

This article was downloaded by:

On: 25 January 2011

Access details: *Access Details: Free Access*

Publisher *Taylor & Francis*

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



## Separation Science and Technology

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713708471>

### Stability of a Supported Liquid Membrane for Removing Hydrophobic Solutes from Casein Hydrolysate Solution

C. Clément<sup>a</sup>; Md. M. Hossain<sup>a</sup>

<sup>a</sup> NATURAL PRODUCTS PROCESSING INDUSTRIAL RESEARCH LIMITED, LOWER HUTT, NEW ZEALAND

**To cite this Article** Clément, C. and Hossain, Md. M.(1997) 'Stability of a Supported Liquid Membrane for Removing Hydrophobic Solutes from Casein Hydrolysate Solution', *Separation Science and Technology*, 32: 16, 2685 — 2703

**To link to this Article:** DOI: 10.1080/01496399708006964

**URL:** <http://dx.doi.org/10.1080/01496399708006964>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

## Stability of a Supported Liquid Membrane for Removing Hydrophobic Solutes from Casein Hydrolysate Solution

C. CLÉMENT and MD. M. HOSSAIN

NATURAL PRODUCTS PROCESSING

INDUSTRIAL RESEARCH LIMITED

PO BOX 31-310, LOWER HUTT, NEW ZEALAND

### ABSTRACT

The stability of a liquid membrane containing a solution of an ionic carrier (Aerosol OT, AOT) in oleyl alcohol and loaded on a commercial support, Celgard 2500, was examined. The experiments were conducted in this flat-sheet support to continuously remove hydrophobic solutes from a feed of casein hydrolysate solution with a strip solution of sodium chloride. Three approaches were investigated to study flux stability of the membrane: i.e., by 1) varying AOT concentrations (10–40% w/w), 2) using a different solvent (decanol instead of oleyl alcohol), and 3) applying an interfacial surface layer on the membrane support. At higher AOT concentrations the flux through the membrane was stable up to 40 hours; the flux declined rapidly beyond this period to about half the initial value and slowly decreased to low values after 120 hours. The use of decanol (100% pure) instead of oleyl alcohol (85% pure) as the membrane solvent increased the flux and improved the stability without significant loss of performance up to about 70 hours. The application of an interfacial gel layer at the feed, strip, or both interfaces did not improve the stability of the AOT/oleyl alcohol membrane. The generation of a polymerized layer at the interface between the organic and aqueous phases of the membrane showed better stability. However, the solute flux through the polymerized membrane was reduced to a low value.

### INTRODUCTION

Supported liquid membranes (SLMs) are a potential alternative to many liquid-liquid extraction and other separation techniques (e.g., chromatog-

raphy and ion exchange) for selective removal of ions or neutral molecules from liquid solutions and gas mixtures. The advantages of SLMs over other techniques are high selectivity, rapid extraction capacity, modest capital and operating costs, low energy consumption, and easily scalable modules for commercial application (1–5). Liquid membrane technology has been comprehensively studied in a few areas: 1) in the recovery of heavy metal ions (6–10), 2) in the separation of bioproducts (11–17), and 3) in the removal of contaminant from wastewater (18–22). The efforts in the area of extraction of metals have been commercially successful (23).

Despite the technical advantages of SLMs, their wide-scale application in industry is still to come. One of the major reasons for this is the membrane stability or the effective lifetime of membrane systems is not long enough for further development to an industrial scale process. The instability of SLMs is mainly caused by the loss of carrier and/or membrane solvent from the support pores, which changes the flux and selectivity of the membrane (24–29). This loss of performance could be due to (30, 31):

- The pressure difference over the membrane
- The presence of an osmotic pressure gradient over the membrane
- The solubility of a liquid membrane in the adjacent solutions
- The restricted diffusion of a carrier–solute complex due to pore blockage
- Emulsion formation of the liquid membrane in water
- The support pores being wetted by the aqueous solution

Tanigaki et al. (32) reported that the liquid membrane was unstable when the feed and strip solutions were unsaturated with the organic phase. Substantial improvement was possible by either intermittent reimpregnation or continuous impregnation of the organic phase to the support. Increasing the thickness of the membrane and/or the pore size and using a phase modifier in the organic phase could also provide a significant increase of membrane stability in continuous operation (33, 34).

An SLM system for the removal of hydrophobic solutes from protein hydrolysates was previously developed (35, 36) and was effective in removing hydrophobic solutes from a protein hydrolysate solution. The system consisted of a solution of Aerosol OT (AOT as carrier) in oleyl alcohol (solvent) loaded on a commercial support, Celgard 2500. The effects of various operating parameters such as feed solution pH, feed flow rate and concentration, and carrier concentration to improve the flux through the SLMs were examined. The optimum process parameters for selective removal were determined (37).

Long-term studies of membrane performance need to be carried out to assure the commercial viability of the process. The purpose of this

investigation was therefore to examine the stability of the membrane (AOT in oleyl alcohol) in a continuous flow module for a casein hydrolysate feed. The stability experiments were carried out at various feed and carrier concentrations over a period of 3–4 days. The decline in flux was considered to be an indication for membrane instability (24). Since oleyl alcohol is of technical grade (85% pure), a pure solvent, decanol, was tried as the liquid membrane to study the stability. In addition, interfacial gels (25, 30) were applied on the feed–membrane interface to prevent leakage of the membrane phase and thus to retain the initial flux for a long time of processing.

