

## Characterization of water-in-oil emulsions produced with microporous hollow polypropylene fibers

GORAN T. VLADISAVLJEVIĆ\*, SABINE BRÖSEL\*\* and HELMAR SCHUBERT\*\*

*\*Institute of Food Technology and Biochemistry, Faculty of Agriculture, University of Belgrade, P. O. Box 127, YU-11081 Belgrade-Zemun, Yugoslavia, and \*\*Institute of Food Process Engineering, Faculty of Chemical Engineering, Universiti of Karlsruhe (TH), Kaiserstrasse 12, D-76128 Karlsruhe, Germany*

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The preparation of fine and monodispersed water-in-oil (W/O) emulsions by utilizing hydrophobic hollow polypropylene fibers with 0.4  $\mu\text{m}$  pores was investigated in this work. The experiments were carried out using demineralized water as the disperse phase, mineral oil Velocite No. 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 the water droplets in the prepared emulsions and the droplet size distribution strongly depend on the content of the disperse phase, the transmembrane pressure difference, and the emulsifier concentration. Stable emulsions with a very narrow droplet size distribution and a mean droplet diameter lower than 0.27  $\mu\text{m}$  were produced using 10 wt % PGPR 90 at a pressure difference below 30 kPa.

*Keywords:* emulsification, membrane emulsification, water-in-oil emulsions, hollow fiber, polypropylene hollow fibers.

### INTRODUCTION

Emulsions are disperse multiphase systems consisting of at least two immiscible liquid phases, e.g., water and oil. The stability of an emulsion is obtained by dispersion of very fine droplets of one liquid, called the disperse phase, through the other liquid, called the continuous phase. Depending on which is the disperse and which the continuous phase there are two types of two-phase emulsions: oil-in-water (O/W) and water-in-oil (W/O). Systems containing an emulsion as the disperse phase are called double emulsions. Typical food O/W emulsions are milk and mayonnaise, while typical food W/O emulsions are butter and margarine. Low calorie mayonnaise is an example of a W/O/W type double emulsion in which the dispersed aqueous drops themselves contain dispersed oil droplets.<sup>1,2</sup> For macroemulsions, the droplet size of the disperse phase is between 0.1 and 50  $\mu\text{m}$ . These emulsions are thermodynamically unstable and have to be stabilized by emulsifiers and/or stabilizers. Emulsifiers are surfactants which lower the interfacial tension between the

\* Serbian Chemical Society active member.

phases and stabilize the droplets by inducing steric and/or electrostatic repulsion between the droplets. Stabilizers are macromolecules which prevent coalescence primarily by increasing the viscosity of the continuous phase.

Emulsification is usually performed using ultrasonic homogenizers, high-pressure homogenizers or rotor/stator systems, such as stirring vessels, colloid mills and toothed disc dispersing machines.<sup>3</sup> 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 poor system stability. Membrane emulsification is a new emulsification technology based on the use of a microporous membrane. In this process, the disperse phase is pressed through the membrane pores into the continuous phase where the droplets are formed. By using membranes having a uniform pore diameter, emulsions with a very narrow droplet size distribution can be produced. The production of monodispersed emulsions is important in the preparation of uniform metal oxide particles by the hydrolysis of alkoxide,<sup>4</sup> in the preparation of a liquid crystal/polymer composite film which is the heart of a liquid crystal display device,<sup>5</sup> in the hydrolysis of olive oil by lipase,<sup>6</sup> in the preparation of liposomes,<sup>7</sup> and in the synthesis of uniform polymeric microspheres by suspension polymerization.<sup>8,9</sup> These uniform microspheres can be used as carriers for enzymes, cells or catalysts, or as packing for analytical or preparative columns,<sup>10</sup> *etc.*

The application of a microporous membrane has several advantages over conventional emulsification devices. Firstly, the membrane emulsification method enables very fine and monodisperse emulsions of controlled mean droplet size to be obtained. Secondly, although an appropriate amount of emulsifier in the continuous phase is indispensable, successful emulsification can be obtained with much less emulsifier and much less energy consumption than is necessary with conventional methods. Thirdly, because of the low shear stress at the membrane surface, membrane emulsification enables the use of shear sensitive ingredients, such as starch and proteins. The microporous membrane employed for emulsification must have a narrow pore size distribution with a mean pore diameter between 0.1 and 10  $\mu\text{m}$ . Also, the membrane surface must not be wetted by the disperse phase. Therefore, a W/O emulsion is produced using either a hydrophobic membrane or a hydrophilic membrane previously treated with the oil phase to render it hydrophobic. The Shirasu porous glass (SPG) membrane developed by Nakashima and Shimizu<sup>11</sup> is the most suitable membrane presently available for use in membrane emulsification systems. Monodisperse O/W emulsions have also been successfully prepared using microporous alumina ceramics membranes<sup>12,13</sup> and microporous polysulfone hollow fibers.<sup>14</sup>

