Demulsification of Water/Oil/Solid Emulsions by Hollow-Fiber Membranes

Neena Pradhan Tirmizi, Bhavani Raghuraman, and John Wiencek
Dept. of Chemical and Biochemical Engineering, Rutgers University, Piscataway, NJ 08855

The demulsification techniques investigated use preferential surface wetting to allow separation of oil and water phases in ultrafiltration and microfiltration membranes. A hydrophobic membrane allows the permeation of an oil phase at almost zero pressure and retains the water phase, even though the molecular weight of the water molecule (18) is much smaller than that of the oil molecule (198 for tetradecane, used in this study). Hydrophobic membranes having pore sizes from 0.02 to 0.2 μm were tested for demulsification of water-in-oil emulsions and water/oil/solid mixtures. The dispersed (aqueous)-phase drop sizes ranged from 1 to 5 μm. High separation rates, as well as good permeate quality, were obtained with microfiltration membranes. Water content of permeating oil was 32−830 ppm depending on operating conditions and interfacial properties. For emulsions with high surfactant content, simultaneous operation of a hydrophobic and hydrophilic membrane, or simultaneous membrane separation with electric demulsification was more efficient in obtaining complete phase separation.

Introduction

Emulsions of water, oil, and solids are formed in a number of industrial settings where immiscible organic and aqueous phases contact. Dilute oil-in-water emulsions are frequently encountered as waste streams from metal-working plants using cutting and grinding oils, emulsified spinning oils from textile plants, and wash water from automotive industry, refineries, and petrochemicals plants (Lissant, 1983). Before discharging these streams to sewers, the oil must be demulsified and separated from the water phase along with any other objectionable substances such as solids. Water-in-oil emulsions, which are the main focus of this study, are often encountered in the petroleum industry, especially during crude-oil production. Demulsification and water removal is a critical requirement before downstream processing of oil. Water-in-oil emulsions are also encountered in liquid-membrane treatment processes for metal extraction or waste water treatment. The emulsions used in liquid-membrane processes are formulated to remain stable under the process operating conditions, and are therefore difficult to break (Hsu and Li, 1985). The recovered-oil phase is reused for making emulsions for the liquid membrane process and should not contain any demulsifying chemicals.

Typical demulsification methods found in literature are additions of demulsifying agents; pH adjustment; gravity or centrifugal settling; filter coalescers; heater treaters; electrostatic coalescers; and membranes (Lissant, 1983). There are advantages and disadvantages to each of these demulsification techniques. In processes using additives, there are additional problems of disposal of adsorbent or additive, or contamination of recovered oil or water with the additive. pH effects can sometimes be used to break oil-in-water emulsions, but effects of pH and salts are not significant in water-in-oil emulsions. Gravity settling, centrifuging, or heating can break some emulsions. Centrifuges are efficient for some emulsions, but are capital intensive and expensive to run and maintain. Electric field methods have been used to demulsify water-in-oil emulsions and electrostatic coalescers are widely used in the petroleum industry (Hsu and Li, 1985; Cottrell, 1911; Taylor, 1988; Larson et al., 1994). The electric field method is also used for breaking emulsions used in liquid-membrane technology (Hsu and Li, 1985; Taylor, 1988). Extremely high voltages (10 to 20 kV) are required to cause droplet coalescence. Hsu and Li (1985) showed that using insulated electrodes with a nonwater wettable coating pre-

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Correspondence concerning this article should be addressed to J. Wiencek.
Current address of J. Wiencek: Chemical and Biochemical Engineering Dept., University of Iowa, Iowa City, Iowa 52242.

vented sparking, thus making it possible to use voltages as high as 20 kV. Larson et al. (1994) also used a high-voltage cell with insulated electrodes for demulsification of coarse and microemulsions.

Membrane modules for demulsification are compact and can be run continuously. The advantages of splitting emulsions by membrane processes in contrast to other processes are:

- Low energy cost, especially with microfiltration membranes that operate at low pressures
- No moving parts
- No contamination of phases by additives
- No degradation due to heating
- No extra safety considerations as in high-voltage demulsification.

All instances of the use of membrane technology for demulsification found in the literature are for oil-in-water emulsions using hydrophilic ultrafiltration and hydrophilic microfiltration membranes. Kirjasoff et al. (1980) used ultrafiltration (Abcor HFD membranes) to treat aqueous waste streams containing 0.353% oil and grease and 0.758% solids. Strathmann (1976) gave a review of membrane methods for treatment of industrial effluents using reverse osmosis and ultrafiltration, as well as demonstrated an ultrafiltration process to clean up oily waste streams. Bhave and Fleming (1988) investigated dilute suspensions of oil-in-water containing up to 5% oil using hydrophilic alumina (Membralox) membranes. Lee et al. (1984) used hydrophilic ultrafiltration membranes (Iris 3042, Rhone Poulenc) to remove soluble oils. Kutowy et al. (1981) used cellulose acetate (hydrophilic) membranes for treatment of oily wastes containing 5 to 35% oil. Scott et al. (1992) studied emulsions having up to 40% oil using hydrophilic membranes (cellulose acetate, regenerated cellulose, and coated regenerated cellulose). Zaidi et al. (1992) and Chen et al. (1991) used ceramic and hydrophilic membranes to remove oil from oil field brines. In all of these studies the permeating phase was water. The transport mechanism in these hydrophilic-membrane demulsification studies was not related to any measurable property of the emulsion system.

Hydrophobic membranes have been used in extraction processes by Kiani et al. (1984) and Teramoto and Tanimoto (1983). Kiani et al. (1984) used polypropylene membranes to keep the organic phase from dispersing into the aqueous phase in a solvent-extraction process. Teramoto and Tanimoto (1983) used hydrophobic polypropylene, Teflon, and polyacrylonitrile membranes to support an organic liquid membrane. Composite hydrophilic and hydrophobic membranes were used by Prasad and Sirkar (1987) for dispersion-free solvent extraction. These composites were formed by stacking thin sheets of cellulose acetate or regenerated cellulose over polypropylene or Teflon membrane sheets.

Membrane techniques are generally based on separation due to size exclusion phenomena or selective dissolution in the membrane matrix. This work presents an investigation on separation due to preferential wetting, which implies that the wetting phase will permeate through the pores while the nonwetting phase will be retained. Membrane pore sizes are much larger than molecules of either phase. We have investigated the use of hydrophobic membranes for demulsification and oil–water separation by exploiting the preferential wetting principle. The nonwetting phase requires a certain minimum pressure (breakthrough pressure) to force it through the membrane pores, and the demulsification operation can be carried out below this "breakthrough pressure." There were no instances in literature of the use of hydrophobic membranes for demulsification. The use of hydrophobic membranes for demulsification enables us to recover the oil phase in a very pure form as a permeate. Thus, water-in-oil emulsions that cannot be separated by a hydrophilic membrane, can be demulsified by hydrophobic membranes.

A range of modules and emulsion types was studied to verify the effectiveness of the proposed oil–water separation. Emulsion characteristics that lead to successful demulsification were identified. The permeation rates and permeate quality were measured for emulsions at various surfactant concentrations. The effect of pore size on permeation rate was evaluated by running emulsions with the same composition through membranes of different pore sizes. Permeation rates were also compared with batch gravity-settling rates at the same temperature. For emulsions with a high surfactant content, a combination of hydrophobic membranes, hydrophilic membranes, and electric field separation were investigated in order to get complete separation and to recover both phases. Parameters that affect the separation such as interfacial tension and contact angles were measured for a number of emulsions. A range of interfacial tensions was obtained by varying surfactant type and concentration. Water–oil mixtures without surfactant were also studied over a range of 1% (v/v) oil–99% (v/v) water to 80% (v/v) oil–20% (v/v) water. If oil permeation is possible at low oil content, then the hydrophobic membrane method could be used for processes requiring recovery of small amounts of organics from oil–water mixtures or for water polishing applications.

This article shows that oil–water separation can be obtained using the preferential wetting principle, and microfiltration membranes give high separation rates without diminishing permeate quality, provided the separation is carried out below the breakthrough pressure. At high surfactant content up to 90% (v/v) of oil can be removed from the emulsion with the membrane process. However, the recovery of pure water from emulsions having high surfactant content requires the use of electrostatic coalescence.

