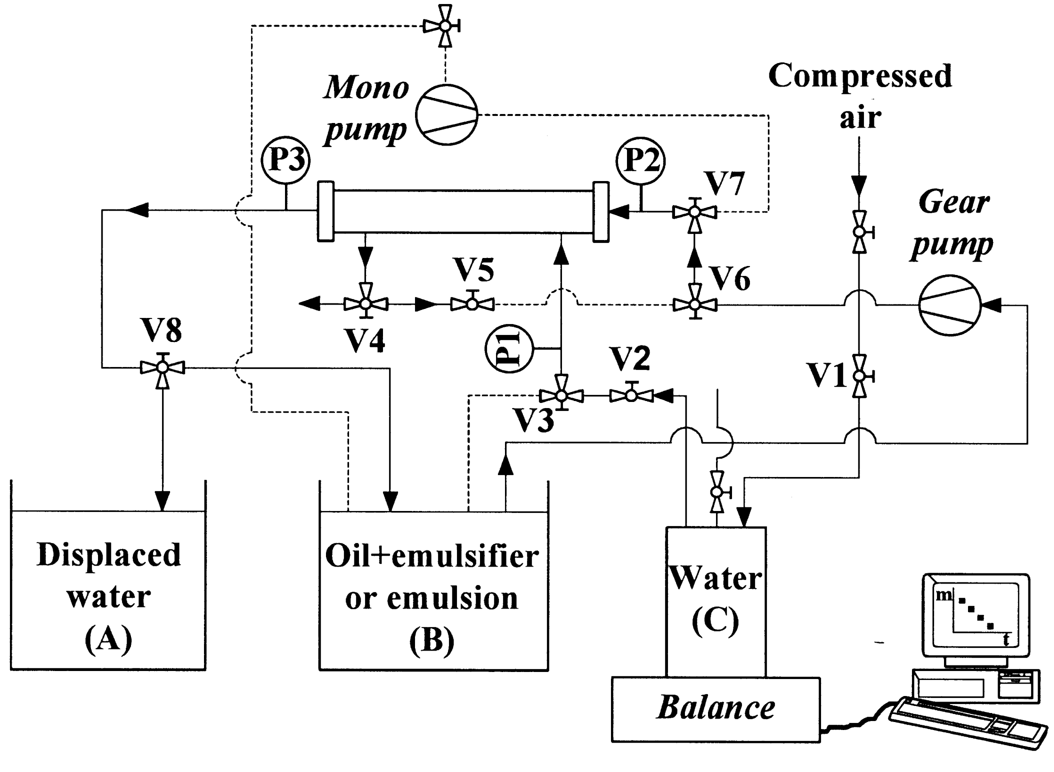

Fig. 1. Schematic view of the experimental set-up used in this work.

pumped from the reservoir B through the inside of a module to the reservoir A. When water was completely displaced with the oil phase, the setting of a three-way valve (V8) was changed to allow the oil phase to recycle between the module and the reservoir B. The flow-rate of the oil phase was maintained constant at about 130 $\mathrm{dm}^3\ \mathrm{h}^{-1}$ with a gear pump (Multifix, model MEL 3000). On the other hand, in a pressure vessel (C) with a volume of 850 cm^3, the disperse phase (water) was pressurized to a specified pressure with a compressed air and introduced to the outside of the fibres. At the beginning of each experiment, the air bubbles were released from the shell side of the module through a three-way valve (V4). The system was operated until a disperse phase content of 25 vol. % was reached in the emulsion. The disperse phase pressure was adjusted by valve V1 and monitored by a gauge (P1) located at the entrance of the module. The tube-side pressures at the module inlet and outlet were measured by means of pressure transducers P2 and P3 and used to calculate the transmembrane pressure Δp_{tm} according to the following equation

$$\Delta p_{\mathrm{tm}} = p_{\mathrm{g,d}} + 100 - (p_{\mathrm{c,in}} + p_{\mathrm{c,out}})/2 \qquad (1)$$

where $p_{\mathrm{g,d}}$ is the disperse phase gauge pressure outside the hollow fibres, and $p_{\mathrm{c,in}}$ and $p_{\mathrm{c,out}}$ are the continuous phase absolute pressures at the module inlet and outlet, respectively (all in kPa).

