

## PREPARATION OF WATER-IN-OIL EMULSIONS USING HYDROPHOBIC MICROPOROUS HOLLOW FIBERS

**G. Vladisavljević, Sabine Brösel and H. Schubert\***

**Abstract:** The preparation of fine and monodispersed water-in-oil (w/o) emulsions by utilizing hydrophobic polypropylene hollow fibers with 0.4  $\mu\text{m}$  pores was investigated in this work. The experiments have been carried out using demineralized water as the disperse phase, mineral oil Velocite 3 as the continuous phase, and polyglycerol polyricinoleate (PGPR 90) in the concentration range of 2.5-10 wt% as the oil-soluble emulsifier. The size of water droplets in the resulting emulsions and the droplet size distribution strongly depended on the disperse phase content, the transmembrane pressure difference and the emulsifier concentration. The stable emulsions with a very narrow droplet size distribution and the mean droplet size lower than 0.27  $\mu\text{m}$  were produced using 10 wt% PGPR 90 at the pressure difference below 30 kPa.

**Key words:** emulsification, membrane emulsification, water-in-oil emulsions, hollow fibers.

### Introduction

Emulsions are disperse multiphase systems containing at least two immiscible liquid phases, e.g., water and oil. Depending on which is the disperse and which the continuous phase there are two types of emulsions: oil-in-water (o/w) and water-in-oil (w/o). Systems containing an emulsion as the disperse phase are

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called double emulsions (w/o/w or o/w/o). The typical food o/w emulsions are milk and mayonnaise, while w/o emulsions are butter and margarine. The low calorie mayonnaise is an example of w/o/w emulsion in which a w/o emulsion is dispersed as droplets in the outer water phase (Bams et al., 1987; Takahashi et al., 1986). For macroemulsions the droplet size of the disperse phase is between 0.1 and 50  $\mu\text{m}$  (Schröder et al., 1998). These emulsions are thermodynamically unstable and have to be stabilized by emulsifiers and/or stabilizers. Emulsifier molecules lower the interfacial tension between the two phases and stabilize droplets by inducing electrostatic and/or steric repulsion between the droplets. Stabilizers are macromolecules soluble in the continuous phase which prevent droplet coalescence primarily by increasing the viscosity of the continuous phase.

Emulsification is usually performed using high-pressure homogenizers and rotor/stator systems, such as stirring vessel, colloid mill, and toothed disc dispersing machine (Karbstein and Schubert, 1995). In the dispersing zone of these machines high shear stresses are applied to deform and disrupt large droplets of a premix. Therefore, shear-sensitive ingredients such as proteins or starch may lose their functional properties resulting in a system instability. In a membrane emulsification process the stress induced is much lower, because small droplets are directly formed at the micropores of a membrane without any premix formation. Besides the possibility of using shear-sensitive ingredients, very fine emulsions with a narrow droplet size distribution can be produced. The production of monodispersed emulsions is especially important in the preparation of uniform metal oxide particles by the hydrolysis of alkoxide (Kandori et al., 1992), in hydrolysis of olive oil by lipase (Shiomori et al., 1995), and in the synthesis of uniform polymeric microspheres by suspension polymerization (Omi, 1996). These uniform microspheres can be used as carriers for immobilized enzymes or cells and as packings in gel permeation chromatograph (GPC) columns (Hatate et al., 1995).

The microporous membrane used for emulsification must have a narrow pore size distribution and the membrane surface should not be wetted with the disperse phase. It means that a w/o emulsion should be prepared using a hydrophobic membrane and an o/w emulsion must be prepared using a hydrophilic membrane. The Shirasu porous glass (SPG) membrane developed by Nakashima and Shimizu (1986) is the most suitable microporous membrane presently available for a membrane emulsification process. In addition, monodispersed o/w emulsions were successfully prepared using microporous ceramic membranes (Schröder et al., 1998; Schröder and Schubert, 1999) and polysulfone hollow fibers (Schröder, 1998).

