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Journal of Colloid and Interface Science
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A membrane method for degassing nonaqueous liquids

M. Rzechowicz, R.M. Pashley *

Department of Chemistry, The Faculties, The Australian National University, Canberra, ACT 0200, Australia

Received 29 September 2005; accepted 1 December 2005

Abstract

Degassing of nonaqueous solvents is useful for their applications in chemical synthesis and in maintaining purity (against oxidative degradation) during long term storage. In addition, degassed solvents have been found to be of value in the production of oil and water emulsions. Currently, there are three main methods for degassing solvents. These are the freeze–pump–thaw process, partial degassing using sonication under slight vacuum and purging, where one active gas (usually oxygen) is replaced with an inert gas (e.g., nitrogen). In this work we have demonstrated the potential application of hollow-fibre membranes to efficiently degas water-immiscible, hydrophobic liquids. Mixtures of dodecane and water, separately degassed using membranes, show an enhanced dispersion of dodecane, similar to that previously reported for freeze–thaw degassed mixtures.

Keywords: Membranes; Degassing; Nonaqueous liquids; Laplace pressure; Ultrahydrophobic

1. Introduction

The shape of a meniscus in a capillary depends on the degree of wetting of the walls of the capillary. Water makes a zero contact angle (θ) with clean glass and so wets the walls of a glass capillary. If the walls are coated with grease or made hydrophobic in some way, the water forms a higher angle and the water does not rise as much in the capillary. If the contact angle was greater than 90° the water would not enter the capillary at all and a substantial pressure would have to be applied to force water into the capillary. This situation is the basis of the water proofing action of Goretex. Water has a contact angle of 110° on Goretex (a Teflon porous membrane) and so will not easily enter the pores [1]. Polypropylene is equally hydrophobic and so water repellent membranes are also made of this material.

The Laplace equation gives the pressure difference (ΔP) across any curved fluid interface, $\Delta P = 2\gamma/R$, where γ is the surface tension of the liquid and R is its radius (assumed spherical). If r is the radius of the capillary tube or pore, it follows from simple geometry, again assuming that the meniscus is spherical, that this pressure is then given by

$$\Delta P = \frac{2\gamma \cos\theta}{r}.$$

One industrial application of the Laplace pressure generated in a pore is the use of Teflon porous membranes to remove dissolved gases from water down to the ppb range [2,3]. This process depends on the Laplace pressure preventing water flow into the Teflon pores. One side of the porous membrane has water at roughly atmospheric pressure and on the other side is a vacuum, as illustrated in Fig. 1.

The Laplace pressures generated depend critically on the water contact angle on the Teflon surface, as illustrated in Fig. 2. Thus, the Laplace pressure generated across the curved water meniscus in Fig. 1 (i.e., between points A and B) in a Teflon pore of 1 µm diameter is about 1 atm. This pore size (or less) will therefore allow liquid water on one side to be in equilibrium with a vacuum on the other side (or water vapour). The water will therefore not boil and will not flow across the membrane. However, the dissolved gases in the water are free to travel across the membrane and will do so because of their absence on the vacuum side of the membrane. The levels of dissolved oxygen and nitrogen (and carbon dioxide) in the water initially correspond to atmospheric pressure values and so are very far from equilibrium. Assuming that the vacuum is main-

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[*] Corresponding author.
E-mail address: richard.pashley@anu.edu.au (R.M. Pashley).

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doi:10.1016/j.jcis.2005.12.001

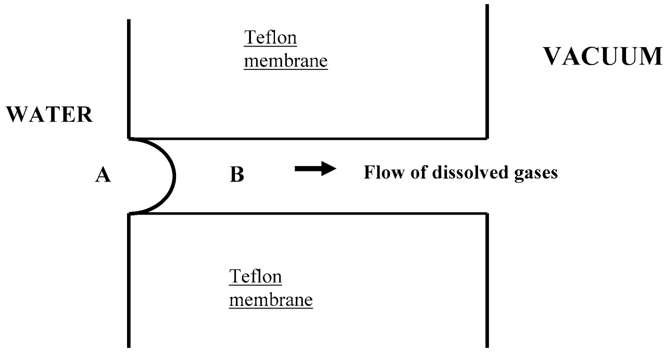

Fig. 1. Schematic diagram of the hollow-fibre membrane used to degas water.