Theoretical Background

Some data on measurement of breakthrough pressure for organic–water systems is available in literature. The breakthrough pressure for a membrane depends on the pore-size distribution, the interfacial tension between the two liquids, the contact angle of the aqueous (nonwetting) phase on the membrane wetted by the organic (wetting phase), and the size and shape of the openings in the membrane. A membrane with a wide pore-size distribution would have some pores much larger than the average pore size, and fluid would break through these large pores first. In order to force a nonwetting fluid through the pores of a membrane the applied pressure should be at least equal to the pressure drop across the interface $P_A - P_B$ given by the Young–Laplace equation:

$$P_A - P_B = 2\gamma \cos\theta (1/r_1 + 1/r_2), \tag{1}$$

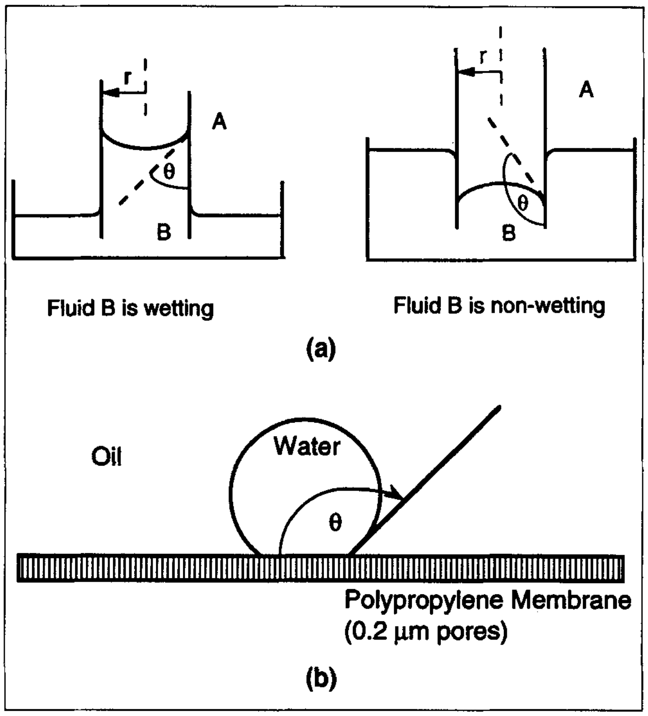


Figure 1. Contact angles at three phase boundaries.

(a) Capillary rise principle for wetting and nonwetting fluids showing the phases, contact angles, and interface. (b) A drop of water on the membrane with oil as the surrounding medium showing the contact angle.

where P_A is the pressure in phase A, P_B is the pressure in phase B, γ is the interfacial tension, θ is the angle at which the interface meets the capillary wall (contact angle) as measured in phase B (Figure 1a), and r_1 and r_2 are the two radii of curvature for the surface. The contact angle of a fluid with a solid is a measure of the wettability of the solid by the fluid. The interfacial tension is a liquid–liquid property while the contact angle is a liquid–liquid–solid property. For the two-liquid system with a hydrophobic membrane, the contact angle of a water droplet is the angle as measured through the organic phase that is formed at the junction of the three phases as shown in Figure 1b (the membrane is a porous surface). A contact angle of 0° indicates complete wetting and 180° indicates complete nonwetting.

Prasad and Sirkar (1987) made measurements of the breakthrough pressure for the nonwetting fluid (water), but did not measure interfacial tension and contact angles. Lee et al. (1984) measured permeability of water through hydrophilic membranes at increasing levels of oil fouling. They used the capillary equation to estimate the pressure required to force oil droplets into the membrane:

$$P_A - P_B = 2\gamma \cos \theta / r, \tag{2}$$

where r is the capillary radius. Increased membrane fouling (and reduced water permeability) was observed for operation above the calculated capillary pressure.

Kim and Harriot (1987) have modeled the breakthrough pressure for the nonwetting fluid in the pores of a hydrophobic membrane by combining the model by Purcell (1949) (for doughnut-shaped pores) with the model of Crisp and Thorpe (1948) (for thin elongated pores between an array of parallel cylindrical fibers) and obtained the following equation:

$$\Delta P_{\text{brk}} = 2\gamma \cos \theta_{\text{eff}} / r, \tag{3}$$

where θ_{eff} accounts for the shape of the pore and was calculated from measurements of the contact angle θ on the membrane surface. Their experimental data for breakthrough of liquid–air systems fit the theoretical equation, but the experimental data for liquid–liquid systems showed nonlinear behavior that is not predicted by Eq. 3. Equation 3 does not include the internal shape of the pore given by radii r_1 and r_2.

In the present work, the interfacial tensions, contact angles, and breakthrough pressures were measured for a hydrophobic membrane (0.2-μm polypropylene) and a hydrophilic membrane (0.8-μm regenerated cellulose). The fit to the capillary Eq. 2 was checked by plotting ΔP_{brk} vs. $\gamma \cos \theta$. The pore structure of the two membranes used for the breakthrough pressure tests resembles a spongy material with capillary-like pores (Microdyn Technologies, Inc., 1994). Both membranes are symmetric membranes (uniform pore size through the entire membrane thickness). The simple capillary equation was used, with contact angle measurements on the membrane surface, since the inside of the capillary is also a porous surface. The doughnut-shaped pore model was not used, because this model would be applicable to asymmetric (reverse-osmosis-type) membranes where the breakthrough process takes place only near the inlet. The pores of a spongy-type symmetric membrane would resemble long capillaries rather than doughnut-shaped pores.

Experimental Methods

Materials

Membranes. Four hydrophobic and four hydrophilic membrane modules were tested for water–oil separation and demulsification. Modules were selected based on membrane material, pore size, fiber internal diameter, and configuration. Each system was selected based on the information provided by the manufacturer regarding hydrophobicity/hydrophilicity and pure solvent fluxes if available. The membrane materials selected were polypropylene, regenerated cellulose, ceramic, and polysulfone. Details of the membrane modules tested (Table 1) give manufacturer data such as membrane area, pore size, and tube internal diameter, as well as performance data collected in the present work, such as pure component breakthrough pressure and permeate purity. The ceramic module is hydrophobic or hydrophilic, depending on the fluid initially used to wet it. The 0.02-μm ceramic module was tested as a hydrophobic module, by wetting it first with an organic, while the 0.2-μm ceramic module was tested as a hydrophilic module, by wetting it first with water. For the purpose of contact angle measurements, flat-sheet membranes of the same material, porosity, and pore size as the hollow fiber 0.2-μm membrane were obtained from Microdyn Technologies.

Emulsions and Surfactants. Water-in-oil emulsions were made using oil-soluble surfactants such as ECA 5025 (Paramins/Exxon Chemicals) or SPAN 80 (ICI Americas Inc.) with

Table 1. Evaluation of Hollow Fiber Membrane Modules for Oil–Water Separation*

Hydrophobic Modules

Module No.	Manuf. Identif.	Material	Area cm^2	Pore Size μm	Tube ID cm	ΔP_{brkthr}** Tetradecane-Air kPa	ΔP_{brkthr}** Water-Air kPa	Water Content** Permeate for Tetradecane-Water Sep.
A	PC-240/5C (Hoechst Celanese)	Polypropylene	4000	0.05	0.024	0	> 207	49 ppm
B	LM1P06 (Enka)	Polypropylene	400	0.1	0.06	0	> 207	46 ppm
C	Ceramic (Single tube) (U.S. Filter)	Ceramic	55	0.02	0.7	0	> 138	28 ppm
D	LM2P18 (Enka) (2 modules)	Polypropylene	200	0.2	0.18	0	> 138	31 ppm

Hydrophilic Modules

Module No.	Manuf. Identif.	Material	Area cm^2	Pore Size μm	Tube ID cm	ΔP_{brkthr}** Tetradecane-Air kPa	ΔP_{brkthr}** Water-Air kPa	Oil Content** Permeate for Tetradecane-Water Sep.
E	Ceramic (Single tube) (U.S. Filter)	Ceramic	55	0.2	0.7	69	0	8 ppm at 34.5 kPa to 1.3% at 69 kPa
F	BLHP (Enka)	Regenerated Cellulose	500	0.05	0.02	> 172	0	< 1 ppm
G	LM MPES (Enka)	Sulfonated Polysulfone	300	0.2	0.15	> 172	0	< 1 ppm
H	LM PF 100 (Enka)	Regenerated Cellulose	200	0.8	0.033	> 172	0	3.2 ppm

*All characteristics of membrane supplied by manufacturer except those denoted by **, which were measured as part of this work. {pure tetradecane ($C_{14}H_{30}$) and water, no surfactant}

tetradecane as the oil phase. Technical Grade tetradecane was obtained from Humphrey Chemicals (composition: 93.9% tetradecane, with dodecane, hexadecane, and octadecanol as impurities). The surfactant was first dissolved in the oil phase (tetradecane), and then blended with deionized water for two minutes in a high-speed blender. Water-soluble surfactant Igepal CO 610 (Rhone Poulenc Inc.) was used to extend the range of interfacial tensions for breakthrough pressure measurements. All oil-soluble surfactant concentrations throughout the text are in kg/m^3 of the oil phase, and water-soluble surfactant concentrations are in kg/m^3 of the water phase. Water–oil–solids emulsions were prepared by adding 60-μm silica powder (Fisher Scientific) to water, followed by addition of oil and mixing with a magnetic stirrer. The oil–water–silica emulsions were stable and did not separate completely by gravity settling over the course of several days.