## MATERIALS AND METHODS

### Chemicals

Sodium dihydrogen orthophosphate, disodium hydrogen phosphate, Aerosol OT, and dodecane were purchased from BDH Chemicals Co. (England). Trimesoyl chloride, piperazine, *N,N'*-dicyclohexylcarbodiimide, and 1,12-diaminododecane were from ACROS Chemicals (Belgium). Tetrahydrofuran, 1,4—phenylenediamine, PVC-Fluka, PVC-carboxylated, oleyl alcohol, and decanol were obtained from Aldrich Co. (USA). Phosphoric acid and sodium acetate were from Ajax Chemicals Co. (Australia). The stripping agent sodium chloride (regular) was from Prolabo (France). The polymeric support, Celgard 2500, was a gift from Celanese Separation Products, Charlotte, NC, USA. Casein hydrolysate (MPH 955) was obtained as a gift from New Zealand Dairy Board.

### Spiral Membrane Module

The spiral system was designed and fabricated according to the literature (38). It consists of two half-cell Perspex faceplates between which the SLM is placed. The faceplates contain rectangular channels in a spiral form, through which the two solutions feed and strip are pumped in a crossflow direction. The dimensions of the membrane module are presented in Table 1.

For all experiments a commercial grade membrane support, Celgard 2500, with slit-type pores was used. The characteristics of the support are given in Table 2 and the experimental setup is shown in Fig. 1.

### Feed and Strip Solutions

Feed solutions were prepared by dissolving casein hydrolysate powder in sodium acetate–phosphoric acid buffer. Casein hydrolysate is a complex mixture of amino acids (e.g., tryptophan, phenylalanine, leucine,

TABLE 1  
Dimensions of the Spiral Membrane  
Module

Width	3.16 mm
Depth	1.6 mm
Length	940 mm
Cell area	$29.7 \times 10^{-4} \text{ m}^2$
Cell volume	4.75 mL/cell

etc.) and polypeptides (mostly di- and tripeptides) of these amino acids. Some of these solutes contain hydrophobic side chains.

Previous work (35–37) found that the hydrophobic peptides can be selectively removed by using a feed solution pH in the 4.5–5.0 range. A pH of 4.5 was chosen for each experiment. The feed solutions were casein hydrolysate in acetate buffer and had two different concentrations: 10 and 30 g/L. The hydrolysate feed solution for both concentrations were centrifuged to remove the undissolved solids using a Sorval RC-5B refrigerated superspeed centrifuge (Dupont Instruments). This was followed by a filtration using a serum capsule filter of pore size  $0.45 \mu\text{m}$  (Gelman Sciences).

A 1 M solution of NaCl in 0.1 M sodium phosphate buffer was used as the strip solution. The buffer solution was used to guarantee a stable pH of 5.5 and a constant pH gradient from the feed to the strip solution (36, 37).

### Preparation of Supported Liquid Membrane

The SLMs were prepared by soaking the Celgard 2500 support with a 10–30% AOT solution in oleyl alcohol or 10% AOT in decan-1-ol for 5 minutes followed by placing the contents under vacuum for about 30 minutes (36, 37). The membrane was then gently wiped with tissue paper to remove the attached liquid.

TABLE 2  
Characteristics of the Membrane Support

Support	Celgard 2500
Porosity	37–48%
Pore size	$0.05 \mu\text{m} \times 0.19 \mu\text{m}$
Thickness	$20 \mu\text{m}$

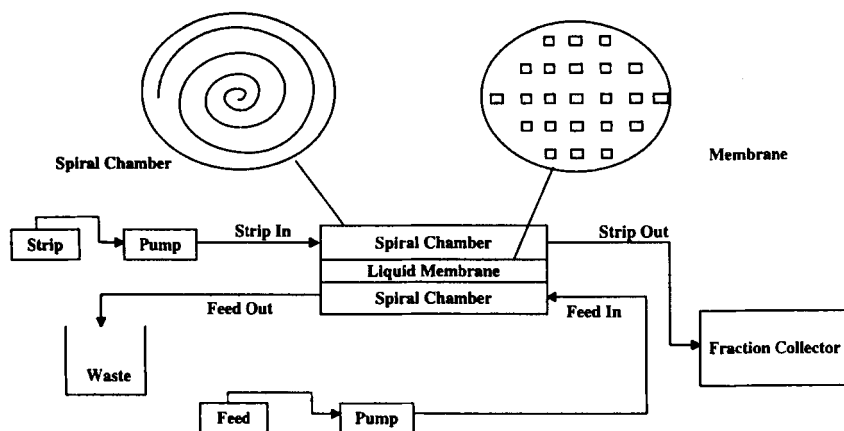


FIG. 1 Schematic diagram of the experimental setup of a continuous supported liquid membrane (SLM) process.

### Preparation of an Interfacial Dense Gel Layer

The method of preparation of a gel layer was obtained from Neplenbroek et al. (24–26). They applied thin, crosslinked PVC gels on the feed side of their membranes. These top layers were found to be very effective in stabilizing SLMs for nitrate removal from water.

To apply a dense gel layer at the interface of the membrane, a liquid SLM was first prepared. The gel-forming polymers (PVC-Fluka and PVC-carboxylated) were dissolved by stirring in a volatile solvent, tetrahydrofuran (THF) (ca. 10 mL THF/g polymer).

The activator [*N,N'*-dicyclohexylcarbodiimide (DCC)] and crosslinking agents [1,12-diaminododecane (DDDA) and 1,4-phenylenodiamine (PDA)] were added to the polymer solution. The gel layer was spread over the membrane surface with a tissue wetted with the gel-forming solution. The THF evaporated during this treatment.

The following amounts were used in each experiment according to the stoichiometry of each reaction (8): DCC (30 mg), DDA (15 mg), and PDA (8 mg) added to the tetrahydrofuran. Then 1 g of PVC-carboxylated was dissolved in THF but with difficulty because this PVC curdled. Lastly, 1 g of PVC-Fluka was dissolved in this solution.