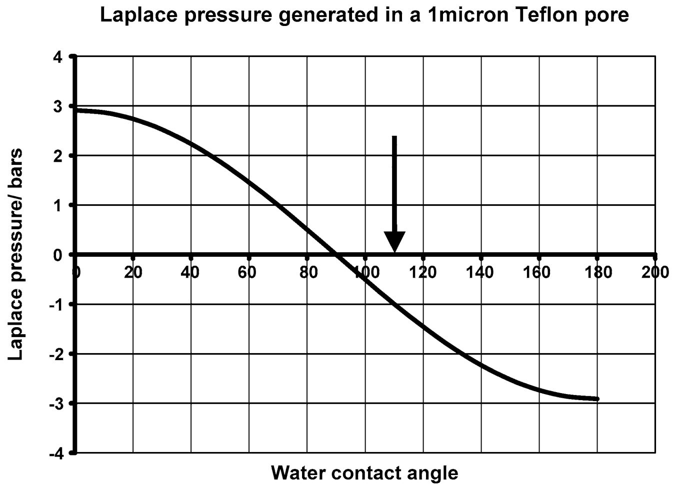

Fig. 2. Calculated Laplace pressure generated across a water meniscus in a 1 μm diameter pore with different wetting angles.

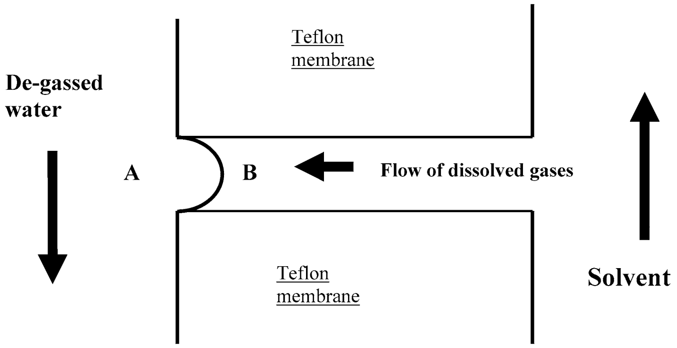

Fig. 3. Schematic diagram of the use of counterflow degassed water to degas nonaqueous solvents using hollow-fibre membranes.

tained, all of the dissolved gases will eventually be drawn from the water. In practice, residual levels of oxygen are typically about 1 ppb, which corresponds to a degassing level of about 99.985%.

This method works because water has a high surface tension (73 mJ m^{-2}) and Teflon has a very low tension (of about 18 mJ m^{-2}). The water–Teflon interfacial tension is also high at about 45 mJ m^{-2} (see later) and hence the water contact angle on Teflon is very high, at 110°. However, water immiscible liquids such as hydrocarbons and fluorocarbons have low surface tension values, close to the Teflon value, and so will have low contact angles on Teflon (see data later) and so will wet the pores. Hence this degassing method will not work for these liquids, when a vacuum exists on the other side of the membrane. However, in the present work we have studied the novel use of degassed water in place of the vacuum on the outer of the hollow-fibre membrane, with gassed nonaqueous solvent inside the fibres. This situation is illustrated in Fig. 3.

When the porous hydrophobic membrane (e.g., Teflon or polypropylene) has degassed water on one side and gassed solvent on the other, the solvent will not flow into the water (and vice versa) when a slight differential pressure (greater than the Laplace pressure) is maintained. However, dissolved gases in the solvent will flow out into the degassed water until the degree of degassing is similar in both liquids. This situation also has the advantage that since the solvent and water are immiscible, there will be no loss of solvent through the pores. For maximum efficiency, the degassed water (outside) and the gassed solvent (inside) should flow in opposite directions, to produce a counterflow solute exchange process.