However, only a small number of investigations dealing with the preparation of W/O type emulsions by membrane emulsification method have been reported. This can be explained by the fact that the preparation of a monodisperse W/O type emulsion is difficult compared to a O/W emulsion because it is difficult to stabilize the water droplets by an electrical double layer repulsion force in an oil phase with a low dielectric constant.<sup>15</sup> In this study, the preparation of monodisperse W/O type emulsions using microporous polypropylene hollow fibers has been investigated for the first time. Until now, these fibers have been

used for membrane distillation,<sup>16</sup> dispersion-free solvent extraction,<sup>17</sup> bubbleless gas absorption,<sup>18</sup> and other nondispersive phase contact processes.

### EXPERIMENTAL

W/O emulsions containing demineralized water as the disperse phase and mineral oil Velocite 3 (Mobil Oil, Hamburg, Germany) as the continuous phase were stabilized using polyglycerol polyricinoleate (PGPR 90, Danisco, Denmark) as the emulsifier. The emulsions were prepared in a Microdyn membrane module (Wuppertal, Germany), type MD 020 CP4N. The module consists of 40 microporous hollow fibers made of polypropylene with an inner diameter of 1.7 mm and a mean pore

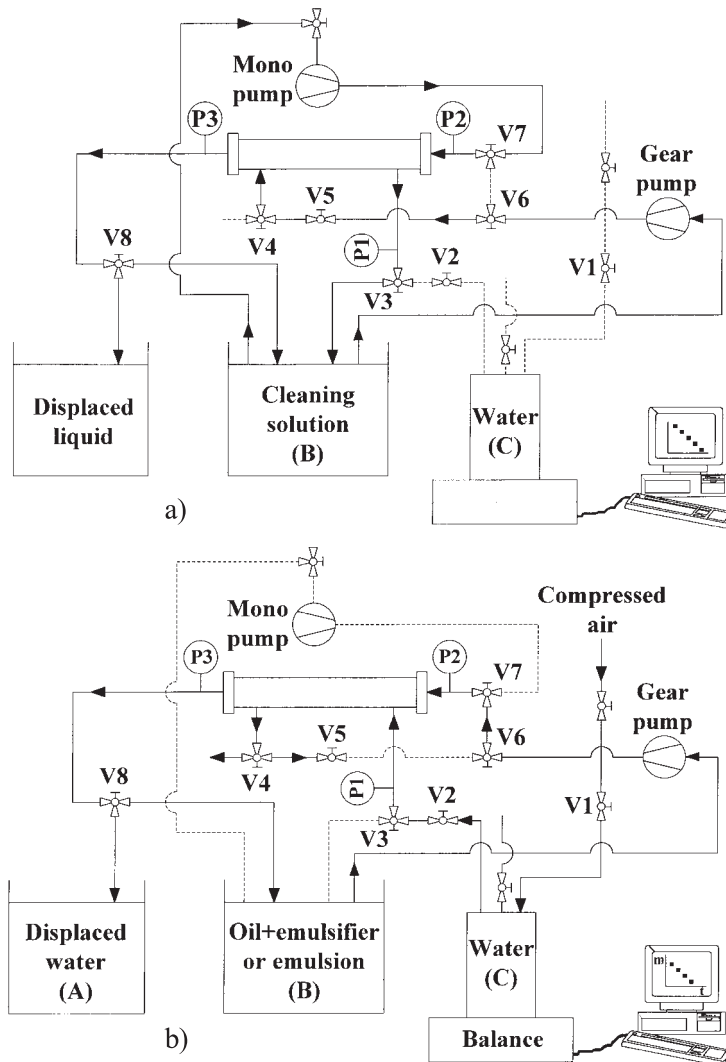


Fig. 1. a) Schematic view of the experimental set-up used in this work;  
b) Cleaning cycle of the membrane emulsification system.