### Preparation of an Interfacial Polymerized Layer

Interfacially polymerized layers of piperazine (PIPA) and trimesoyl chloride (TMCI) were able to improve the stability of SLMs for the removal of nitrate from water (33).

Each interfacial polymerization was carried out as described by Kemperman (30). The support material was impregnated with 0.2 M organic acid chloride (TMCl was heated in an oven to liquify it for better handling). Excess solution was wiped off the surface of the impregnated support with a tissue paper. The support was then placed on top of a 0.2 M PIPA solution. After a polymerization time of 15 or 7 minutes, the membrane was removed from the diamine solution and washed, first with ethanol and then with water to remove unreacted species. The composite membrane was then dried in air overnight.

For these composite membranes a longer time for impregnating the support with AOT in oleyl alcohol was necessary for the SLM preparation. A contact time of 2 hours under vacuum was used.

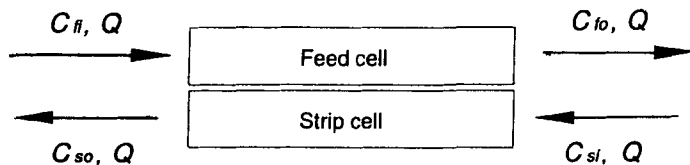
### Transport Measurements

The experiments were carried out for 2 to 4 days without recycling of feed or strip solutions. The membrane module, including the connecting tubes, was filled with feed and strip solutions at maximum pump speed set to the desired value of 0.20 mL/min (7). Samples of the strip solution were taken every 1 or 2 hours in a fraction collector (RediFrac, Pharmacia).

The transport of peptides and amino acids across the membrane was monitored by measuring the change in concentration of the initially peptide-free strip solution. The absorbance of strip solution was measured spectrophotometrically at 280 nm using a UV-visible spectrophotometer (Shimadzu UV-160). The feed samples were diluted and their absorbance values were also measured at 280 nm.

The pH of feed and strip samples was measured with a PHM-4 Research pH meter (Radiometer Co., Copenhagen) at the beginning and at the end of each experiment to check the integrity of the membrane. The variation was from 5.5 to 5.4 for the strip samples and from 4.5 to 4.6 for the feed samples.

### Calculation of Flux



The average flux of solute (peptides or amino acids),  $J_s$ , through the SLM to the strip solution is calculated from

$$J_s = \frac{Q(C_{s_o} - C_{s_i})}{A} \quad (1)$$

where  $Q$  is the strip flow,  $C_{s_o}$  and  $C_{s_i}$  are the outlet and inlet solute concentrations of the strip phase respectively, and  $A$  is the effective membrane area.

The relation between the solute concentration ( $C_{s_o} - C_{s_i}$ ) and the UV absorbance values of the feed ( $Abf_i$ ) and strip solutions ( $Abs_o$  and  $Abs_i$ ) is given in

$$C_{s_o} - C_{s_i} = C_{f_i} \times \frac{(Abs_o - Abs_i)}{Abf_i} \quad (2)$$

where  $C_{f_i}$  is the initial feed concentration.

Combining Eqs. (1) and (2), we obtain the final expression of the solute flux  $J_s$ :

$$J_s = \frac{Q}{A} \times \frac{(Abs_o - Abs_i)}{Abf_i} \quad (3)$$

## RESULTS AND DISCUSSION

The experimental operating conditions are listed in Table 3. The pH of the casein hydrolysate solution and the strip solution conditions were chosen on the basis of previous results (36, 37). Under these conditions the hydrophobic peptides are selectively removed from casein hydrolysate solution (38). The effects of various factors, 1) the carrier concentration

TABLE 3  
Operating Conditions for the Stability Experiments

Feed phase:	
Casein hydrolysate concentration	10–30 g/L (for AOT/oleyl alcohol system) 30–35 g/L (for AOT/decanol system)
pH	4.5
Flow rate	20 mL/h
Strip phase:	
Concentration of sodium chloride	1 M
pH	5.5
Flow rate	20 mL/h
Temperature of both phases	293 K
Liquid membrane:	
AOT concentration in oleyl alcohol	10–40% w/w
AOT concentration in decanol	10% w/w



(% w/w AOT in oleyl alcohol), 2) decanol as membrane solvent, 3) gel layers on the interfaces, and 4) interfacial polymerized layer on SLM stability, are presented below.

### Effect of AOT Concentration on SLM Stability

The flux stability through SLMs containing 10 to 40% AOT in oleyl alcohol was observed using 10 g/L casein hydrolysate feed solution. The results are shown in Fig. 2. For SLM with 10% AOT the flux decreased sharply after 5 hours to about 30–35% of the initial flux in 15 hours and then was stable up to 2 days of operation. For SLMs with 20–40% AOT the initial flux was maintained for about 20–25 hours and then it decreased to about 50% of the initial flux in 2 days. For SLM with 40% AOT the initial high flux (3 g/m<sup>2</sup>·h) was lower than that for the SLM with 30% AOT (flux is about 4 g/m<sup>2</sup>·h). This could be due to reduced diffusion (as the viscosity increases with the increase in carrier concentration), change in interfacial tension, and the partition coefficient at the interfaces in this higher range of AOT concentration.