Successful and efficient degassing of solvents will depend on using a process with a very high surface area of contact per unit volume of fluid. Commercially this is achieved by the use of hollow-fibre filters. These have been successfully used to degas water for the last ten years, using microporous Teflon and polypropylene hollow fibres [2,3]. Recently, a related technology has been developed called the "hollow-fibre-contained liquid membrane" (HFCLM). In this process two liquids are used to strip solutes from one to the other. This process could be easily adapted to run degassed water either inside or outside of the fibres, with the solvent flow either outside the fibres or inside. Hydrocarbon solvents would be degassed using Teflon fibres, whereas fluorocarbons would be degassed using polypropylene fibres. This type of filtration device is illustrated in Fig. 4.

It should be noted that before membrane systems were developed, vacuum towers were used to degas water via a system of increasing vacuum, as water droplets fall through the various pumping and outgassing stages. In principle, this method could also be used for solvents, although there appears to be little evidence of any commercial examples. Laboratory techniques for degassing all liquids typically involve a freeze–thaw, pumping process, repeated until completely degassed [4]. However, this process is unlikely to be suitable for large scale commercial applications. It would also be possible to sequentially degas water immiscible solvents by stepped equilibration with degassed water. The liquids would be shaken together to equilibrate dissolved gas levels and then separate by centrifugation. The process could then be repeated with degassed water until the solvent was similarly degassed.

During gas transfer between the degassed water on the outside of the porous hollow fibres and the gassed solvent within the fibres, a modest hydrostatic pressure difference (its value depends on the pore size) must be maintained on the water side to prevent flow of the solvent through the pores. However, once complete degassing has occurred it might be possible to actually produce an oil in water dispersion continuously simply by removing this pressure and allowing oil droplets to be released into the degassed water. This situation is illustrated in Fig. 5.

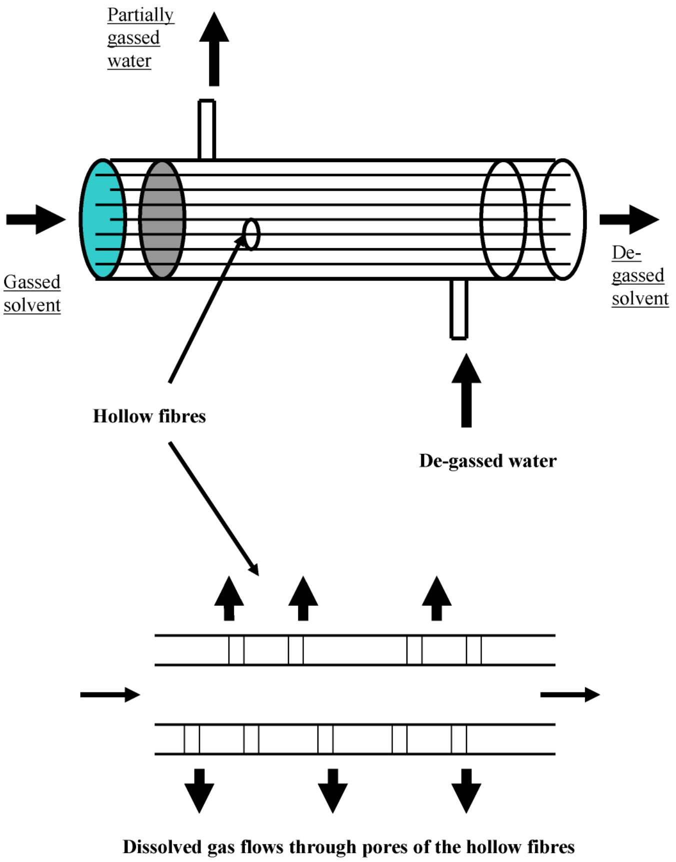

Fig. 4. Schematic diagram of a hollow-fibre cartridge used to degas nonaqueous solvent by the counterflow process.

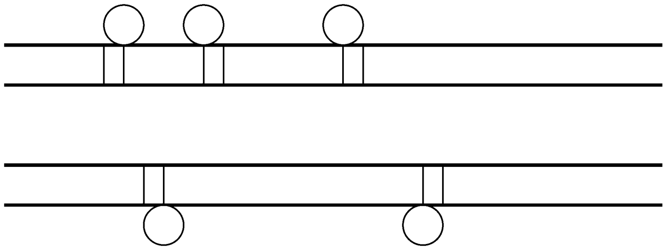

Fig. 5. Schematic diagram of the use of the hollow-fibre membrane to create an emulsion.