The preparation of monodispersed w/o emulsions using microporous polypropylene hollow fibers have been investigated in this paper for the first time in the literature. These fibers have been extensively used for membrane distillation (Laganà et al., 1999), membrane-based gas absorption and stripping, membrane-based solvent extraction, etc.

## Material and Methods

W/O emulsions containing demineralized water as a disperse phase and mineral oil Velocite no. 3 (Mobil Oil, Hamburg, Germany) as a continuous phase were stabilized using polyglycerol polyricinoleate (PGPR 90, Danisco, Denmark) as an 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 fibers made of polypropylene with an inner diameter of 1.7 mm and a mean pore size of 0.4  $\mu\text{m}$ . The effective fiber length is 468 mm and the effective membrane area is 0.1  $\text{m}^2$ . The fibers were potted with polyurethane resin inside a cylindrical polypropylene shell with an outer diameter of 25 mm and a length of 500 mm.

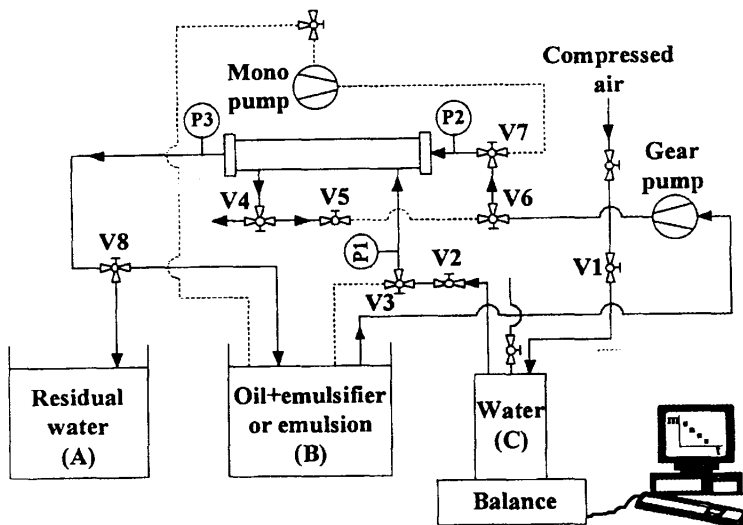


Fig. 1a - Schematic view of the experimental set-up used in this work

The experimental set-up used for membrane emulsification is shown in Figure 1a. The continuous phase or emulsion from the reservoir B was pumped inside the fibers using a Multifix model MEL 3000 gear pump and returned back to the reservoir B. The liquid flow rate inside the fibers was maintained constant at about 130  $\text{L}\cdot\text{h}^{-1}$  for all experiments. In order to remove water from the interior of the fibers, pump and tubings, the first 3-4 l of mineral oil was collected in the reservoir A. After that, the setting of a three-way valve V8 was changed allowing the continuous phase to recycle between the module and the reservoir B. The disperse phase (demineralized water) from a 850 ml volume pressure vessel C was introduced at the shell side of the module with compressed air. At the beginning of each experiment the air bubbles remaining outside the fibers were released in the atmosphere through the valve V4. The disperse phase pressure was adjusted

is in accordance with Darcy’s law. At  $\Delta p_{TM} = 28\text{-}76\text{ kPa}$  and emulsifier concentration of 10%, the steady-state flux of the disperse phase ranges from 0.8 to  $3.2\text{ mL}\cdot\text{m}^{-2}\cdot\text{min}^{-1}$ . It must be noted here that the pure water flux at the same