The mass of water passing through the pores into the continuous phase was measured continuously by a digital balance on which the pressure vessel rested. The balance was connected to a PC computer for data acquisition. The disperse phase flux was calculated as

$$J_{\mathrm{d}} = \dot{m}_{\mathrm{d}}/(\rho_{\mathrm{d}} A) \qquad (2)$$

where A is the effective membrane area, ρ_{d} is the disperse phase density, and $\dot{m}_{\mathrm{d}}$ is the mass flow-rate of the disperse phase determined from the slopes of the *m vs. t* plots (Fig. 3) using the least-squares regression analysis method.

The mean droplet size and the droplet size distribution were measured using a laser light scattering system (Malvern Mastersizer X, Malvern Instruments, Germany), allowing the detection of droplets with a minimum diameter of 0.1 μm. The mean droplet diameter was expressed as the mean Sauter diameter, $d_{3,2}$, which is the diameter of a spherical droplet which has the same area per unit volume, S, as that of the total collection of droplets in the emulsion

$$d_{3,2} = \frac{6}{S} = \left(\sum_{1}^{k_{\mathrm{s}}} \frac{v_i}{d_i}\right)^{-1} \qquad (3)$$

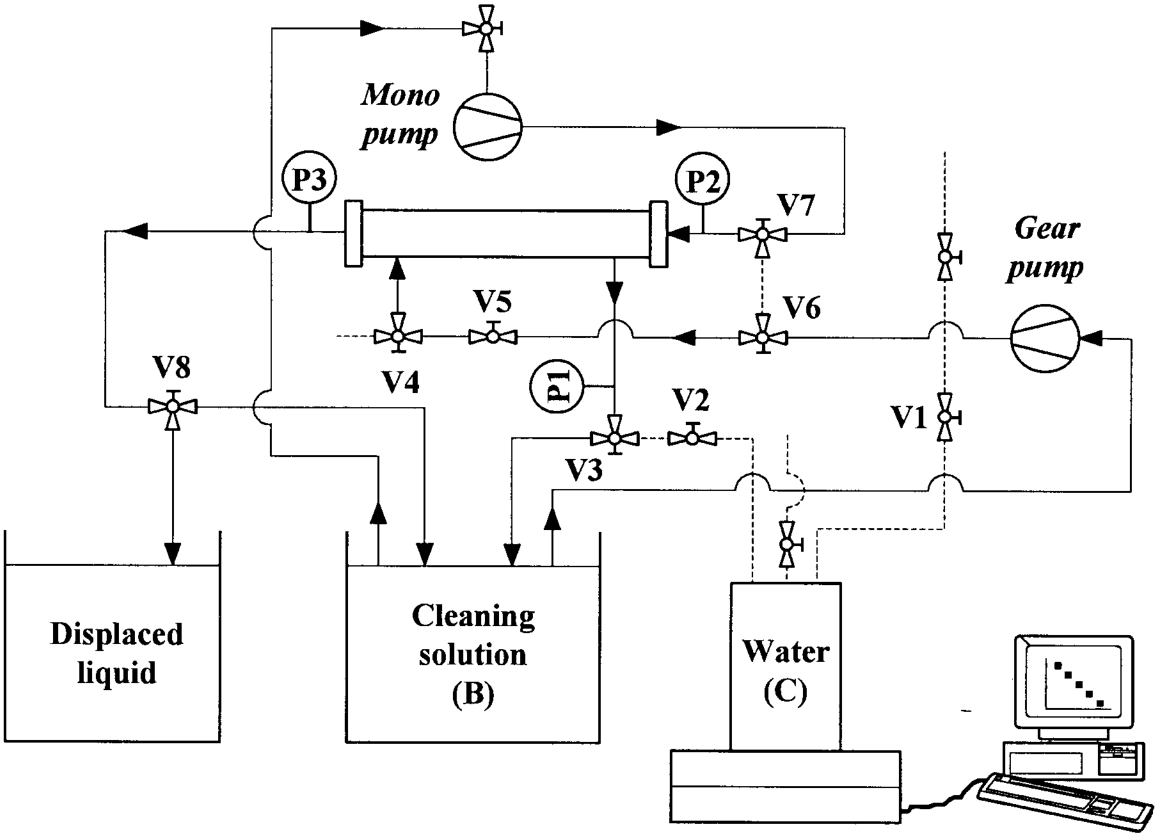

Fig. 2. Cleaning cycle of the membrane emulsification system.

where v_i is the volume fraction of droplets in the i-th range of sizes, the mean diameter of which is d_i, and k_s is the number of size ranges.