The pore sizes could be varied to obtain different droplet sizes. This method could be used to produce a continuous flow of concentrated emulsion, without the use of detergent.

In this study we have measured the wettability of water on smooth Teflon and polypropylene substrates, when immersed in a range of nonaqueous, water-immiscible, solvents. This data was then used to estimate the range of differential pressures required to prevent flow through the porous membranes and so enable the removal of dissolved gases from these solvents. We have demonstrated the use of this counterflow process to degas nonaqueous solvents. We have also examined the enhanced dispersion of fine oil droplets in water using membrane degassing for the first time.

2. Methods and materials

Water was prepared by activated charcoal and reverse osmosis filtration prior to distillation and storage in Pyrex vessels in a laminar flow filtered air cabinet. Dodecane was purchased as 99.9% purity and used as supplied. Wherever possible, liquids and equipment were handled in a laminar flow cabinet to reduce airborne contamination. The Teflon hollow-fibre cartridges were small MiniModule units supplied by Membrana, Charlotte, USA. The hollow fibres had an internal diameter of 220 μm and pores of 0.03–0.05 μm. Typically, the units contained between 2000 and 7000 fibres of 140 mm active length. The InPro 6900 dissolved oxygen electrode system was supplied by Mettler–Toledo Ltd., Melbourne, Australia. This system had a high accuracy (∼1%) and detection limit down to 1 ppb and could measure dissolved oxygen levels in water, air and liquid solvents. The vacuum pump used to evacuate the outer chamber of the hollow-fibre unit was an Alcatel diaphragm pump rated at 9 millibars. Conductivity measurements were obtained using a CDM 210 radiometer with CDC866T four-pole probe. Turbidity measurements were obtained using a HF-Micro 100 unit supplied by HF Scientific, Florida, USA. The atomic force microscope (AFM) study was carried out using a Nanoscope IIIa supplied by Digital Instruments (Veeco), Santa Barbara, USA. Tapping mode analysis was carried out using NT-MDT cantilevers. All images were produced in air.

Contact angle measurements were carried out manually using a microscope and protractor system to image a sessile droplet on a flat plate substrate housed in a sealed glass cell. This system gave a typical contact angle accuracy of about 1–2°. The Teflon substrates were obtained by polishing the rough surface with finely powder Teflon manually for long periods of time. Earlier studies used fine alumina powder but it is likely that this powder can become entrapped in the Teflon surface [5]. The polypropylene surfaces were prepared by melting the plastic against a smooth glass slide in a nitrogen gas environment.

In the dispersion experiments, mixtures of oil in water were usually achieved by vigorous shaking of the mixture for 8–10 s in a sealed Pyrex tube. All of the oil and water dispersions experiments were carried out on liquid samples which came from the hollow-fibre system, so that any contamination should not affect the comparative validity of these results. The "blank" samples used water and oil collected from the hollow-fibre cartridges whilst the vacuum was not running. The nondegassed blank oil and water mixtures were simply shaken. Whilst the freeze–thaw degassed samples were degassed for four freeze cycles [4], then shaken for 10 s and recorded. In the freeze–thaw process liquid nitrogen was used to freeze the oil and water mixtures, followed by pumping down to a pressure of 0.01 mbar. Any dissolved gas produced on each melting cycle was removed upon refreezing and pumping. Typically, no further bubbling, on melting, was observed after 3–4 cycles. The vacuum pressure of 0.01 mbar corresponds to a degassing level of about 99.999%, if it is assumed that the final pressure achieved after several cycles of freeze/thaw/pumping is given by the pressure in equilibrium with the final frozen liquid, which on being melted does not give any visible bubbling or outgassing.