Analytical methods

The water content of tetradecane was measured on a Coulometric Titrator Aquastar 2000 (EM Science). Higher water contents, such as those of the emulsion ($\sim$ 20%), were measured by Volumetric Karl Fisher Tiration (Mettler DL18). Tetradecane in aqueous permeate streams or demulsified retentate streams was extracted into hexane and measured by gas chromatography on a HP 5890 Series II instrument. Tetradecane has a very high solubility in hexane and is completely extracted into hexane. A gas chromatogram of the aqueous phase showed no residual tetradecane after the extraction.

A variety of techniques were used to measure interfacial tension at the oil–water interface. Some results are shown in Table 2 for interfacial tensions in the region of interest. Although there was some variability in results, the techniques agreed to within 10 to 20%. The Du Nouy ring tensiometer was used for measurements above 6.0 mN/m. Low interfacial tensions were measured by a spinning drop tensiometer (Model 500, University of Texas). Spinning tubes with 0.2-mm internal diameter, were used for the low interfacial tension range, and 0.4-mm internal diameter tubes were used to extend the capability of the spinning drop technique up to 10 mN/m.

Liquid–liquid–membrane contact angles were measured by taking photographs using an Olympus SZ-PT microscope with a video attachment. A horizontal microscope stand was used to view the drop that was placed on a flat-sheet membrane

Table 2. Interfacial Tension Measurements by Various Methods

	Method	Interfacial Tension mN/m
Water–Pure Tetradecane	Du Nouy ring	47.30
	Wilhelmy plate	47.80
	Drop wt. (0.07 cm capillary)	45.00
	Drop wt. (0.143 cm capillary)	51.10
Water–Tetradecane with 3% ECA 5025	Du Nouy ring	8.79
	Spinning drop tensiometer	10.33
	Drop wt. (0.07 cm capillary)	9.15
	Drop wt. (0.143 cm capillary)	11.09

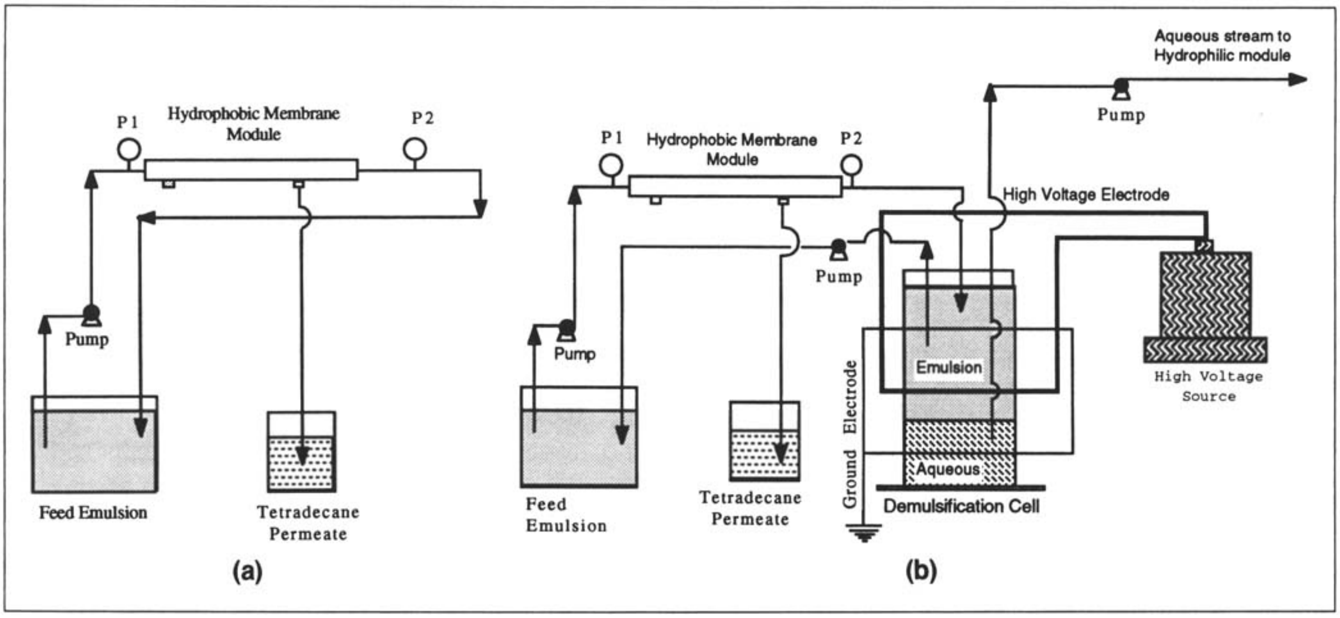


Figure 2. Experimental setup.

(a) Membrane demulsification where the membrane module is either a hydrophobic module alone or hydrophilic and hydrophobic modules in series for the combined separation case. (b) Membrane separation with electric field coalescence.

surface in a glass chamber filled with the second liquid. Measurements of contact angles were made from the photographs.

Measurements of dispersed-phase drop size in the emulsion were obtained using an Olympus BH-2 microscope with a video attachment at a magnification of 1,250. Emulsion drop sizes were measured and found to be in the range of 1 to 5 μm for freshly prepared emulsions having surfactant contents of 5.0 to 30 kg/m^3. In emulsions having lower surfactant content, droplets were seen to be coalescing to form larger drops.

Experimental setup and procedure

Membrane Demulsification (Figure 2a). Membrane modules were connected with Viton and polypropylene tubing to a Masterflex 0–600 rpm peristaltic pump (Cole Parmer). The permeate side was open to the atmosphere and the transmembrane pressure drop was controlled manually using a valve on the retentate side. Except for the values reported in Table 3, flux measurements reported in Figures 3–6 were collected by recirculating both the permeate and retentate streams back to the feed tank, which maintained a constant emulsion composition. All other demulsification experiments (including data reported in Table 3) were carried out in batch mode by removing the permeate while recirculating the retentate back into the feed tank, which results in a variable feed composition.

Characterization of Breakthrough Pressures. Hydrophobic and hydrophilic modules were initially tested for the minimum pressure required for breakthrough of the nonwetting phase through the membrane in air (membrane–air–liquid). The wetting phase permeates at essentially a zero transmembrane pressure. [The precision of the pressure gauges was ±3.5 kPa (±0.5 psi). For all practical purposes, pressures having measured values less than 5 kPa can be viewed as zero pressure.] Table 1 shows the breakthrough pressures for the

Table 3. Separation Rates and Permeate Quality for Various Membrane Pore Sizes*

Surfactant Content of Emulsion (kg/m^3 in $C_{14}H_{30}$)	Pore Size of Membrane					
	0.02 μm (Module C)		0.1 μm (Module B)		0.2 μm (Module D)	
	Permeate (Oil) Flux (cm/s)	Water in Permeate	Permeate (Oil) Flux (cm/s)	Water in Permeate	Permeate (Oil) Flux (cm/s)	Water in Permeate
0.0	1.22×10^{-3}	28 ppm	3.69×10^{-3}	45.5 ppm	5.79×10^{-3}	31 ppm
0.5	0.20×10^{-3}	30 ppm	0.68×10^{-3}	47.8 ppm	1.88×10^{-3}	48.3 ppm
20	0.14×10^{-3} at 103 kPa**	4.1%	0.22×10^{-3}	384.1 ppm	0.25×10^{-3}	296.3 ppm

*Initial emulsion composition: 80% (v/v) tetradecane ($C_{14}H_{30}$), 20% (v/v) water, surfactant ECA 5025 as indicated below. {All tests at 34.5 kPa (5 psi) average transmembrane pressure drop in batch mode (i.e., variable feed composition to a final composition of 50% (v/v) tetradecane, 50% (v/v) water, see Methods).}

**No flux at 34.5 kPa to compare with data for other modules.

membrane–liquid–air case. Most of the modules show a large difference (> 138 kPa) between the breakthrough pressure for the wetting and nonwetting fluids except the ceramic 0.2-μm module.

Breakthrough pressures for liquid–liquid conditions were measured by circulating the organic phase on the shell side and the aqueous phase on the tube side for hydrophobic membranes. The aqueous phase was slowly pressurized and the water content of the organic phase was measured by Karl Fisher Titration as a function of pressure. A range of interfacial tensions and contact angles was obtained by varying the surfactant type and concentration. The hydrophobic membranes were flushed through with the oil phase (shell side to tube side) before each experiment to fill all pores with oil. For the hydrophilic membrane, the organic phase was circulated on the tube side and slowly pressurized, while the aqueous phase was circulated in a closed loop on the shell side. Aqueous-phase samples were analyzed for oil content by gas chromatography to determine the breakthrough pressure.