After each experiment the system was cleaned (Fig. 2). The emulsion was first removed with a large amount of water flowing in an open cycle. Water was then replaced with 4 dm^3 of 1 mass % aqueous solution of alkaline cleaning agent P3-ultrasil 11 (Henkel, Düsseldorf, Germany) flowing in an open cycle. After that, the system was cleaned with additional 4 dm^3 of 1 mass % P3-ultrasil 11 solution flowing in a closed cycle between the module and the reservoir B at 50 °C. The cleaning solution was simultaneously recycled outside the fibres using a gear pump and inside the fibres using a Netzsch mono-pump (Waldkraiburg, Germany), type NL 20. After about 60 min, the alkaline cleaning agent was removed from the system with 4 dm^3 of 1 mass % aqueous solution of neutral cleaning agent P3-ultrasil 53 (Henkel). The system was then cleaned with additional 4 dm^3 of 1 mass % P3-ultrasil 53 solution flowing in a closed cycle at 50 °C for 60 min. Finally, the system was thoroughly rinsed out with demineralized water until the pure water flux at the given transmembrane pressure was restored to the initial value.

RESULTS AND DISCUSSION

In Fig. 3 the mass removal of demineralized water from the pressure vessel is plotted against time for two typical experiments. The similar dependences were also obtained for other operating conditions, but for the picture simplicity they are omitted in Fig. 3. The disperse phase flux decreased with time but after some period of time a steady state was established. The disperse phase flux during the first minute of operation was 1.4 dm^3 m^{-2} h^{-1} and 3.3 dm^3 m^{-2} h^{-1} at 28 kPa and 78 kPa, respectively, which is more than 10 times higher than the fluxes in the stationary state. The flux decline was more rapid at lower transmembrane pressures. As an example, after 10 min of operation, the water fluxes were 19 % and 40 % of their initial values at 28 kPa and 78 kPa, respectively. The reduction in water flux with time is an indication that the fraction of pores permeable for water diminished with time due to oil blockage.

As shown in Fig. 4, the steady-state disperse phase flux increased linearly with increasing the transmembrane pressure Δp_{tm}, which is in accordance with Darcy's law. At Δp_{tm} = 28—76 kPa and the emulsifier content of 10 mass %, the disperse phase flux ranged from 0.05 to 0.2 dm^3 m^{-2} h^{-1}. For the experiments in which pure water was fed at both sides of the membrane, the water flux was in the range of 480—1200 dm^3 m^{-2} h^{-1} at the same transmembrane pressures. It is 4 orders of magnitude higher than the disperse phase flux. Assuming that the flux reduction is due to complete blocking of some of the pores, while the rest remain unaffected by the oil, it follows that only 0.01 % of the pores took part in permeation of disperse phase through the membrane.

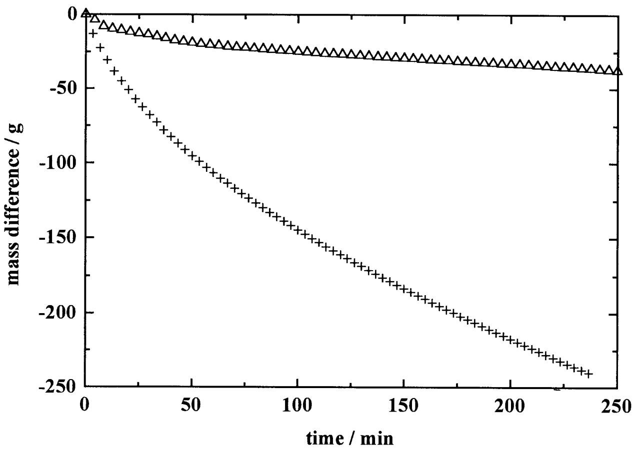

Fig. 3. Mass removal of disperse phase (water) from the pressure vessel, measured as a difference of the immediate and initial masses of disperse phase, as a function of time: + 78 kPa, 2.5 % PGPR; △ 28 kPa, 10 % PGPR.