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.

The experimental set-up used in this work is shown in Fig. 1a. In order to remove water from the interior of the fibers, tubes, and the gear pump, the oil phase was first pumped from reservoir B through the inside of the module to reservoir A. Then, the setting of the three-way valve V8 was changed allowing the oil phase to recycle between the module and the holding reservoir B with the gear pump (Multifix, model MEL 3000). The flow rate of the oil phase was maintained constant at about  $130 \text{ L h}^{-1}$ . In the pressure vessel C, on the other hand, the dispersed phase (water) was pressurized to a specified pressure with compressed air and introduced to the outside of the fibers. At the beginning of each experiment the air bubbles from the extracapillary space were released to the atmosphere through the three-way valve V4. The disperse phase pressure was adjusted with the regulating valve V1 and monitored by the gauge M1 located at the entrance of the module. The tube-side pressures at the module inlet and outlet were measured by means of the pressure transducers M2 and M3 and used to calculate the transmembrane pressure difference  $\Delta p_{\text{tm}}$  according to the following equation:

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

where  $p_{\text{g,d}}$  is the disperse phase gauge pressure outside the fibers, and  $p_{\text{c,in}}$  and  $p_{\text{c,out}}$  are the continuous phase absolute pressures at the module inlet and outlet, respectively (all in kPa). The weight of water passing through the pores into the continuous phase was measured continuously by a digital balance on which the pressure vessel rested. The digital balance was connected to a PC computer for data acquisition. The disperse phase flux was calculated as:

$$J_{\text{d}} = m_{\text{d}}/\rho_{\text{d}}A \quad (2)$$

where  $A$  is the effective membrane area,  $\rho_{\text{d}}$  is the disperse phase density, and  $m_{\text{d}}$  is the mass flow rate of the disperse phase determined from the slopes of the  $m$  versus  $t$  plots (Fig. 2) using the least-squares regression analysis method. The mean droplet size and the droplet size distribution were measured using

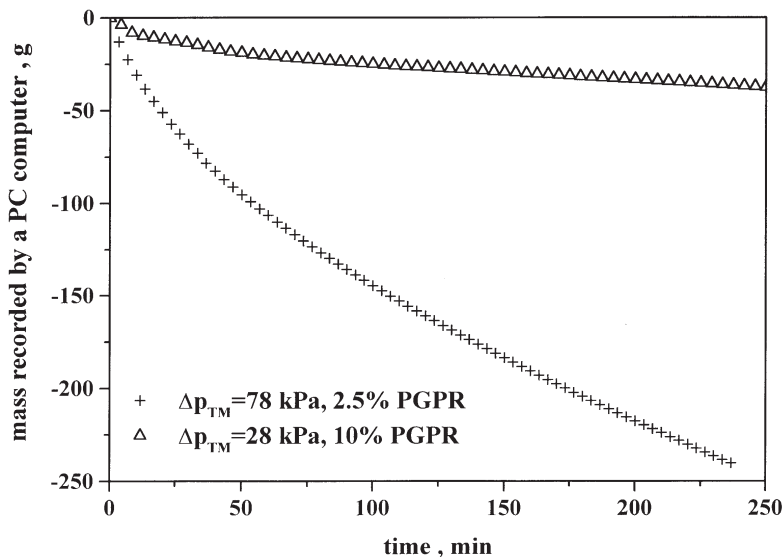


Fig. 2. Mass removal of disperse phase (water) from the pressure vessel as a function of time.

a laser scattering system (Malvern Mastersizer X, Malvern Instruments, Germany), which allows the detection of droplets with a minimum diameter of  $0.1 \mu\text{m}$ . 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 sum of droplets in the emulsion:

$$d_{3,2} = \frac{6}{S} \left( \sum_i^{k_s} \frac{V_i}{d_i} \right)^{-1} \quad (3)$$

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

After each experiment the system was cleaned *in situ* with cleaning agents (Fig. 1b). The emulsion was first removed with a large amount of water flowing in an open cycle. The water was then replaced with 4 L of a 1 wt % aqueous solution of the alkaline cleaning agent P3-ultrasil 11 (Henkel Hygiene, Düsseldorf, Germany) flowing in an open cycle. Afterwards, the system was cleaned with an additional 4 L of 1 % P3-ultrasil 11 solution flowing in a closed cycle between the module and reservoir B at a temperature of  $50^\circ\text{C}$ . The cleaning solution was simultaneously recycled outside the fibers using a gear pump and inside the fibers 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 L of a 1 wt % aqueous solution of the neutral cleaning agent P3-ultrasil 53 (Henkel Hygiene). The system was then cleaned with an additional 4 L of a 1 wt % P3-ultrasil 53 solution flowing in a closed cycle at  $50^\circ\text{C}$  for about 60 min. Finally, the system was thoroughly rinsed with demineralized water until the pure water flux at the given transmembrane pressure difference was restored to its initial value.