Membrane Separation with Electrostatic Coalescence. The membrane unit was operated simultaneously with the electrostatic cell as shown in Figure 2b. A clarified-oil phase was collected as permeate from the membrane unit, and the aqueous phase was collected from the bottom of the electrostatic cell. The electrostatic coalescence cell previously used and described by Larson et al. (1994) and Larson (1993) was used. The demulsification cell consisted of a specially constructed plexiglas chamber having a volume of 260 cc, through which the high voltage and ground wires were passed. The high-voltage electrode was a polyvinyl chloride (PVC)-coated (insulation) hookup wire of 0.635 cm dia. (0.25 in. nominal OD, Newark Electronics). The PVC coating was 0.1 cm thick. The surface of the wire was made hydrophobic by covering it with heat-shrink Teflon (Newark Electronics). The ground electrode was stainless steel tubing of 0.15875 cm dia. (1/16 in. OD). The power source was in Hipotronics AC Dielectric Test Set Model 730-1. The maximum rating of the unit was 30 kV, but was operated below 20 kV, which was the rating of the insulation wire. As a safety precaution the automatic power shutoff was set at 3 mA.

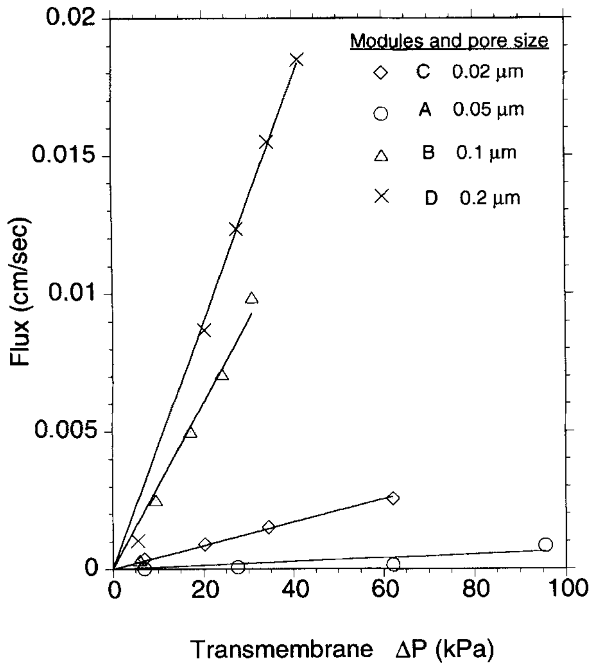


Figure 3. Pure tetradecane (oil) flux from hydrophobic modules for four pore sizes.

Modules A, B, and D have polypropylene membranes, and module C is a ceramic membrane.

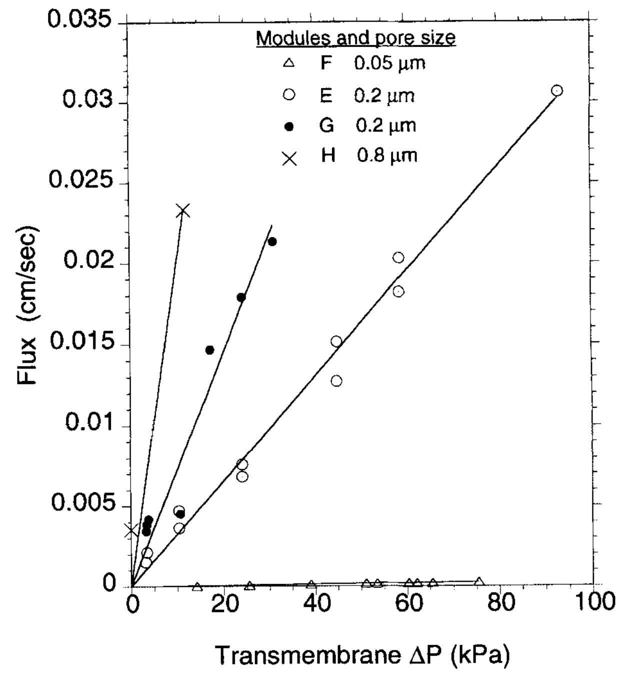


Figure 4. Pure water flux from hydrophilic modules for four pore sizes.

Module E is ceramic, modules F and H are regenerated cellulose, and module G is polysulfone.

Results and Discussion

Pure component fluxes

Figure 3 shows a comparison of pure tetradecane flux through the four hydrophobic membranes tested, and Figure 4 shows the same for hydrophilic membranes. The flux was calculated based on total surface area of the membrane. Flux increases linearly with the transmembrane ΔP as expected. Comparing modules of the same material, the fluxes dramatically improve as the average pore size increases from 0.05 μm (which is considered ultrafiltration) to 0.2 μm (a microfiltration membrane). This supports our premise that flux will be much higher with the MF membranes and, as will be shown later, this increased flux can be achieved without any degradation in the permeate quality. Modules B and D have the same porosity. Fluxes from different membrane materials cannot be compared directly on the basis of pore size because the pore density differs.

Permeate quality vs. pore size

Table 1 also shows the permeate quality for tests with water–tetradecane mixtures (no surfactant). The permeating tetradecane from all hydrophobic modules was a single clear phase with a water content below 50 ppm. The ceramic 0.2-μm membrane, which was tested as a hydrophilic module, became partially wetted by oil as the pressure was increased, and the permeating water had a high oil content.

Water-in-oil emulsions were tested in hydrophobic membrane modules having three different pore sizes (0.02, 0.1 and 0.2 μm). The average batch flux (see Experimental Setup and Procedure for description) and water content of the permeating oil (tetradecane) were measured. The results are shown in Table 3 for three emulsions: (a) zero surfactant, that is, water-oil physical mixture with 20% (v/v) water; (b) 0.5-kg/m^3 surfactant ECA 5025 in oil with 20 (v/v)% water; and (c) 20-kg/m^3 surfactant ECA 5025 in oil with 20% (v/v) water. Tests were conducted at an average transmembrane pressure drop of 34.5 kPa (5 psig). Note that the permeate quality for the 0.1-μm module (module B) with 20 kg/m^3 surfactant emulsion is worse than that for the 0.2-μm membrane (module D). The smaller tube diameter of module B resulted in a higher pressure loss with the 20-kg/m^3 surfactant emulsions (6 kPa or 8.7 psi), so that the inlet side of module B was at 65.5 kPa to get an average transmembrane pressure drop of 34.5 kPa. The higher inlet pressure probably caused the higher permeation of water. The 0.02-μm module C (ultrafiltration range) did not show oil permeation at 34.5 kPa, so the pressure was increased to 103 kPa, at which point large amounts of water permeated through, due to partial wetting by the aqueous phase. The ceramic modules were found to be inefficient for demulsification of water-in-oil emulsions containing surfactants. The results in Table 3 show that the higher pore size polypropylene membrane gives a much higher permeate flux, without diminishing permeate quality. The dispersed phase drop size in the emulsions was in the range of 1 to 5 μm, which is much higher than the pore size of all the membranes.

Module B (0.1 μm, polypropylene) and module D (0.2 μm, polypropylene) are from the same company (Microdyn Technologies) and are reported by the manufacturer to have the same porosity (70% to 80%). The theoretically expected fluxes from the two modules can be compared by calculating the flow through the pores using the Hagen-Poiseuille equation

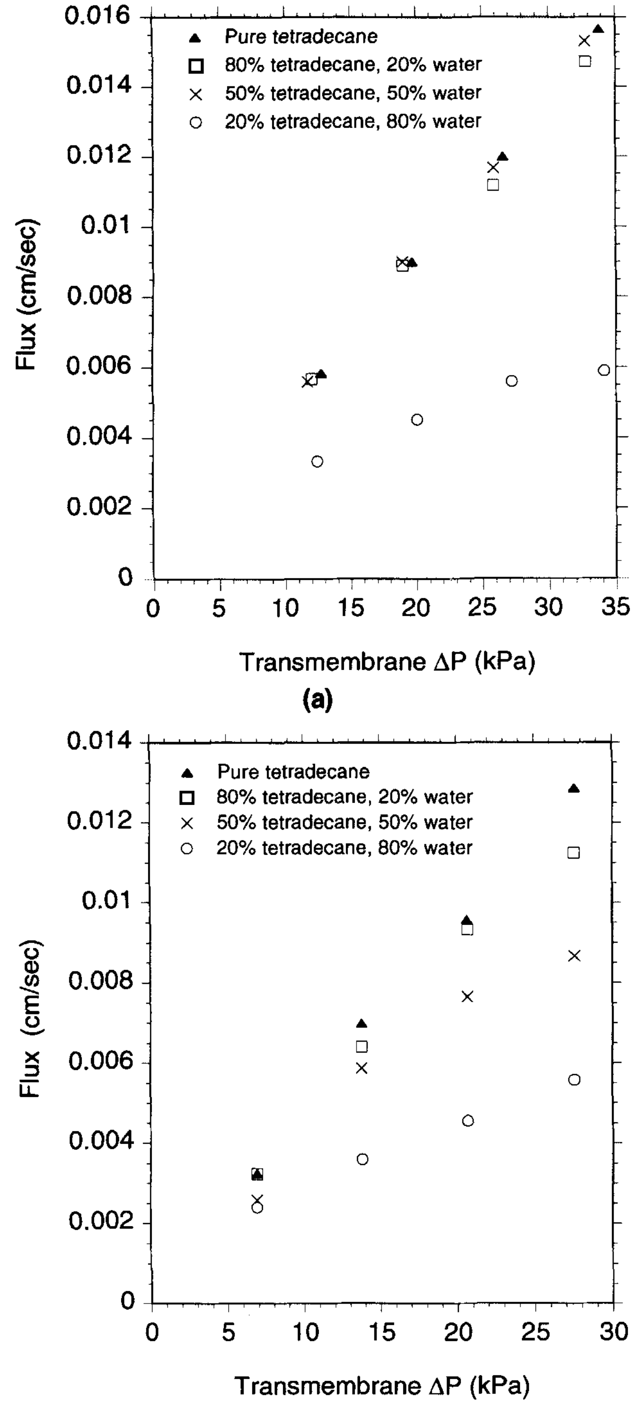
$$Q = nq = n\Delta P\pi r^4/8\tau\mu L, \qquad (4)$$