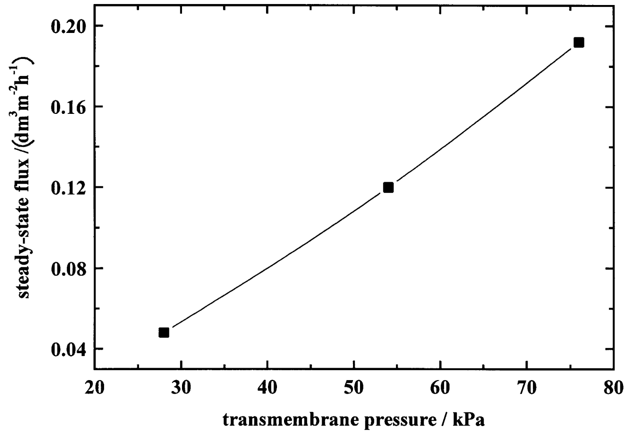

Fig. 4. Steady-state disperse phase flux as a function of transmembrane pressure. PGPR content of 10 mass %.

The effect of disperse phase content on the mean droplet size is shown in Fig. 5. The mean droplet size decreases rapidly with increasing time as the disperse phase content increases up to 10 vol. %, when the mean droplet size reaches an almost constant value. At PGPR content of 2.5 mass % and 28 kPa, the disperse phase flux reached its steady value after about 150 min of operation and, during this period, 180 cm^3 of water were emulsified (Fig. 3). The initial volume of continuous phase in the system was about 2.3 dm^3. It means that disperse phase content reached 7.3 vol. % when flux reached a steady value. Therefore, droplet size reached a constant value for the time in which the flux reached steady state.

The highest droplet diameter for disperse phase

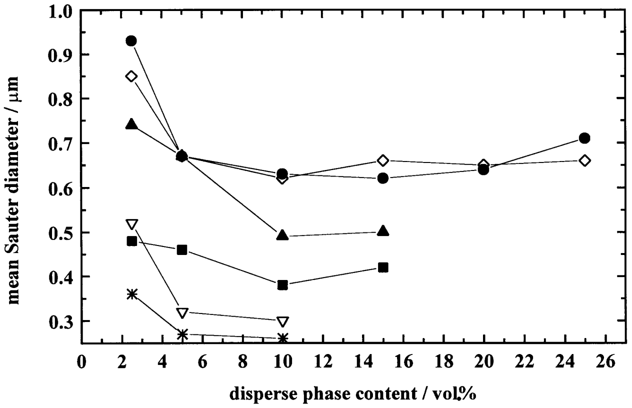

Fig. 5. Mean droplet diameter as a function of disperse phase content: ◇ 2.5 % PGPR, 77 kPa; ● 5 % PGPR, 77 kPa; ▲ 7.5 % PGPR, 77 kPa; ■ 10 % PGPR, 77 kPa; ▽ 10 % PGPR, 54 kPa; ∗ 10 % PGPR, 28 kPa.

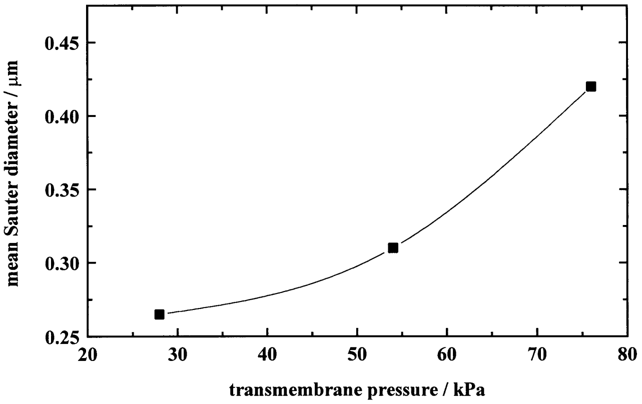

Fig. 6. Mean droplet diameter as a function of transmembrane pressure. PGPR content of 10 mass %.