The hollow-fibre-degassed samples used both oil and water degassed by the cartridges. The oil (0.2 ml dodecane) was syringed into a tube which was then evacuated. This vacuum was then used to suck the (degassed) water (25 ml) into the tube. The tube was then quickly evacuated again. As soon as the liquids were observed bumping (2–3 s after opening the vacuum tap), the tube was closed, the mixture was shaken for 10 s and the turbidity recorded over time.

3. Results and analysis

The results for the AFM study of the surface roughness of polypropylene and Teflon surfaces (using tapping mode) show that the rms roughness value for each substrate was 1.8 nm for polypropylene and 52 nm for Teflon. The polypropylene melted surface was clearly much smoother than the polished Teflon. However, in both cases a 1:1 image showed a featureless image of slightly undulating hills and valleys.

From the various interfacial tensions, the Young equation for the contact angle θ is given by

$$\gamma_{\mathrm{ap/ss}} = \gamma_{\mathrm{ap/d}} \cos\theta + \gamma_{\mathrm{ss/d}},$$

where $\gamma_{\mathrm{ap/ss}}$, $\gamma_{\mathrm{ap/d}}$ and $\gamma_{\mathrm{ss/d}}$ are the interfacial tensions for the ambient phase/solid substrate, ambient phase/droplet and solid substrate/droplet, respectively.

It follows that water droplets on Teflon and polypropylene immersed in air, should have a very high contact angle, as is demonstrated by the results given in Tables 1 and 2 and the photograph in Fig. 6. The relatively low contact angle hysteresis observed for the polished Teflon substrates and the melted polypropylene substrate indicates that both surfaces were reasonably smooth and clean. By comparison, the results obtained for water droplets immersed in dodecane, on both polypropylene and Teflon, are remarkable because in both cases the angle observed was close to 180°, with no apparent hysteresis. In both cases the droplets readily roll off the substrate, when tilted even a few degrees. A photograph of a typical droplet is shown in Fig. 7. Ultrahydrophobic surfaces for water droplets in air have only been reported previously on rough surfaces [6].

These observations for polypropylene substrates are consistent with the Young equation because for the case of water droplets immersed in dodecane, the ambient phase is chemically similar to the solid substrate. Hence, it is expected that $\gamma_{\mathrm{ap/ss}}$ will be close to zero and since $\gamma_{\mathrm{ap/d}} \approx \gamma_{\mathrm{ss/d}}$, it follows that $\cos\theta \Rightarrow -1$ and hence $\theta \Rightarrow 180°$.

Table 1
Contact angle measurements on polypropylene surfaces

Droplet	Ambient phase	Contact angle advancing	Contact angle receding
PFH	Air	<10	<10
PFH	Water	78	32
Water	Air	120	80
Dodecane	Air	10	10
TCE	Air	12	0
TCE	Water	35	0
Water	Dodecane	180	180

Table 2
Contact angle measurements on Teflon surfaces

Droplet	Ambient phase	Contact angle advancing	Contact angle receding
PFH	Air	10	10
PFH	Water	90	21
Water	Air	116	95
Dodecane	Air	38	17
TCE	Air	55	30
TCE	Water	95	<10
Water	Dodecane	180	180

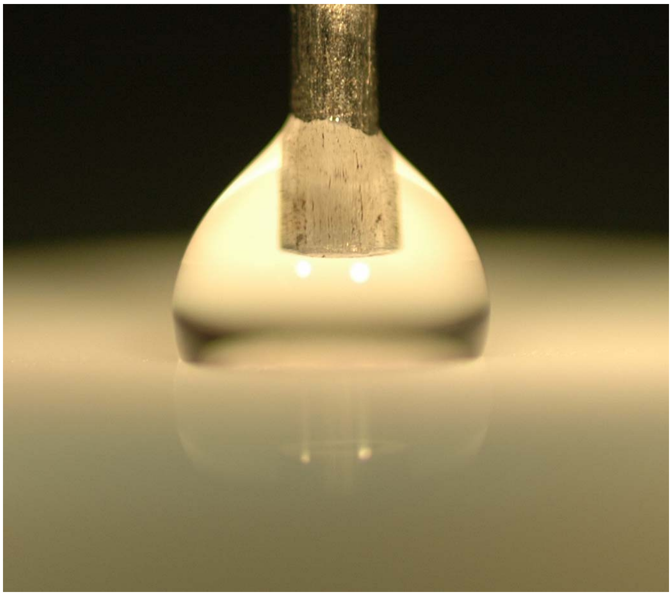

Fig. 6. Photograph of a water droplet on Teflon in air.