where Q is the permeate flux, n is the number of pores per unit area, q is the volumetric flow rate through each pore, ΔP is the pressure drop across the pore or transmembrane pressure drop, r is the pore radius, μ is the fluid viscosity, τ is the tortuosity of the pores, and L is the pore length. If both membranes have equal porosities, then the 0.1-μm module has four times as many pores per unit membrane area as the 0.2-μm module. We assume that the actual pore lengths are in the same ratio as the membrane thicknesses, which are 0.2 mm for module B and 0.5 mm for module D. We also assume that the two membranes have the same tortuosities, since they are of the same material and made by a similar process (ACCUREL process: Microdyn Technologies, Inc.). Thus, for the same transmembrane pressure drop, the Hagen-Poiseuille equation shows that the permeate flows from modules B and D should be in the ratio of 5:8. The data of Figure 3 for pure oil fluxes and the values in Table 3 for the zero surfactant case all show this same ratio between fluxes for the two modules. This calculation highlights the reason for higher fluxes through larger pore-size membranes: a few large-diameter pores offer less resistance to flow than many small diameter pores.

Permeation characteristics

Mixtures of water-tetradecane containing 0% (v/v) to 80% (v/v) water (no surfactant) were passed through module D (polypropylene, 0.2 μm). The flux was measured at various transmembrane pressure drops, at constant crossflow velocity, while recirculating the permeate and retentate back to the feed tank, to maintain constant feed properties. Figure 5a shows the permeate flux as a function of the transmembrane pressure drop. At 50% (v/v) tetradecane content, the flux is essentially equal to the pure tetradecane flux. At 20% (v/v) tetradecane, the flux is noticeably reduced. This flux reduction is attributed to the change in continuous phase, from a tetradecane-continuous phase at high tetradecane content, to a water-continuous phase at high water content. This transition from an oil-continuous (water-dispersed) state, to a water-continuous (oil-dispersed) state, is known as phase inversion. When tetradecane is the dispersed phase rather than the continuous phase, permeation is dependent on collisions between the oil droplets with the membrane surface, which results in a concomitant flux reduction. Phase inversion often occurs at about 74% (v/v) of the initially dispersed phase or 26% (v/v) tetradecane, since this is the volume occupied by closely packed spheres. The flux reduction due to phase inversion was found to depend on the feed flow rate. At low crossflow rates the oil permeation may be sufficiently complete (due to increased residence time) to cause the mixture to reach the phase inversion composition at some point within the module. Figure 5b shows fluxes for oil permeation from oil-water mixtures at a lower inlet velocity of 0.1052 m/s and flux reduction is observed even for the 50%-50% (v/v) oil-water mixture.

Figure 6 shows permeation data for 80% (v/v) oil-20% (v/v) water emulsions, for various surfactant contents ranging from zero to 30 kg/m^3 in module D at an emulsion inlet velocity of 0.239 m/s. Emulsions containing surfactant display a limiting flux that is independent of the applied pressure (driving force). This phenomenon is known as limiting flux behavior. When the flux of tetradecane containing 30 kg/m^3 surfactant (ECA 5025) and no water (i.e., no emulsion formation) was compared to pure tetradecane flux, a flux drop of about 4.5% was observed over a comparable range of transmembrane pressures and this mixture did not display limiting flux behavior. Thus, limiting flux behavior is exhibited only by the emulsions most probably caused by the formation of a concentrated emulsion layer at the membrane surface, due to depletion of the oil phase by permeation. As the oil phase is removed from the emulsion, the water droplets become closely packed at the membrane surface, and this concentrated emulsion layer hinders the flow of the oil phase. Limiting flux behavior is not observed for oil-water mixtures without surfactant as in Figure 5a and 5b, because the water droplets are able to coalesce in the absence of surfactant as evidenced by gravity settling and do not form a stable emulsion layer at the membrane surface. As the surfactant concentration increases, droplet coalescence is increasingly inhibited, leading to a more stable concentrated emulsion layer at the membrane surface.



(a)

(b)

Figure 5. Permeation of tetradecane (oil) from water-tetradecane mixtures (no surfactant) in module D.

Flux of oil decreases when the mixture phase inverts from oil continuous to water continuous. (a) Crossflow velocity: 0.239 m/s. (b) Crossflow velocity: 0.1052 m/s. Oil changes from continuous phase to dispersed phase at a higher inlet oil content.

Membrane fouling

Although the permeation rate with emulsions was lower than pure tetradecane flux as shown in Figure 6, the original flux could be recovered after flushing the modules with hexane or methanol. Module C (ceramic) showed some permanent fouling due to irreversible surfactant adsorption, and flux could not be recovered after repeated cleaning with aqueous surfactant solutions or solvent flushing (methanol, hexane).

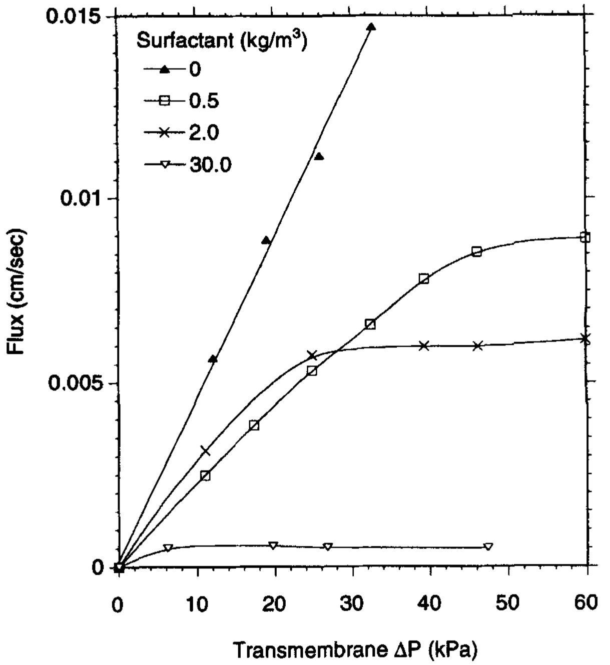


Figure 6. Permeation of tetradecane through Module D using emulsions with surfactant content from 0 to 30 kg/m^3 at a feed velocity of 0.239 m/s.

Emulsion composition: 80% (v/v) tetradecane, 20% (v/v) water, +surfactant (ECA 5025). Limiting flux behavior is exhibited by water-in-oil emulsions.

Among the hydrophilic modules, module E (ceramic) showed the maximum oil contamination in the permeate due to partial wetting of the membrane with the oil phase. Flux drop for module E was on the order of 82% due to partial oil wetting. The hydrophilic modules F and H (regenerated cellulose) showed high-purity permeate and minimal fouling due to oil. Module G (polysulfone) was mildly fouled in the presence of oil, but was severely fouled by the surfactant and initial flux could not be recovered after repeated flushing with methanol and water. For the remainder of this article, only the polypropylene and regenerated cellulose modules A, B, D, F, and H will be discussed.