The flux stability of SLMs with 10–40% AOT in oleyl alcohol using 30 g/L of casein hydrolysate is presented in Fig. 3. The evolution of flux in the strip solution was similar to that in Fig. 2, but a longer time was needed in the latter case to attain the initial steady state. An improvement in the period of stable performance was observed at this higher feed concentra-

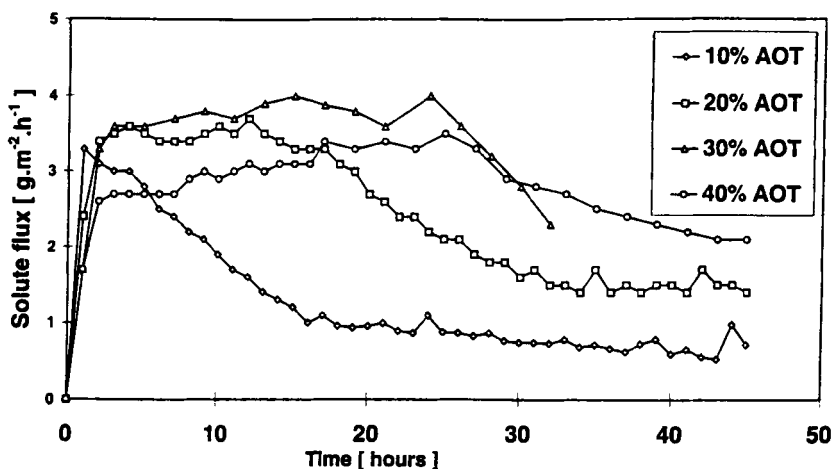


FIG. 2 Stability of SLMs with different concentrations of AOT (%w/w) using 10 g/L casein hydrolysate solution.

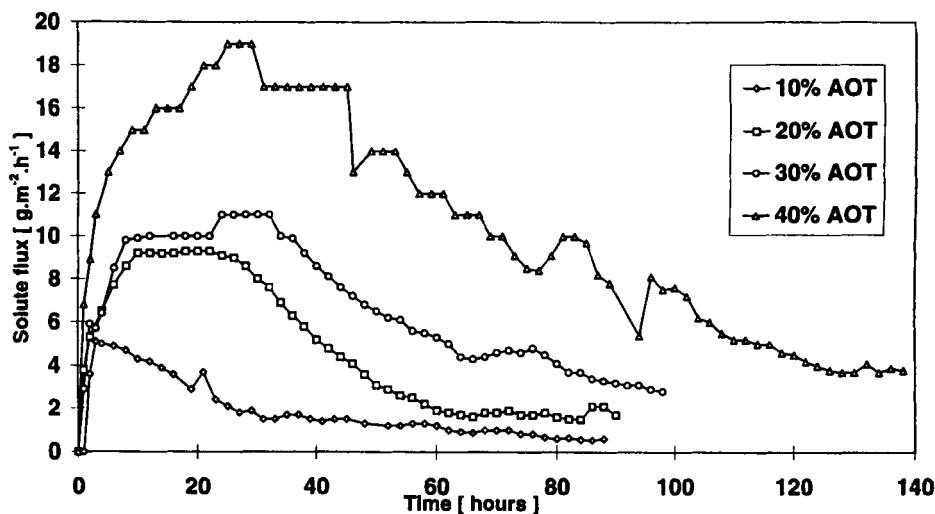


FIG. 3 Stability of SLMs with different concentrations of AOT (%w/w) using 30 g/L casein hydrolysate solution.

tion. The flux started declining at a later time (after 35–40 hours) compared to that of 20–25 hours for processing at lower feed concentration.

A comparison of flux stability through the SLM (20% AOT in oleyl alcohol) at low (10 g/L) and high (30 g/L) casein hydrolysate concentrations is shown in Fig. 4. A strong influence of the feed concentration on

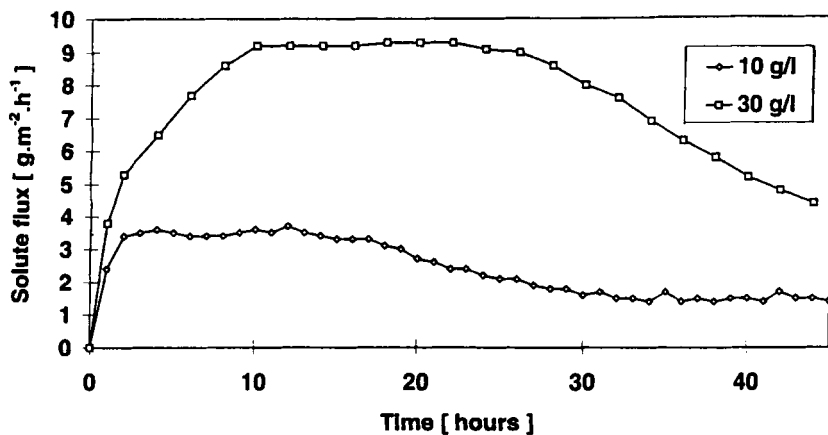


FIG. 4 Comparison of flux stability through the SLM (20% AOT in oleyl alcohol) using two (10 and 30 g/L) casein hydrolysate solutions.

the initial steady flux is observed as the flux is increased threefold with a similar increase in the feed concentration.

### Organic Solvent in Strip Solution

The effect of adding 1 and 0.2% oleyl alcohol in strip solution on the solute flux through 10% AOT membrane for a feed concentration of 10 g/L is shown in Fig. 5. This addition of organic solvent increased the flux stability up to 20 hours (instead of 5 hours) and moderated the progressive decline in flux over a period of 45 hours. The effect of the higher amount of oleyl alcohol was comparatively better although the improvement was not great.

### Effect of Membrane Solvent (decanol instead of oleyl alcohol)

Oleyl alcohol (85% technical) contains water-soluble impurities which may introduce SLM instabilities. Decanol (a pure solvent) was therefore used as a liquid membrane to observe its flux stability. The results of the decanol membrane experiments (with 10% AOT and 30–35 g/L of casein hydrolysate) along with those of oleyl alcohol are presented in Fig. 6.