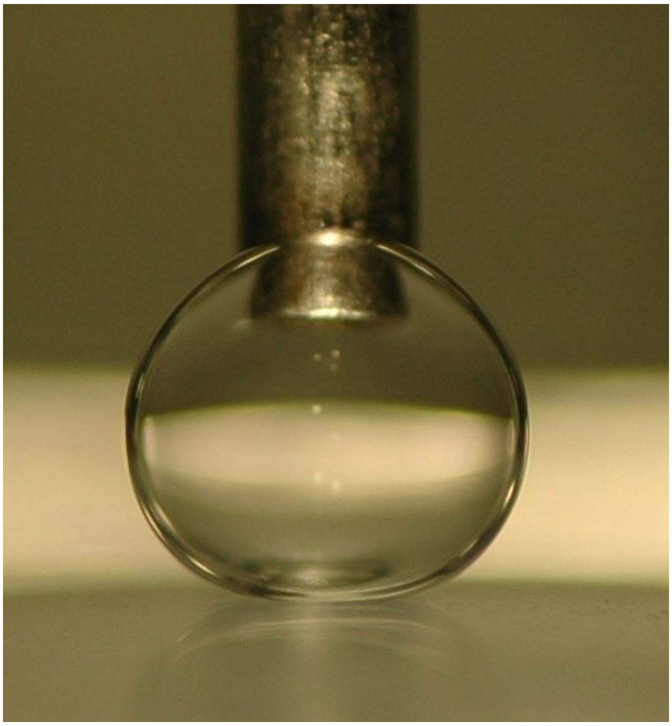

Fig. 7. Photograph of a water droplet on polypropylene immersed in dodecane.

However, a similar situation was also observed for water droplets on Teflon immersed in dodecane. In this case it is expected that the interfacial tension between the droplet and the ambient phase should be about 53 $\text{mJ}\,\text{m}^{-2}$ (i.e., water/dodecane [7]) and between the droplet and solid substrate about 43 $\text{mJ}\,\text{m}^{-2}$ (i.e., water and Teflon). This latter value was calculated from the critical surface tension for Teflon of 18 $\text{mJ}\,\text{m}^{-2}$ and the water droplet contact angle on Teflon, of 110°, using the Young equation [8]. A small interfacial tension between the ambient phase and the solid substrate would therefore produce a high contact angle, of about 140° according to the Young equation but not the 180° value observed. It is possible that dodecane penetrates or is retained in some way by the Teflon surface, and hence the droplet is actually advancing over essentially a dodecane surface.

The measured contact angles reported in Tables 1 and 2 can be used to predict the ability of vacuum degassing, or counterflow degassing, to degas nonaqueous liquids. For example, the high contact angle ($>90°$) observed for water on polypropylene and Teflon surfaces in air, shows that vacuum degassing of water is possible with either membrane material. By comparison, the results in Table 1 indicate that perfluorohexane (PFH), dodecane (DD) and tetrachloroethylene (TCE) cannot be degassed using polypropylene membranes because these liquids will readily flow through the pores, drawn by the vacuum. However, the contact angles of water droplets on polypropylene, immersed in several nonaqueous liquids, indicate that the use of the counterflow process, with degassed water as the gas absorbent, will allow retention of the nonaqueous liquid (PFH, DD and TCE), with the application of a modest hydrostatic pressure. As an example, PFH should be retained by water with an applied pressure of about 0.4 bars, for a micrometre-sized polypropylene membrane.

Similar results obtained using polished Teflon substrates also indicate that this material can be used in a counterflow process with degassed water to remove gases from PFH, DD and TCE. As an example, TCE should be retained by water by the application of a modest differential pressure of about 0.14 bar.