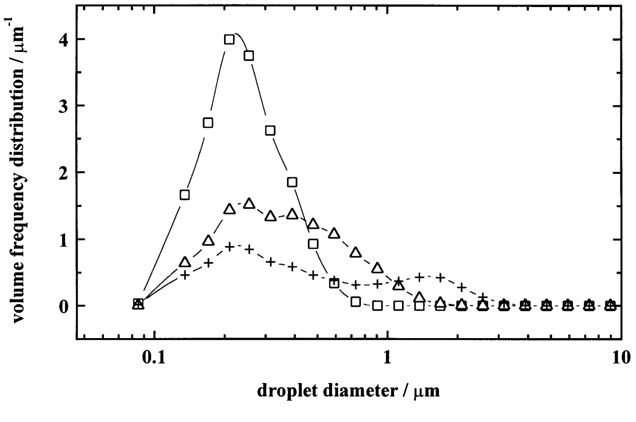

Fig. 7. Droplet size distribution curves for the prepared emulsions: ☐ 28 kPa, 10 % PGPR; △ 77 kPa, 10 % PGPR; + 78 kPa, 2.5 % PGPR.

content of 2.5 vol. % can be attributed to a relatively high disperse phase flux at the beginning of each experiment. Larger droplets are formed at higher fluxes because the emulsifier is not able to stabilize the new interfaces fast enough.

Obviously, the mean droplet size increases with increasing transmembrane pressure and with decreasing the emulsifier concentration. That phenomenon is also observed in the preparation of O/W emulsions [12, 19]. Using emulsifier content of 10 mass % and transmembrane pressure of 28 kPa, one obtains the mean droplet diameter of 0.27 μm (Fig. 6). It is 33 % lower than the mean pore size. One of the possible explanations is that pores were filled with oil at the beginning of each experiment, because water was pressurized for 30—60 min after the introduction of the oil phase. However, water cannot completely displace oil from the interior of the pores due to high oil viscosity. Therefore, some amount of oil phase was retained inside the pores in the form of a film reducing the effective pore diameter [24]. The correlation between the water droplet size and filter pore size was also reported by *Kandori et al.* [18, 25]. They prepared a monodispersed W/O emulsion with a mean droplet size of 0.67 μm by using 2 mass % poly(oxyethylene-oxypropylene) type surfactant (PE-64) and a hydrophilic SPG filter with a mean pore size of 0.98 μm. This result is opposite to that obtained for O/W emulsions in which the mean diameter of the oil droplets is several times larger than the mean pore size [11, 13].

The typical droplet size distribution curves for the prepared emulsions are shown in Fig. 7. The most frequently occurring droplet size lies in the range between 0.21 μm and 0.26 μm, and is independent of the operating conditions. As can be seen from Fig. 7, W/O emulsion with very narrow droplet size distribution was obtained at 28 kPa using 10 mass % PGPR. This emulsion contained more than 98 vol. % of water droplets smaller than 0.65 μm. However, at higher transmembrane pressures the emulsions with broader droplet size distributions were obtained. For example, the emulsion prepared at a transmembrane pressure of 77 kPa contained 77 vol. % of water droplets smaller than 0.65 μm. On the other hand, the emulsion prepared at the same transmembrane pressure and stabilized using 2.5 mass % PGPR contained only 35 vol. % of water droplets smaller than 0.65 μm.

CONCLUSION

The water-in-oil (W/O) emulsions with a narrow droplet size distribution and a water content between 2.5 vol. % and 25 vol. % were successfully prepared using microporous polypropylene hollow fibres with 0.4 μm pore size. Both the disperse phase flux and the mean droplet size increased with increasing the transmembrane pressure. In addition to that, the mean droplet size decreased with increasing the emulsifier concentration. The disperse phase flux decreased with time until a steady state was established. The steady-state disperse phase flux was 4 orders of magnitude lower than the pure water flux indicating that a great majority of pores were partially or completely blocked by the oil phase during the water permeation through the membrane.

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