The SLM (AOT in decanol) maintained its initial flux for a longer time (about 60 hours). After this period the flux increased beyond the initial value. This might be due to a loss of the LM phase, resulting in a decrease of the liquid membrane thickness.

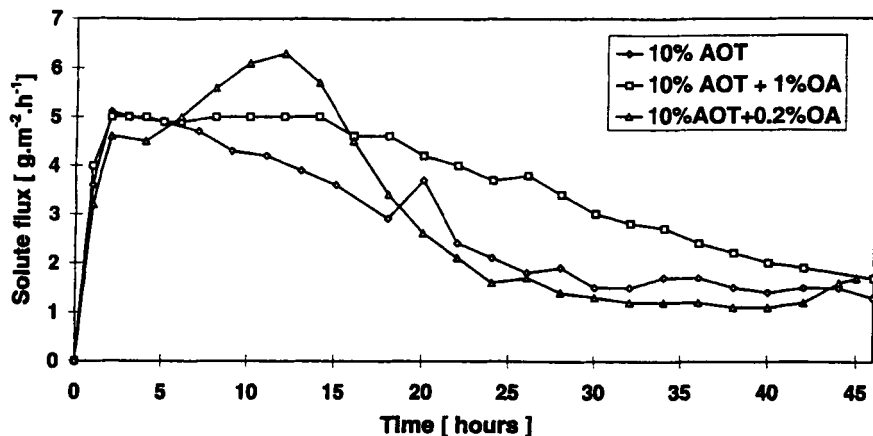


FIG. 5 Comparison of flux stability for addition of oleyl alcohol in the strip solution for processing of 10 g/L casein hydrolysate solution.

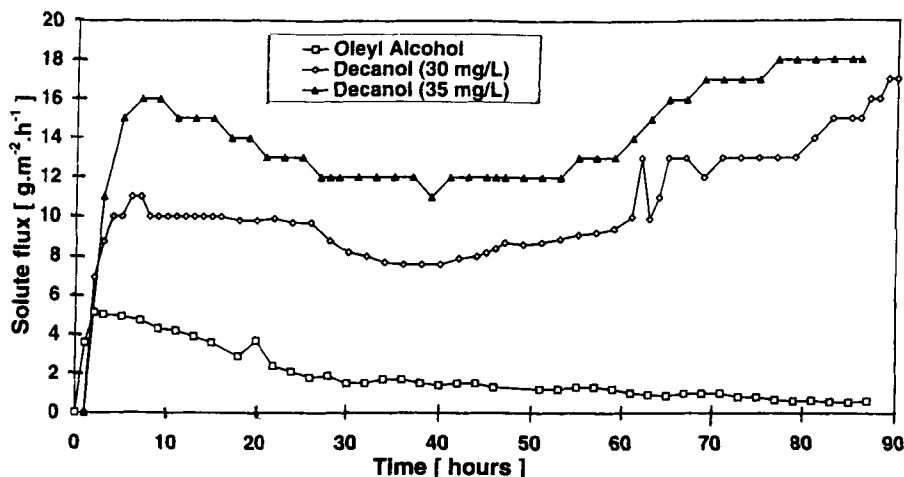


FIG. 6 Comparison of flux stability through the SLM (10% AOT) in two organic solvents: oleyl alcohol and decanol using 30 g/L casein hydrolysate solution.

A strong influence of the feed concentration on the initial flux was observed: a higher feed concentration (35 g/L) gives a greater initial flux through the decanol-oleyl alcohol membrane. This increase of the solute flux value could be due to the availability of more solutes and not due to a higher activity gradient of complexed carriers through the membrane. In order to show that, we calculated the solute diffusivity coefficient  $D_s$  from Fick's law:

$$D_s = \frac{\bar{J}_s \times l}{(K_f \bar{C}_f - \bar{C}_s / K_s)} \quad (4)$$

where  $\bar{J}_s$  is the solute average flux,  $\bar{C}_f$  and  $\bar{C}_s$  are the average feed concentration ( $\bar{C}_f \approx C_{fi}$ ) and the average strip concentration ( $\bar{C}_s \approx C_{so}$ ), respectively,  $K_f$  and  $K_s$  are the partition coefficients at the feed and strip interfaces, respectively, and  $l$  is the membrane thickness.

Using  $K_f = 1$  and  $K_s = 0.2$  (obtained from measurements of the partition coefficient for Trp at pH 4.5) and the experimental feed and strip concentrations, the diffusivity values were calculated. At both feed concentrations the values of  $D$  were very close to each other. This means that only the activity gradient of solute was involved in the increase of flux value. Furthermore, at high feed concentration the osmotic pressure gradient is stronger and thus it might increase the instability of the system.

The stability of the SLMs with decanol is better than with oleyl alcohol since the stable operational time was increased by 6 times compared to

the later one (SLMs with oleyl alcohol were stable for only 10 hours). Furthermore, the initial flux with decanol membrane was at least twice as higher as that with oleyl alcohol. This could be due to the lower viscosity and higher partition coefficient of decanol compared to those of oleyl alcohol (16). The impurities in the 85% oleyl alcohol system could have some effect on the flux through the SLM. However, in the absence of pure oleyl alcohol in the market and because of its food industry acceptability, we continued the experiments with technical grade oleyl alcohol.

### Interfacial Gel Dense Layer

Based on the emulsion formation hypothesis for membrane degradation, Neplenbroek et al. (25) used gelation of the LM phase to stabilize SLMs for the removal of nitrate from water. By gelling the membrane liquid, its viscosity increases and the resistance against liquid displacement out of the support is enhanced. They carried out the gelation in two ways: a homogeneous gel network in the support pores and a thin, dense gel layer at the feed side. Better results were obtained when a PVC layer was applied as a thin layer ( $<2\text{ }\mu\text{m}$ ) on the feed side of the support and cross-linked after preparation.