Using the Teflon hollow-fibre MiniModule unit at a water flow rate of about 140 ml/min, a degassing level of typically about 99.6% was obtained, corresponding to about 33 ppb dissolved oxygen. The pH value of this water increased from 5.8 to 7.0–7.1, due to the removal of dissolved carbon dioxide. When this water was used as the outer fluid in a second hollow-fibre unit, with gassed dodecane inside the fibres flowing in the opposite directions, a degassing rate of typically about 99.2% was observed for dodecane, in a single pass process (i.e., 65 ppb dissolved oxygen). These results demonstrate that the process, even in a single stage, efficiently removes dissolved gases from nonaqueous liquids to a high degree. The dodecane flow rate used in these minimodules was relatively low, at about 2 ml/min. However, this rate could obviously be substantially increased using larger units. The higher flow rate (140 ml/min) counterflow of degassed water was continuously recycled through the first HF vacuum membrane system, during the process, to improve efficiency and save water. This recycled, degassed water remained completely clear during the exchange process, which shows that the dodecane was completely retained inside the HF exchange membrane during the process. The efficiency of the exchange process could, of course, be further improved by using a higher capacity vacuum pumping system, to degas the feed water to a higher degree.

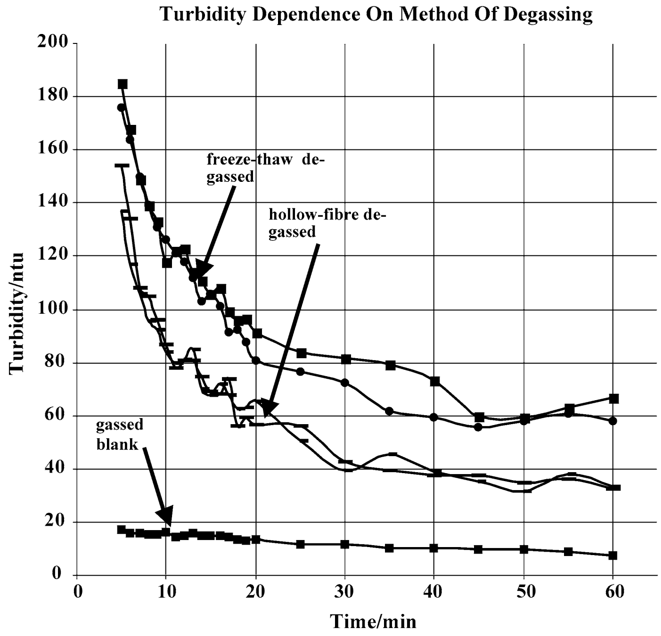

Fig. 8. The turbidity of dodecane and water mixtures following vigorous shaking for samples both gassed and degassed. Degassing was carried out by the freeze–thaw process for mixtures of oil and water (upper curves) and via separate degassing of the two liquids, using the membrane process (middle curves).

Water and dodecane degassed by the HF membrane process were mixed and shaken and their dispersion compared with the gassed case and mixtures degassed by the freeze–thaw technique. The results obtained are shown in Fig. 8 and clearly demonstrate that degassing dodecane and water separately, using the novel membrane system, is sufficient to cause enhanced dispersion, significantly above that for gassed, "blank" mixtures. The best dispersion results were obtained by the freeze–thaw process, which gives a better opportunity to mix than 10 s of shaking and, in addition, degases the two liquids to a higher degree. These results are also of interest because they clearly demonstrate that degassing, by whatever method, causes the enhanced dispersion of oil in water.

4. Conclusions

The present study has demonstrated that hollow-fibre membranes can be used to degas nonaqueous solvents in a continuous counterflow process using degassed water to remove the dissolved gases via hydrophobic pores. This process offers a further use for the degassed, concentrated brine produced commercially in the vacuum distillation process used to desalinate sea water. The results presented here also demonstrate that the enhanced dispersion of fine oil droplets in water can be obtained without the use of the freeze–thaw technique to degas the two liquids. It has also been shown that contact angles close to 180°

can be produced using water droplets on smooth surfaces, when the droplets are immersed in a suitable water-immiscible liquid.

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