## RESULTS AND DISCUSSION

In Fig. 2 the mass of demineralized water removed from the pressure vessel is plotted against time for two typical experiments. Similar dependencies were also ob-

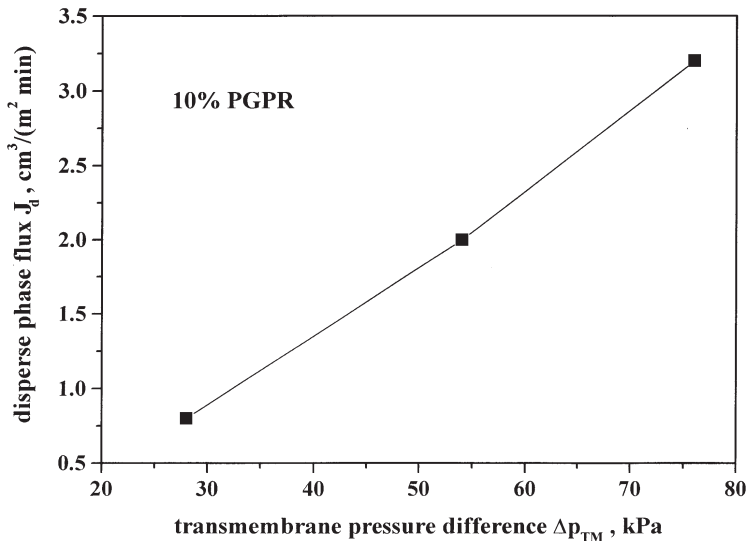


Fig. 3. Steady-state disperse phase flux as a function of transmembrane pressure difference at an emulsifier (PGPR 90) concentration of 10 wt %.

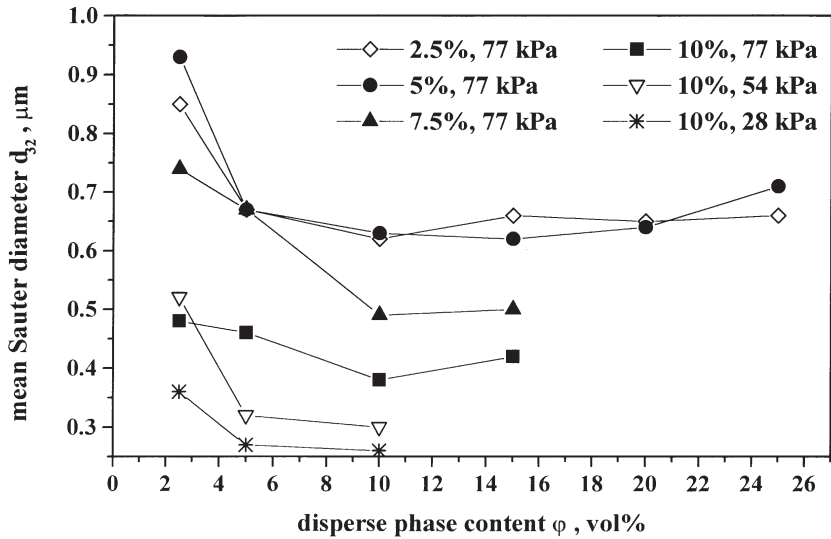


Fig. 4. Mean droplet diameter as a function of the disperse phase concentration.

tained for other operating conditions, but for the sake of clarity these dependencies are omitted from Fig. 2. The disperse phase flux initially decreased with time but after a certain period a steady-state was established. As shown in Fig. 3, the steady-state flux of the disperse phase increases linearly with increasing transmembrane pressure difference  $\Delta p_{tm}$ , which is in accordance with Darcy's law. At  $\Delta p_{tm} = 28 - 76$  kPa with an emulsifier concentration of 10 wt %, the steady-state flux of the disperse phase ranges