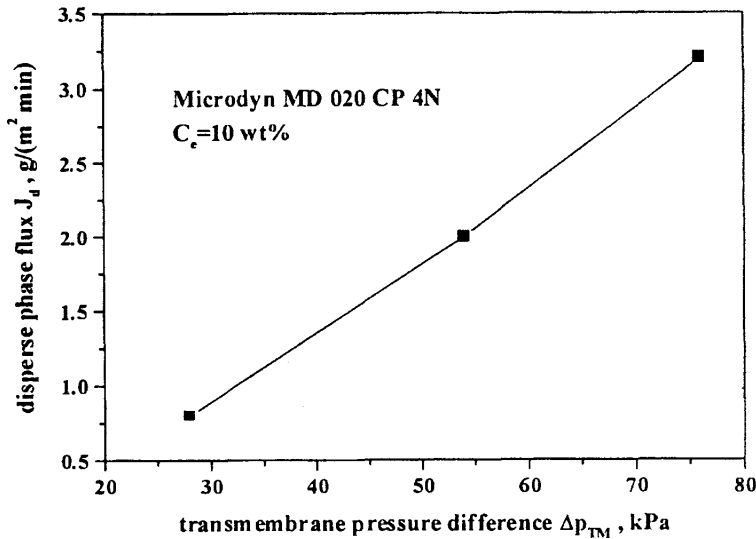


Fig. 3. - Disperse phase flux in the steady-state as a function of transmembrane pressure difference at emulsifier (PGPR 90) concentration of 10 wt%

$\Delta p_{TM}$  values was in the range of  $(8.3\text{-}20.1) \times 10^3\text{ mL}\cdot\text{m}^{-2}\cdot\text{min}^{-1}$ , which is 3-4 orders of magnitude higher than the disperse phase flux. Therefore, a very small percentage of the pores took part in the permeation of disperse phase through the membrane.

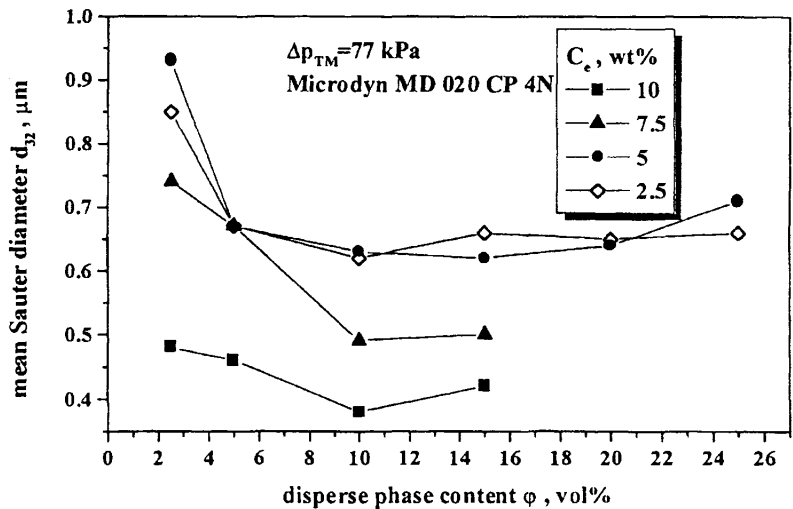


Fig. 4. - Mean droplet diameter as a function of emulsifier (PGPR 90) concentration and disperse phase content at transmembrane pressure difference of 77 kPa

The influence of disperse phase content on the mean droplet size is shown in Figs. 4 and 5. In most cases, the mean droplet size highly decreases with increasing the disperse phase content from 2.5 to 5 vol% and above a disperse phase content of about 10 vol% reaches an almost constant value which is independent on the