We decided to try the above gel layer technique. The application of the gel layer at various interfaces of the support pores can be represented by the diagrams in Fig. 7(A–C). A thin gel layer at the feed–membrane interface (and without any gel at the strip interface) is shown in Fig. 7(A), a thin gel layer at the strip–membrane interface (and without any gel at the feed interface) is shown in Fig. 7(B), and gel layers at both interfaces are shown in Fig. 7(C). All the subsequent stability experiments were carried out with SLM (10% AOT in oleyl alcohol) at a 10 g/L feed concentration because this provides the worst performance conditions.

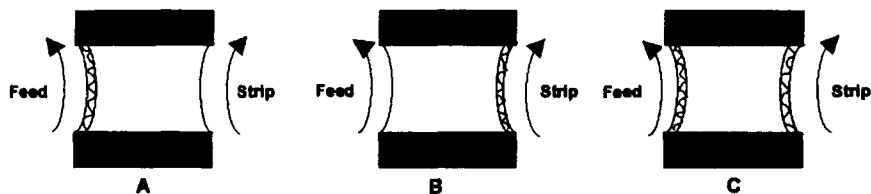


FIG. 7 Representation of interfacial gel layers at the feed interface (A), at the strip interface (B), and at both interfaces (C).

### ***Thin Gel Layer at Either Feed or Strip Side and at Both Sides***

The stability of flux through the uncoated SLM is compared with those obtained with a gel layer either at the feed side or at the strip side in Fig. 8. The flux-time behavior of the SLM with gel at the feed side is similar to the one without gelation. The maximum flux through the gelled SLM was  $2 \text{ g/m}^{-2}\cdot\text{h}^{-1}$ , lower than that ( $3 \text{ g/m}^{-2}\cdot\text{h}^{-1}$ ) without gelation. The flux through the SLM with gel at the strip side was even lower, and there was a drastic drop in flux after attaining the maximum value. This could be due to the greater thickness of the gel (formed at  $20 \text{ mg}$  gel layer) at the strip side compared to that on the feed side (formed at  $10 \text{ mg}$  gel layer).

The stability of flux through the SLM with gel layers at both interfaces (feed and strip) is also shown in Fig. 8. The crosslinking step was avoided in order to formulate gels with a larger mesh size. Even then the stability did not improve, rather the maximum flux decreased compared to the one without gelling. The flux was lower over the entire period of 45 hours.

There was no improvement of flux stability by applying gel at either feed, strip, or both interfaces. The solute flux decreased both with an increase in the gel thickness and with an increase in the processing time. The reduction in diffusivity of the carrier-solute complex due to the gel

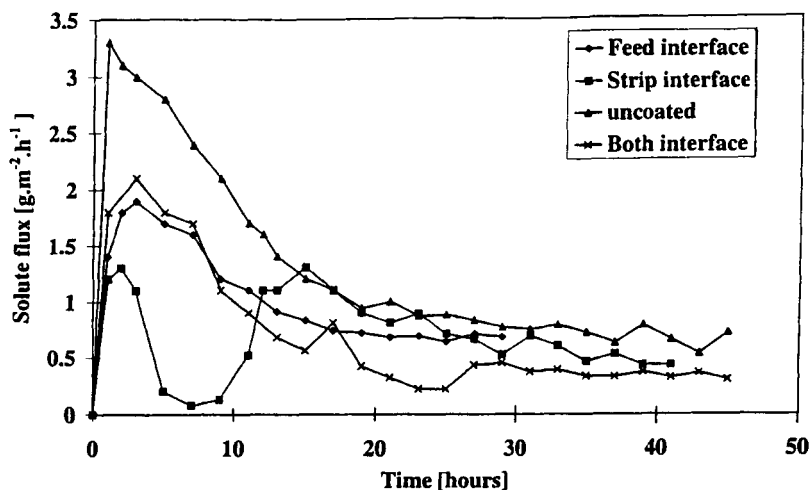


FIG. 8 Comparison of flux stability of the uncoated SLM (10% AOT in oleyl alcohol) with the gel layer at either the feed or the strip interface using  $10 \text{ g/L}$  casein hydrolysate solution.

network and the loss of SLM components are thought to cause the flux decrease.

Stabilization of membranes by gelation worked for relatively stable systems (24–26). These systems consisted of tetraoctyl ammonium bromide (TeOA) and trioethylmethyl ammonium chloride (TOMA) as carriers dissolved in *o*-nitrophenyl octyl ether (O-NPOE) and supported on Acurel. The gelling was accomplished with selected PVC for which the solvents were plasticizer. It is not known whether oleyl alcohol is a plasticizer for the polymers used in this study. Because of the above reason and also due to the lack in reproducibility of the gelling method, the technique of the interfacial polymerized layer by Kemperman (30) was tried and the results are discussed below.

### Interfacial Polymerized Layer

The interfacial polymerization technique was used as an alternative to the previous gel technique. Kemperman (30) worked with a different SLM (using a different carrier) system from the one Neplenbroek et al. (25) used for the removal of nitrate from water, and he found that the gelation technique didn't work for his system.

This technique has several advantages: the reproducibility of the results is better than with the gelling technique, and this method can be applied not only for coating flat membranes but also at the lumen side of hollow fibers.

The stability experiments through the SLM with a polymerized top layer were carried out at 10% AOT and at a 10 g/L feed concentration.