Demulsification of water-in-oil emulsions using hydrophobic membranes

Water–Oil Mixtures without Surfactant. It was shown in Figure 5 that there is a large drop in flux when the continuous oil phase becomes the dispersed phase. Figure 7 shows the rate of recovery of tetradecane from mixtures of tetradecane and water for various oil–water ratios in the feed. There is an initial region of rapid recovery where the tetradecane content is high, after which the recovery rate diminishes. This observation is consistent with our premise that flux will be dependent on collisions of tetradecane droplets with the membrane, when tetradecane is the dispersed phase. Even though flux drops when tetradecane becomes the dis-

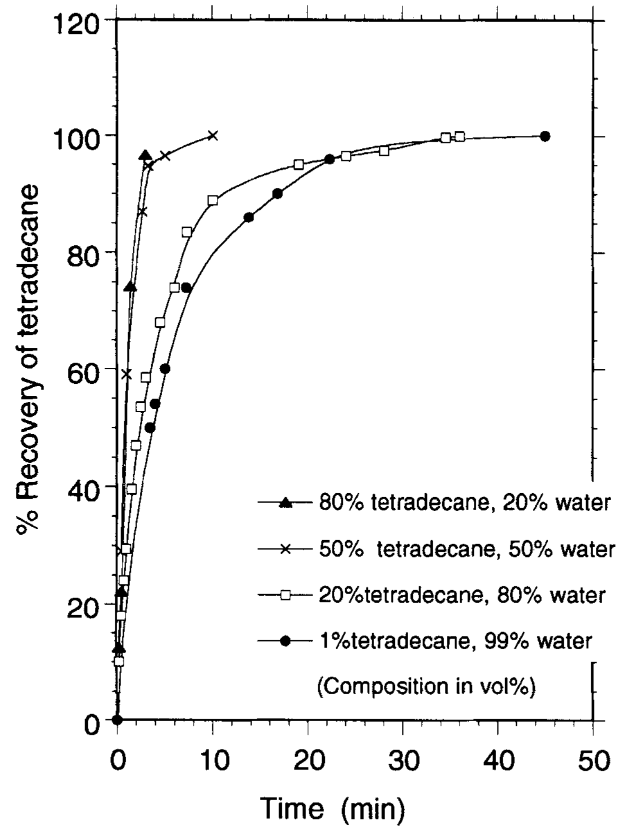


Figure 7. Recovery of tetradecane from water–tetradecane mixtures (no surfactant) in module D.

Feed velocity: 0.239 m/s; transmembrane pressure = 34.5 kPa. Rate of recovery reduces as oil goes from continuous to dispersed phase, but appreciable rates of recovery are observed even at low oil content.

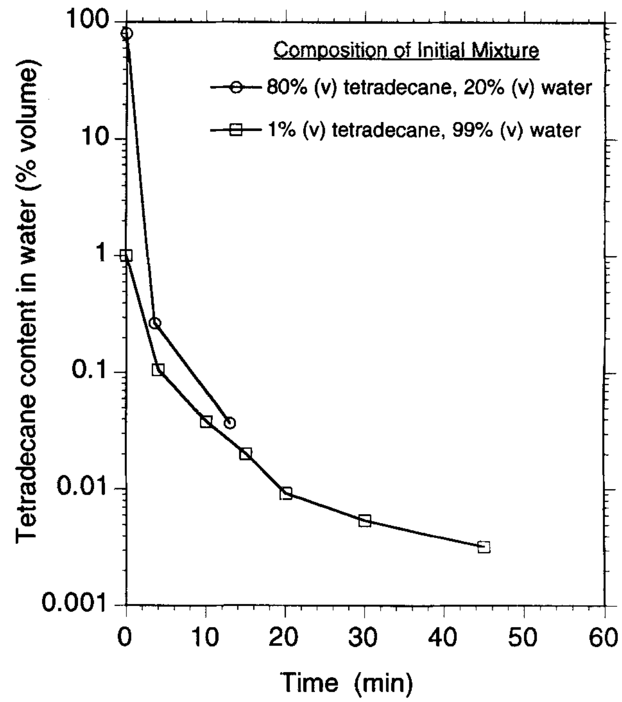


Figure 8. Tetradecane content of retentate as a function of time during permeation of tetradecane from water–tetradecane mixtures in Module D (no surfactant).

Removal of oil can be obtained even at low oil content so that the method can be applied to water purification.

persed phase, the permeate rate is still quite appreciable and the permeating oil has a very low water content. This suggests that oil may be removed as permeate from an aqueous stream contaminated by oil. In fact, if the oil can be reduced to the ppm level, such membrane techniques may be a viable option to adsorption. The purity of water was measured as a function of time for oil–water mixtures with low initial oil content. Figure 8 shows the drop in tetradecane content on the retentate side for 80% (v/v) tetradecane–20% (v/v) water and 1% (v/v) tetradecane–99% (v/v) water mixtures. For feed containing 1% (v/v) tetradecane–99% (v/v) water, the retentate-side water could be purified to as low as 25 ppm (32×10^{-4} % v/v) oil content by this method. This proves that at a low tetradecane content (1% of feed), in the absence of surfactant, permeation of tetradecane does take place. One of the potential applications for this process would be in the clarification of oily waste water streams and the recovery of organics from wash water.

Water-in-Oil Emulsions with Surfactant. The emulsions were prepared with oil-soluble surfactants as described in the experimental procedure and were kept stirred during the experiments with a magnetic stirrer. Surfactant concentration was varied from 0.5 to 30 kg/m^3, to form emulsions of varying degrees of stability. In all tests with the hydrophobic modules, the permeating tetradecane was a single clear phase. For emulsions with low surfactant content, phase inversion was observed as the oil phase was removed, whereby the dispersed water droplets became the continuous phase. For higher surfactant concentrations (10, 20, and 30 kg/m^3), phase inversion was not observed. In general, the emulsions appeared to be thickened or viscous as the tetradecane content decreased due to permeation. The viscosity increase causes the inlet pressure to the module to rise (in order to maintain constant flowrate) as the demulsification progresses. For a 30-kg/m^3 ECA 5025/80% (v/v) tetradecane/20% (v/v) water emulsion, the viscosity increased tenfold when 86% (v/v) of tetradecane was removed by permeation. Photomicrographs of the thickened viscous emulsion show the formation of a multiple emulsion (Figure 9). At the phase-inversion point (if it occurred), there was a sharp drop in viscosity indicated by a rapid drop in pressure. For emulsions with surfactant content of 0.5 kg/m^3 ECA 5025, the phase inversion was complete. For emulsions with 2-kg/m^3 and higher surfactant content, partial phase inversion was observed and a mixture of emulsions was formed consisting partly of phase-inverted emulsions and partly of thickened viscous emulsion. Thus, the phase inversion proceeds gradually with portions of the emulsion inverting and then forming an emulsion within an emulsion. A 5-kg/m^3 surfactant emulsion, when passed through module D at room temperature (25°C), did not phase invert even after 92% (v/v) of tetradecane was removed and the retained emulsion phase had 24% (v/v) oil/76% (v/v) water. At that point, the retentate was too viscous to flow through the membrane module. When the same 5-kg/m^3 surfactant emulsion was passed through the module at 50°C, the phase-inversion was observed and 98% (v/v) tetradecane was re-

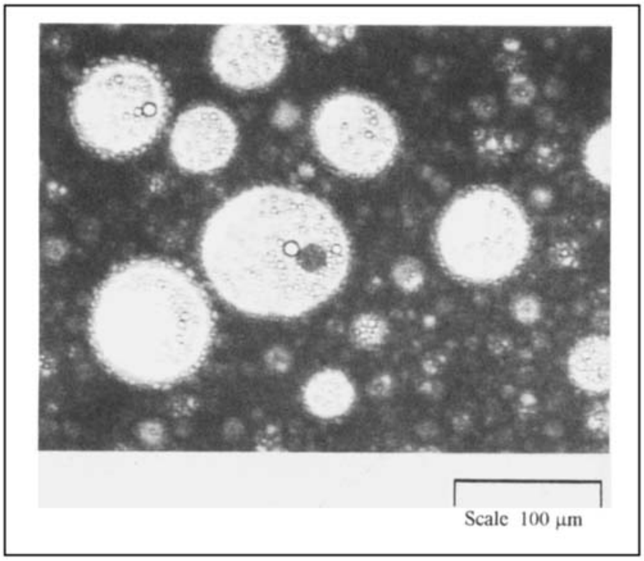


Figure 9. Viscous retentate emulsion after removal of 93% tetradecane.

Initial emulsion composition (before demulsification): 80% (v/v) tetradecane, 20% (v/v) water 20 kg/m^3 ECA 5025 in tetradecane. The concentrated emulsion shows formation of a multiple emulsion.

moved. The increased temperature helped to reduce the viscosity of the emulsion, thus allowing permeation to continue. The retentate had 3.85% tetradecane and 96.15% water. A second treatment step (e.g., with a hydrophilic membrane) is required to obtain high-purity water from the retained mixture.

Table 4 summarizes the results of the demulsification tests with hydrophobic membranes. The permeating tetradecane had a very high purity for all cases (below 500 ppm residual water). Emulsions with surfactant content higher than 5 kg/m^3 that could not be separated to the point of phase inversion by a hydrophobic membrane alone, require some additional separating mechanism to recover the aqueous phase. For cases where only the oil phase needs to be recovered, 85 to 90% recovery can be obtained with a hydrophobic membrane alone. For cases where the additional recovery of the aqueous stream is required, we have investigated the use of hydrophobic and hydrophilic membranes in series as well as hydrophobic and hydrophilic membranes in combination with an electrostatic coalescer.