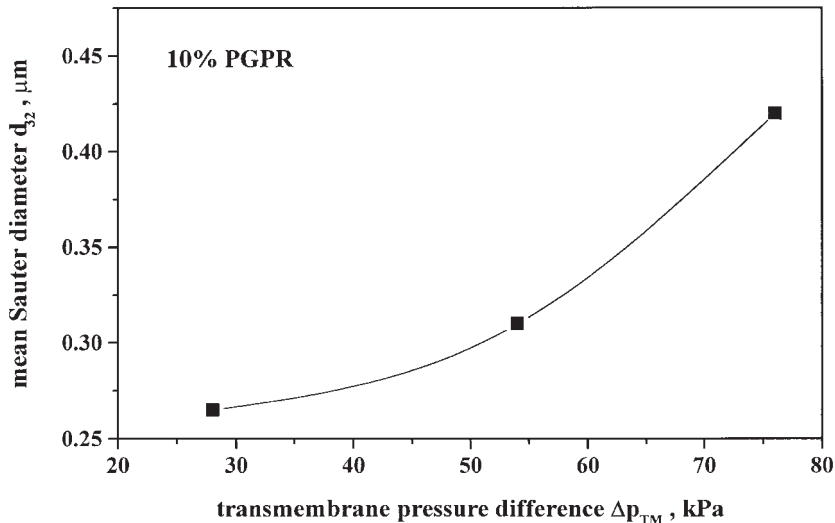


Fig. 5. Mean droplet diameter as a function of the transmembrane pressure difference at an emulsifier (PGPR 90) concentration of 10 wt %.

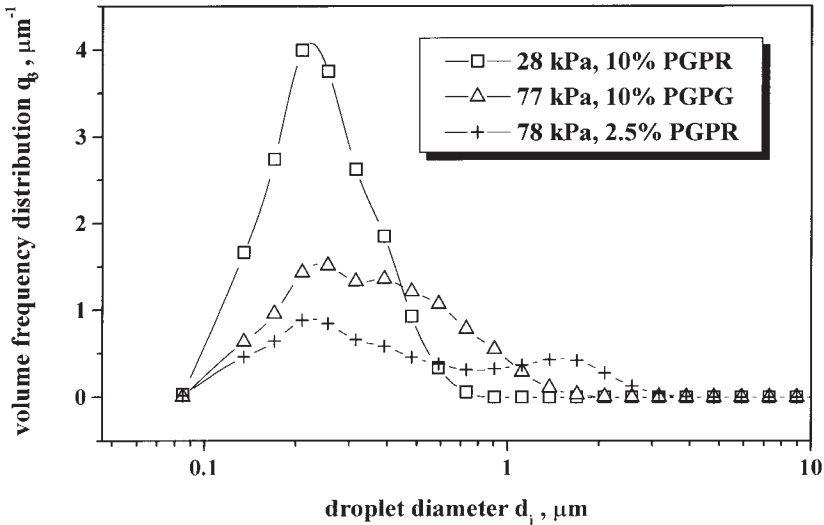


Fig. 6. Droplet size distribution curves for emulsions prepared under different experimental conditions.

from 0.8 to 3.2  $\text{cm}^3/(\text{m}^2 \text{ min})$ . At the same pressures, water flux into the pure water at the other side of the membrane was in the range of  $(0.8 - 2.0) \times 10^4 \text{ cm}^3/\text{m}^2 \text{ min}$ , which is 4 orders of magnitude higher than the disperse phase flux. Therefore, only a very small fraction of the pores take part in the permeation of the disperse phase through the membrane.

The influence of the content of the disperse phase in the emulsion on the mean droplet size is shown in Fig. 4. In most cases, the mean droplet size decreases greatly when the disperse phase content is increased from 2.5 to 5 vol %, but above 10 vol % an almost constant value is attained. The largest mean droplet size at the lowest disperse phase concentration of 2.5 vol % can be attributed to the relatively high disperse phase flux at the beginning of each experiment. Larger droplets are formed at higher fluxes because the emulsifier is unable to stabilize the new interfaces fast enough.