### Polymerization Time

The flux through the SLM with a polymerized layer obtained after contacting for 15 and 5 minutes are presented in Fig. 9. The initial flux increased with the decrease in the polymerization time although the stability was more or less the same. The magnitude of the flux was about 3 times greater for layers formed after polymerization times of 5 minutes over a stability run of 60 hours (the experiment was stopped for logistic reasons).

It is worth mentioning that a barrier was formed instantaneously when the reactants met at the interface after the initial fast formation of the top layer. This means that mass transfer of the diamine through the top layer becomes the rate-controlling step in the polymerization process and that the increase in the weight of the membrane decreased.

The weight of the formed polymer was 6.5 mg for 15 minutes of impregnation and 5.0 mg for 5 minutes. The difference in weight was about 23% for a difference of polymerization time of 67%. This suggests the polymeri-

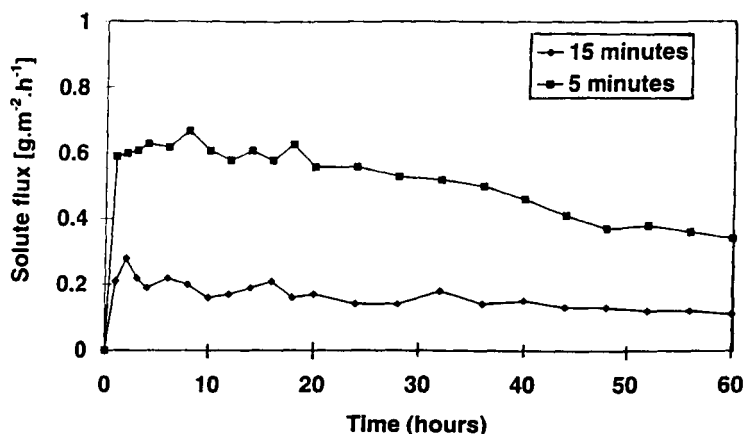


FIG. 9 Comparison of flux stability of the uncoated SLM (10% AOT in oleyl alcohol) with the gel layers on both feed and strip interfaces using 10 g/L casein hydrolysate solution.

zation time should be controlled for improvement of the polymerized layer action.

### Comparison of the Coating Techniques

The stabilities of the fluxes from an uncoated membrane, a gelling membrane, and a polymerized membrane are shown in Fig. 10. The stability behavior were similar for both the uncoated and the gelled membranes, i.e., improvement with the application of a gel layer was insignificant. The formation of polymerized layers on membranes was shown to have stabilized SLM performance. However, the solute flux was very low from a practical point of view and close to the final value in uncoated and gel-formed SLMs. It is noted that the flux could be increased by increasing the AOT concentration and/or feed concentration (as shown in Figs. 2 and 3). For processes where constant flux is needed and higher carrier concentration is allowable, polymerized SLMs could be useful to maintain the performance. It is desirable to develop and use liquid membrane/polymer combinations which would provide higher flux and longer stability. Further research should be carried out to meet these requirements.

It is worthwhile to mention that there are not many chemicals (carrier/solvent) suitable for food industry use. The results in this study demonstrate the flux and stability behavior of a SLM system in which a food-grade liquid membrane has been tried (oleyl alcohol is a nontoxic solvent and a few ppm of AOT is allowed in food products by FDA).



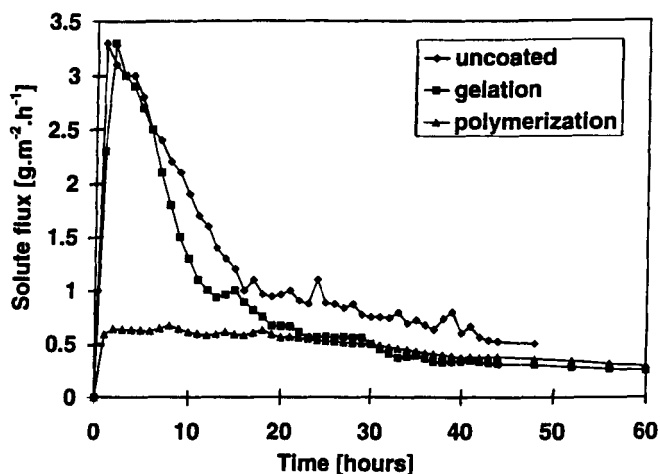


FIG. 10 Stability of the SLM (10% AOT in oleyl alcohol) with a polymerized top layer (obtained at reaction times of 7 and 15 minutes) at the feed interface using 10 g/L casein hydrolysate solution.

## CONCLUDING REMARKS

The SLM prepared with 10% AOT in oleyl alcohol was stable only for a few hours at both high and low casein hydrolysate concentrations. At higher AOT concentrations (20–40%) the stability of the SLM was improved and a stable performance up to 40 hours was achieved.

The flux increased and its stability improved considerably by using a different membrane solvent, i.e., decanol (a pure solvent) instead of oleyl alcohol (a 85% pure solvent). However, the membrane phase was unstable after a few days (about 65 hours) of good performance.

The application of an interfacial gel layer at the feed–strip interface or at both interfaces did not improve the stability of an AOT/oleyl alcohol SLM. Moreover, with these gel layers the flux was lower and decreased with processing time.

The application of a polymerized top layer at the feed–SLM interface improved the stability. However, the flux through the liquid membrane decreased to a low value.

Adding a small concentration (0.25 and 1%) of oleyl alcohol to the strip solution in order to decrease its gradient also improved the stability of the SLM to some extent.