Table 4. Demulsification in Hydrophobic Modules of Tetradecane–Water Emulsions 80% (v/v) Tetradecane, Containing 20% (v/v) Water

Surfactant content kg/m^3 in Tetradecane	Module	Run Time min	% Recovery Tetradecane at 26°C	Water in Permeate ppm
Low Surfactant Content: Phase inversion was observed				
0.5 (ECA 5025)	D	77	98.3	48.3
0.5 (ECA 5025)	B	68	97.1	47.8
2.0 (ECA 5025)	D	26	99.7	66
5.0 (ECA 5025)	D	104	98.1 at 50°C	56
High Surfactant Content: No phase inversion				
5.0 (ECA 5025)	D	30	92.2	47
10.0 (ECA 5025)	D	35	84.5	138
10.0 (ECA 5025)	D	45	90.1 at 50°C	166
10.0 (ECA 5025)	A	75	94	
10.0 (SPAN 80)	A	110	90.1	
20.0 (ECA 5025)	D	66	93	296.3
20.0 (ECA 5025)	B	79	85.8	384.1
30.0 (ECA 5025)	D	169	89.8	340.9

Table 5. Tetradecane Recovery by Gravity Settling vs. Hydrophobic Membrane Separation*

Surfactant Content kg/m^3 in Tetradecane	% Recovery of Tetradecane from Upper Clear Layer after Gravity Settling	% Recovery of Tetradecane by Hydrophobic Membrane (D)
5.0	60	92.2
10.0	40	84.5
20.0	45	93
30.0	20	89.8

*Gravity settling: 25 mL samples for 3 weeks; membrane separation: Module D emulsion composition: 80% (v/v) tetradecane, 20% (v/v) water, surfactant ECA 5025.

Comparison with gravity settling

Gravity-settling tests were conducted with water-in-oil emulsions containing 5, 10, 20 and 30 kg/m^3 ECA 5025 in tetradecane with 80% (v/v) oil and 20 (v/v)% water. Emulsions were allowed to gravity settle for three weeks. After gravity settling, the emulsions separated into three layers—the top clear-oil layer containing less than 280 ppm water, a middle layer containing > 1.0% water, and a bottom thick-emulsion layer containing 58% to 95% water. A clear-water phase was not obtained after gravity settling or centrifuging. Table 5 shows a comparison between gravity settling and membrane separation in module D (polypropylene). The percentage recovery of a clear-oil phase, as a function of surfactant content, is used to compare the two methods. As the surfactant (ECA 5025) concentration increases from 5 to 30 kg/m^3, the stability of the emulsion greatly improves and the recovery by gravity settling drops from 60% to 20%. However, the hydrophobic membrane is able to recover 85 to 90% tetradecane even from stable 30-kg/m^3 ECA 5025 emulsions. Emulsions with as low as 0.5-kg/m^3 surfactant separated out only 10% of the oil in 48 hours of gravity settling, and analysis of the layers showed a top layer with 48-ppm water, a middle cloudy layer with 0.17% water, and the bottom layer with 66% water.

Hydrophilic and hydrophobic modules in series

A water-in-oil emulsion with 2.0-kg/m^3 surfactant was passed through a hydrophobic module (D) and a hydrophilic module (F) in series. The hydrophilic module was placed before the hydrophobic one because of its high transmodule pressure drop. By this method, a pure water permeate was obtained from the hydrophilic module, while a pure tetradecane permeate was obtained simultaneously from the hydrophobic module. The experiment was stopped when the inlet pressure to the hydrophilic module reached its upper operating pressure of 180 kPa. At this point the inlet pressure to the hydrophobic module was 14 kPa. This completely continuous system recovered roughly 93% of the tetradecane and 77% of the water from the original emulsion. The results for

Table 6. Experimental Data: Hydrophilic and Hydrophobic Membranes in Series

Hydrophobic membrane	Module D
Hydrophilic membrane	Module F
Emulsion volume	833 cm^3
Emulsion composition	80% (v/v) tetradecane, 20% (v/v) water 2.0 kg/m^3 ECA 5025 in tetradecane
Run time	75 min
Tetradecane recovery	92.7%
Tetradecane quality	45 ppm water
Water recovery	77.4%
Water quality	less than 1 ppm tetradecane
Comp. of retained emulsion	43.3% water (by mass balance)
Vol. of retained emulsion	129 cm^3

this experiment are summarized in Table 6. When the hydrophobic module alone was used for the same emulsion, phase inversion was observed and 99.7% recovery of tetradecane was achieved. The aqueous phase was not as pure and contained 1.2% (v/v) tetradecane. Although this method is very simple, emulsions with higher concentration of surfactant (> 2 kg/m^3) did not demulsify with this apparatus. The difficulty in permeating water from a water-in-oil emulsion is that the dispersed-water phase is unable to directly contact the membrane surface due to the surrounding film of oil. At low surfactant content, the droplets are able to coalesce and the larger unstable droplets are able to contact the hydrophilic membrane surface. For emulsion with higher surfactant content, the droplets do not coalesce and the emulsified droplets do not wet the membrane surface.

Simultaneous electrostatic and membrane separation

Emulsions with surfactant (ECA 5025) concentrations higher than 2 kg/m^3 were demulsified with a combination of electrostatic and membrane separation techniques. The apparatus shown in Figure 1b was used. Two hydrophobic modules (module D) were operated in parallel to increase the separation rate. The aqueous stream was subjected to secondary purification in a hydrophilic membrane (module H). The electric field causes the coalescence of water droplets and the membranes provide a polishing step to produce high-purity oil and water phases. Experiments were conducted with 1,000 mL of emulsion containing 80% (v/v) tetradecane, 20% (v/v) water, with 30 kg/m^3 ECA 5025. When only the electric cell was used (no membranes), the separated aqueous stream had 1.8% tetradecane and the oil phase had 1.2% water after 60 minutes of operation. When the electric cell with membranes was operated with 1000 mL of emulsion for 60 minutes, 702 mL of oil phase containing 830 ppm water and 154 mL water containing 3.2 ppm were recovered. The results are summarized in Table 7. [The emulsion lost (144 mL) was due to the holdup volume of the apparatus.] If the electric cell had not been used for this emulsion (i.e., only membrane separation), aqueous phase recovery would have been impossible.

Demulsification of water – oil – solid emulsions using hydrophobic membranes

Table 7. Experimental Data*

Hydrophobic membrane	Module D
Hydrophilic membrane for final treatment of water (optional)	Module H
Emulsion volume	1,000 cm^3
Emulsion composition	80% (v/v) tetradecane, 20% (v/v) water, 30 kg/m^3 ECA 5025 in tetradecane
Run time	60 min
Tetradecane recovery	87.8%
Tetradecane quality	830 ppm water
Recovery of water after treatment in module *H*	77%
Water quality	3.2 ppm tetradecane
Comp. of retained emulsion	31.9% water (by mass balance)
Vol. of emulsion retained	144 cm^3

*Simultaneous operation of hydrophobic membrane and electric demulsification.

Water–oil–solids emulsions containing up to 60% (v/v) oil were demulsified by a hydrophobic membrane (module D). Oil permeation was carried out at a low transmembrane pressure of 34.5 to 41.4 kPa (5 to 6 psi) as this prevented plugging of the outlet valve. Microfiltration membranes are well suited for this separation since permeation rates are high at low transmembrane pressures. The pore size of the microfiltration membrane was smaller than the solid-particle size. The inlet velocity of the emulsion was 0.3 m/s. Table 8 shows the percentage recovery of the oil phase (tetradecane) for solids loadings up to 40 kg/m^3 of oil–water mixture. At low oil content (20% v/v), the percentage recovery of oil is low because the oil forms a coating on the solid particles and cannot be recovered. At high oil content, the oil lost in coating the solids is a small percentage of the total oil in the emulsion. The water content of permeating oil was 30 ppm. Emulsions with water–oil–solids and surfactant were not tested.

Effect of interfacial properties on separation

Breakthrough pressures of aqueous solutions through a hydrophobic membrane wetted by the organic were measured as described in the experimental procedure using module D (0.2 μm, polypropylene). Similarly, breakthrough pressures of the oil phase through a hydrophilic water wet membrane were measured using module H (0.8 μm, regenerated cellulose). The relationship between breakthrough pressures, interfacial tension, and contact angles was compared to the predictions of the Young–Laplace equation for uniform capillaries, Eq. 2.