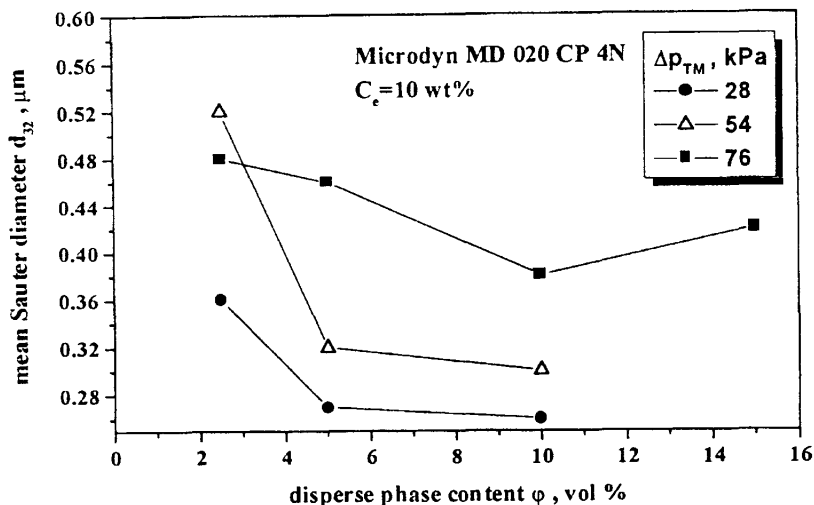


Fig. 5. - Mean droplet diameter as a function of transmembrane pressure difference and disperse phase content at emulsifier (PGPR 90) concentration of 10 wt%

disperse phase content. The highest mean droplet size at the lowest disperse phase content of 2.5 vol% can be attributed to the high disperse phase flux at the beginning of each experiment. The mean droplet size increases with increasing the transmembrane pressure difference and with decreasing the emulsifier concentration. It

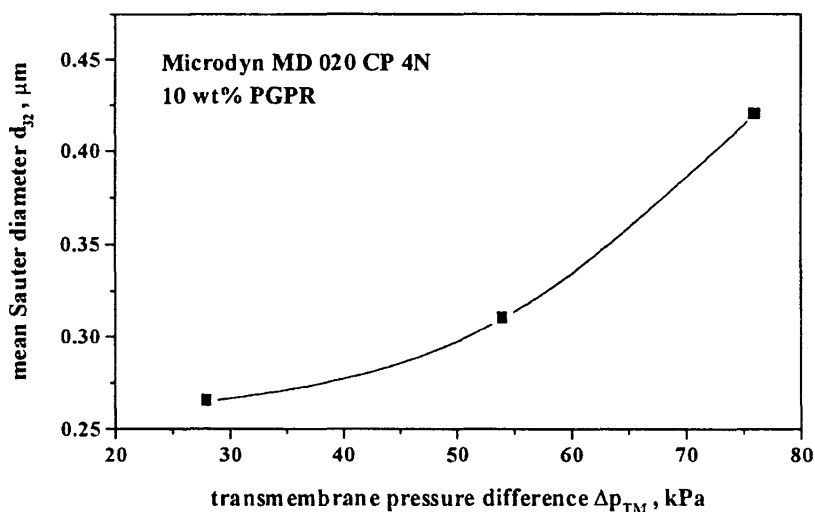


Fig. 6. - Mean droplet diameter as a function of transmembrane pressure difference at emulsifier (PGPR 90) concentration of 10 wt%

should be noted here that at the emulsifier concentration of 10 wt% and transmembrane pressure difference of 28 kPa the mean droplet size is only 0.265  $\mu\text{m}$  (Fig. 6), which is 34% lower than the mean pore size. This type of behavior was also reported by Kandori (1995) and Kandori et al. (1991) for the preparation of w/o emulsions by SPG filter emulsification method using various kinds of SPG filters of different pore diameters and copolymer-type surfactants. For example, Kandori (1995) prepared a monodispersed w/o emulsion with the mean droplet size of 0.67  $\mu\text{m}$  by using a hydrophilic SPG filter with a pore size of 0.98  $\mu\text{m}$  and 2 wt% PE-64 surfactant as an emulsifier. This result is opposite to that obtained for o/w emulsions in which the size of the oil droplets is several times larger than that of the pore diameter (Katoh et al., 1996; Schröder et al., 1998, etc).