Obviously, the mean droplet size increases with increasing transmembrane pressure difference and with decreasing emulsifier concentration, which is also observed in the preparation of O/W type emulsions.<sup>13,19</sup> At an emulsifier concentration of 10 wt % and a transmembrane pressure difference of 28 kPa, the mean droplet diameter is only 0.265  $\mu\text{m}$  (Fig. 5), which is 34 % smaller than the mean pore size. One of the possible explanations of this is that the water which penetrates through the membrane cannot completely displace the oil from the interior of the pores due to the high viscosity of the oil compared to that of water. Therefore, some amount of the oil phase is retained inside the pores in the form of a layer leading to a decrease in the effective pore diameter.<sup>20</sup> This dependency between the mean droplet size and the mean pore size was also reported by Kandori *et al.*,<sup>21,22</sup> for the preparation of W/O emulsion by the SPG filter emulsification method using various kinds of microporous glass filters of different pore

diameters and copolymer-type surfactants. As an example, Kandori<sup>22</sup> prepared a monodisperse W/O emulsion with a mean droplet size of 0.67  $\mu\text{m}$  using a 2 wt % PE-64 surfactant concentration and a hydrophilic SPC filter with a mean pore size of 0.98  $\mu\text{m}$ . This result is opposite to that obtained for O/W emulsions when the mean diameter of the oil droplets is several times larger than the mean pore size.<sup>12,23</sup>

Typical droplet size frequency distribution curves for emulsions prepared under different experimental conditions are shown in Fig. 6. The most frequently occurring droplet size lies in the interval between 0.21 and 0.26  $\mu\text{m}$ , and is independent on the operating conditions in the investigated range. As can be seen from Fig. 6, an emulsion with very narrow droplet size distribution was obtained with a pressure difference of 28 kPa using 10 wt % PGPR in the continuous phase. This emulsion contained more than 98 vol % of water droplets smaller than 0.65  $\mu\text{m}$ . However, at higher transmembrane pressures, emulsions with broader droplet size distributions were obtained. For example, the emulsion prepared with a pressure difference of 77 kPa using 10 wt % PGPR contained 77 vol % of droplets smaller than 0.65  $\mu\text{m}$ . On the other hand, the emulsion prepared under the same pressure difference and stabilized using 2.5 wt % PGPR contained only 35 vol % of droplets smaller than 0.65  $\mu\text{m}$ .

#### CONCLUSION

W/O emulsions with narrow droplet size distributions and 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 transmembrane pressure difference. In addition, the mean droplet size decreased with increasing emulsifier concentration. The disperse phase flux decreased with time until a steady state flux value was established. The steady-state disperse phase flux was 4 orders of magnitude lower than that of the pure water flux, indicating that a large majority of the pores were blocked by the oil phase during the permeation of water through the membrane.

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#### ИЗВОД

#### КАРАКТЕРИЗАЦИЈА ЕМУЛЗИЈА ТИПА ВОДА-У-УЉУ ДОБИЈЕНИХ ПОМОЋУ МИКРОПОРОЗНИХ ПОЛИПРОПИЛЕНСКИХ ШУПЉИХ ВЛАКАНА

ГОРАН Т. ВЛАДИСАВЉЕВИЋ\*, SABINE BRÖSEL\*\* и HELMAR SCHUBERT\*\*

\*Институт за прехрамбену технологију и биохемију, Пољопривредни факултет Универзитета у Београду, б. бр. 127, 11081 Београд - Земун, Југославија и \*\*Институт за прехрамбено процесно инжењерство, Факултет за хемијско инжењерство, Универзитет у Карлсруеу, Немачка

Стабилне монодисперзне емулзије воде у минералном уљу су пропремљене пропуштањем воде под притиском кроз поре полипропиленских шупљих влакана пречника 0,4  $\mu\text{m}$  у континуалну фазу која је рециркулисала унутар влакана. Флуks диспе-



рзне фазе кроз мембрану у присуству уљне фазе унутар влакана је за 4 реда величине мањи од флукса који се добија када се са обе стране мембране налази вода, што указује да је при емулговању велики проценат пора блокиран уљем и као такав не учествује у пермеацији воде кроз мембрану. Средњи пречник капи у припремљеним емулзијама расте са порастом трансмембранске разлике притисака а опада са порастом концентрације емулгатора (полиглицерол-полирицинолеата). Ако се емулговање врши при трансмембранској разлици притисака мањој од 30 kPa и при концентрацији емулгатора од 10 мас % добијају се емулзије са врло уском расподелом величина капи и средњим пречником капи од само 0,27  $\mu\text{m}$ .

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