The aqueous–organic combinations studied along with the measured interfacial tensions, contact angles, and break-

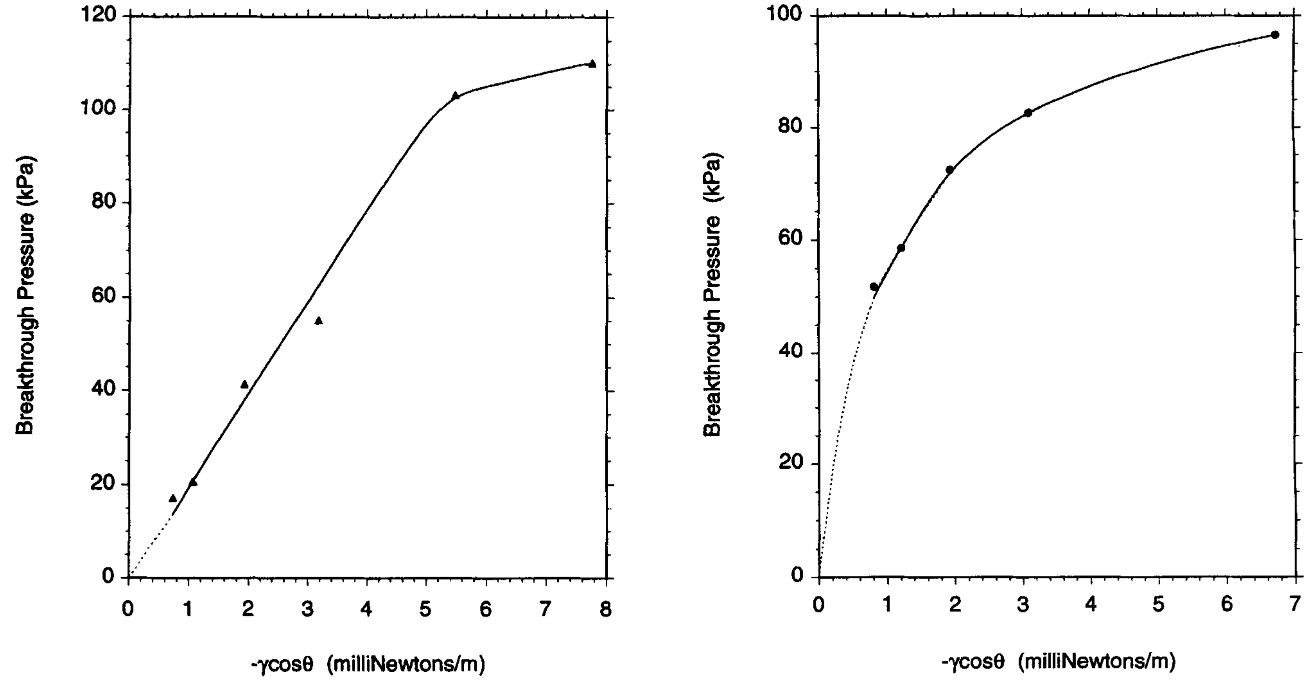
Table 8. Oil Recovery from Water/Oil/Solid Emulsions Using Hydrophobic Membrane (Module D)

Oil % Vol.	Water % Vol.	Solids kg/m^3	Run Time min	Recovery of Oil %
20	80	10	23	84
20	80	20	60	77
20	80	40	60	84.7
40	60	20	20	99.1
40	60	40	23	94.7
60	40	20	15	94.8
60	40	40	17.5	98.7

Table 9. Breakthrough Pressure Tests for Water–Oil Systems

Aqueous Phase (aq)	Organic Phase (org)	Interfacial Tension $\gamma_{aq/org}$ N/m × 1,000	Contact Angle θ, deg. aq/org/Memb.	Breakthrough Pres. kPa
With Module D (Hydrophobic)				
2.0 kg/m^3 Igepal CO610	Tetradecane	0.9093	144	17
1.0 kg/m^3 Igepal CO610	Tetradecane	1.355	142	21
0.5 kg/m^3 Igepal CO610	Tetradecane	2.143	154	41
0.2 kg/m^3 Igepal CO610	Tetradecane	3.452	157	55
0.05 kg/m^3 Igepal CO610	Tetradecane	5.668	165	103
DI Water	Tetradecane with 30 kg/m^3 ECA 5025	8.79	152	110
DI Water	Tetradecane	47.3	178	> 180
With Module D (Hydrophilic)				
2.0 kg/m^3 Igepal CO610	Tetradecane	0.9093	152.5	52
1.0 kg/m^3 Igepal CO610	Tetradecane	1.355	155	59
0.5 kg/m^3 Igepal CO610	Tetradecane	2.143	161.5	72
0.2 kg/m^3 Igepal CO610	Tetradecane	3.452	154	83
DI Water	Tetradecane with 30 kg/m^3 ECA 5025	8.79	140	96

through pressures are given in Table 9a for the hydrophobic membrane and 9b for the hydrophilic membrane at 25°C. Interfacial tension measurements made by the Du Nouy ring and spinning drop techniques are reported. The interfacial tension values reported in the literature for a pure tetradecane–water system are 52.92 mN/m at 25°C (reported by Aveyard and Haydon, 1965), and 54.17 mN/m (reported by Weissberger, 1945). The value of 47.3 mN/m measured in this work is for technical-grade tetradecane (Humphrey Chemicals), which has some dodecane, hexadecane, and octadecane impurities. Breakthrough pressure decreases as the interfacial tension and contact angle decreases. The measured breakthrough pressures as functions of $-\gamma \cos\theta$ for the hydrophobic and hydrophilic membranes are shown in Figure 10a and 10b, respectively. The data for the hydrophobic membrane are linear over most of the range studied. The linear region passes through the origin as predicted by the Young–Laplace equation and has a slope of 19.75×10^6 m^{-1}. Comparing with Eq. 2, the slope is equal to $2/r$, where r is the pore radius. The pore diameter calculated from the slope is 0.203 μm for module D, which has a pore size rating of 0.2 μm. For pure-water–pure-tetradecane, Eq. 2 predicts a breakthrough pressure of 642.6 kPa for water. The water–tetradecane system was tested up to a pressure of 186.2 kPa



(a) **(b)**

Figure 10. Breakthrough pressure as a function of $\gamma \cos\theta$.

(a) Module D, (0.2-μm) hydrophobic membrane. (b) Module H, (0.8-μm) hydrophilic membrane.

and no breakthrough occurred. The system could not be tested above 206.8 kPa due to limitations of the membrane and the experimental setup. The breakthrough pressure plot for the hydrophilic membrane (Figure 10b) is curved over the whole region. Data in the region near the origin are not available (lower contact angles could not be obtained with the selected oil and surfactants), but the curve appears to pass through the origin.

The observed nonlinear behavior of the breakthrough pressure may be caused by changes in pore shape as the pressure is increased. The pore shape has not been taken into consideration in this work. Kim et al. (1987) observed similar behavior for liquid–liquid breakthrough using a Teflon membrane [for systems containing liquid–liquid combinations using water, carbon tetrachloride, hexane, octane, and methyl isobutyl ketone (MIBK)] and their experimental data shows an initial linear region followed by a sharp leveling.

Conclusions

The following conclusions can be drawn from the experimental data presented:

- Organic–water separation by membranes can be obtained due to the preferential wetting phenomenon, which is the basic premise of this study.
- Microfiltration membranes (larger pores than UF) can be utilized to resolve emulsions at high flux without diminishing permeate quality. For the cases studied in this work, the dispersed phase drop size was larger than the membrane pore size.
- Separation of water-in-oil emulsions containing surfactant in a hydrophobic membrane exhibited limiting flux behavior. This reduction in flux was reversible, and flux could be recovered for the polypropylene membranes by backflushing. For these polypropylene membranes, permanent fouling due to surfactant adsorption was not observed. The flux reduction is due to accumulation of a concentrated emulsion layer at the membrane surface.
- Oil removal from water–oil mixtures with no surfactant could be carried out with polypropylene membranes even at oil content as low as 1% (v/v). The water stream could be purified to 25 ppm oil content in a reasonable amount of time.
- Hydrophobic membranes can allow essentially complete permeation of organic phases from emulsions, provided phase inversion occurs. Such phase inversion readily occurs in systems containing < 2 kg/m^3 surfactant. Above 2 kg/m^3 surfactant content, the phase-inversion point could not be reached even though 90% (v/v) recovery of oil phase was possible.
- At surfactant concentrations higher than 2 kg/m^3 ECA 5025, a combination of electric and membrane techniques was successful in recovering both the oil and the aqueous phase. This method gave oil with 830 ppm water content and water with 3.2 ppm tetradecane. Electrostatic coalescence alone does not give high-purity water and oil phases. Membrane separation techniques along with electrostatic coalescence greatly improve the quality of the oil and water phases.
- Hydrophobic polypropylene modules could be used to recover 85 to 90% oil from water–oil–solid emulsions. Microfiltration membranes were especially suitable for this purpose because high fluxes could be obtained at low transmembrane pressure drops.
- Breakthrough pressure of the nonwetting fluid, for a given membrane, is a function of the interfacial tension between the wetting and nonwetting fluids and the liquid–liquid–membrane contact angle. The relationship between experimental measurements for breakthrough pressure, interfacial tension, and contact angle displayed linear behavior as predicted by the Young–Laplace equation for capillary rise in the low-pressure region only.

This work has demonstrated separation of oil–water emulsions by the preferential wetting principle, in a hydrophobic membrane. The technique has obvious applications to demulsification of water-in-oil emulsions, which could not be separated by hydrophilic membrane techniques, and to the recovery of the organic phase in a very pure form. Furthermore, the principle of separation due to preferential wetting can be extended to nonaqueous liquid–liquid systems, provided they are not completely miscible and differ in their wetting properties on a membrane.

Acknowledgments

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