Fig. 7 shows the droplet size frequency distribution curves for the emulsions prepared under different experimental conditions. The most frequently occurring droplet size lies in the range between 0.21 and 0.26  $\mu\text{m}$ . As can be seen from Fig. 7, a monodispersed emulsion with narrow droplet size distribution was obtained under the pressure difference of 28 kPa using 10 wt% PGPR in the continuous phase. This emulsion contained more than 98 vol% of droplets smaller

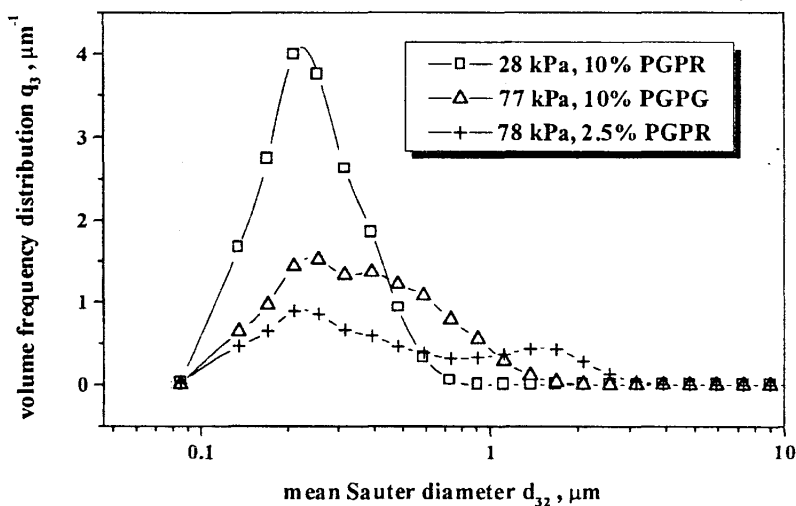


Fig. 7. - Droplet size distribution in the emulsions prepared under different experimental conditions

than 0.65  $\mu\text{m}$ . However, at higher transmembrane pressures the emulsions with broad droplet size distributions were obtained. For example, the emulsion prepared under the pressure difference of 77 kPa contained 77 vol% of droplets smaller than 0.65  $\mu\text{m}$ .

## Conclusion

The monodispersed w/o emulsions with a water content between 2.5 and 25 vol% were successfully prepared using microporous polypropylene hollow fibers. The

emulsification results were expressed as the disperse phase flux, the mean droplet diameter, and the droplet size distribution. Both the disperse phase flux and the mean droplet diameter increased with increasing the transmembrane pressure difference. In addition, the mean droplet size decreased with increasing the emulsifier concentration. The disperse phase flux decreased with time until a steady state flux value was established. The steady-state disperse phase flux was 3-4 orders of magnitude lower than the pure water flux indicating that a great majority of pores were blocked by the oil phase during the water permeation through the membrane.

*Acknowledgement.* This work was supported by Landesamt für Besoldung und Versorgung Baden-Württemberg.

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Received November 26, 1999

Accepted April 24, 2000

## PRIPREMANJE EMULZIJA TIPA VODA-U-ULJU POMOĆU HIDROFOBNIH MIKROPOROZNIH ŠUPLJIH VLAKANA

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### Rezime

Stabilne monodisperzne emulzije vode u mineralnom ulju su dobijene propuštanjem vode pod pritiskom kroz mikropore polipropilenskih šupljih vlakana u kontinualnu fazu koja je recirkulisala unutar vlakana. Fluks disperzne faze kroz membranu u prisustvu kontinualne faze unutar vlakana je 3-4 puta manji od fluksa koji se dobija kada se i unutar vlakana nalazi voda, što ukazuje da je pri emulgovanju vrlo veliki procenat pora blokiran uljem i kao takav ne učestvuje u permeaciji vode kroz membranu. Srednja veličina emulgovanih kapi raste sa porastom transmembranske razlike pritisaka a opada sa porastom koncentracije emulgatora (poliglicerol-poliricinoleata). Ako se emulgovanje vrši pri razlici pritisaka manjoj od 30 kPa i pri koncentraciji emulgatora od 10 mas% mogu se dobiti emulzije sa vrlo uskom raspodelom veličina emulgovanih kapi i srednjom veličinom kapi manjom od 0,27  $\mu\text{m}$ .

Primljeno 26. novembra 1999.

Odobreno 24. aprila 2000.

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