## SYMBOLS

$A$	surface area of membrane ( $\text{m}^2$ )
$Abf$	UV absorbance of the feed solution
$Abs$	UV absorbance of the strip solution
$Aot$	Aerosol OT, sodium di-2-ethylhexyl sulfosuccinate
$C_{fi}$	concentration of casein hydrolysate in initial feed solution (g/L)
$\bar{C}_f$	average concentration of solute in feed solution (g/L)
$C_s$	concentration of solute in strip solution (g/L)
$\bar{C}_s$	average concentration of solute in strip solution (g/L)
$D$	diffusivity of the solute ( $\text{m}^2/\text{s}$ )
$J_s$	flux for solute based on the area of the spiral chamber, defined in Eq. (1), ( $\text{g}/\text{m}^2/\text{h}$ )
$\bar{J}_s$	average solute flux ( $\text{g}/\text{m}^2/\text{h}$ )
$K_t$	partition coefficient at the feed-membrane interface
$K_s$	partition coefficient at the strip-membrane interface
$l$	thickness of the membrane support ( $\mu\text{m}$ )
Trp	tryptophan
Trp-Leu	tryptophan-leucine
$Q$	flow rate (mL/h)

**Subscripts**

i	inlet of the membrane module
o	outlet of the membrane module
s	solute (amino acid or peptide)

## ACKNOWLEDGMENTS

The financial assistance of the Foundation for Research, Science and Technology (FRST), New Zealand, is gratefully acknowledged. Thanks to Glenn Fenton from Analytical Department, Industrial Research Limited, for the HPLC analysis of samples. C.C. wishes to thank his uncle Alain Mauberret, the CROUS of Grenoble (France), and his parents for their financial support during his stay at Lower Hutt, New Zealand. He also conveys special thanks to Lieutenant Colonel Jean Jacques Pluquet of Bureau du Service National de Marseille who granted him a respite to carry out his studies before doing military service.

## REFERENCES

1. R. M. Izatt, J. D. Lamb, and R. L. Bruening, "Comparison of Bulk, Emulsion, Thin Sheet Supported and Hollow Fiber Supported Liquid Membranes in Macrocyclic-Mediated Cation Separations," *Sep. Sci. Technol.*, 23(12&13), 1645 (1988).
2. G. Schulz, "Separation Techniques with Supported Liquid Membranes," *Desalination*, 68, 191 (1988).
3. R. D. Noble and W. D. Way, "Liquid Membrane Technology: An Overview," *ACS Symp. Ser.*, 347, 1 (1987).
4. J. J. Pelligrino and R. D. Noble, "Enhanced Transport and Liquid Membranes in Bioseparations," *Tibiotechnology*, 8, 216 (1990).
5. E. L. Cussler and D. E. Evans, "Liquid Membranes for Separations and Reactions," *J. Membr. Sci.*, 6, 113 (1980).
6. D. Melzner, J. Tilkowski, A. Mohrmann, W. Poppe, W. Halwachs, and K. Schügerl, "Selective Extraction of Metals by Liquid Membrane Techniques," *Hydrometallurgy*, 13, 105 (1984).
7. T. C. Huang and T. H. Tsai, "Separation of Cobalt and Nickel Ions in Sulphate Solutions by Liquid-Liquid Extraction and Supported Liquid Membrane with Di(2-ethylhexyl) Phosphoric Acid Dissolved in Kerosene," *J. Chem. Eng. Jpn.*, 29(1), 126 (1991).
8. S. Taguchi and K. Goto, "Bis[2-(2-pyridylazo)-s-diethylaminophenolato]cobalt(III) Chloride as a New Extraction and Spectrophotometric Reagent for Trace Anions," *Talanta*, 27, 289 (1980).
9. M. Teramoto, H. Atsuyama, H. Takaya, and S. Asano, "Development of Spiral-Type Supported Liquid Membrane Module for Separation and Concentration of Metal Ions," *Sep. Sci. Technol.*, 22, 2175 (1987).
10. M. Teramoto and H. Tanimoto, "Mechanism of Copper Permeation through Hollow Fiber Liquid Membranes," *Ibid.*, 18(10), 871 (1983).
11. M. Bryjak, J. Kozłowski, P. Wieczorek, and P. Kafarski, "Enantioselective Transport of Amino Acid through Supported Chiral Liquid Liquid Membranes," *J. Membr. Sci.*, 85, 221 (1993).
12. P. Deblay, M. Minier, and H. Renon, "Separation of L-Valine from Fermentation Broths Using a Supported Liquid Membrane," *Biotechnol. Bioeng.*, 35, 123 (1990).
13. S. Takeshima, S. Wadd, and H. Sakurai, "Transport Behavior of Basic Amino Acids through an Organic Liquid Membrane System," *Sep. Sci. Technol.*, 29, 2117 (1994).
14. M. P. Thien, T. A. Hatton, and D. I. C. Wang, "Separation and Concentration of Amino Acids Using Liquid Emulsion Membranes," *Biotechnol. Bioeng.*, 32, 604 (1988).
15. P. Wieczorek, A. Kocorek, M. Bryjak, P. Kafarski, and B. Lejczak, "Transport of Dipeptides and Phosphono Dipeptides through an Immobilized Liquid Membrane: Stereoselectivity of the Process," *J. Membr. Sci.*, 78, 83 (1993).
16. M. Matsumura and H. Kataoka, "Separation of Dilute Aqueous Butanol and Acetone Solutions by Evaporation through Liquid Membranes," *Biotechnol. Bioeng.*, 30, 887 (1987).
17. M. Matsumura, S. Takehara, and H. Kataoka, "Continuous Butanol/Isopropanol Fermentation Down-flow Column Reactor Coupled with Evaporation Using Supported Liquid Membrane," *Ibid.*, 39, 148 (1992).
18. A. M. Urtiga, M. I. Ortiz, E. Salazar, and J. A. Irabien, "Supported Liquid Membranes for the Separation-Concentration of Phenol. 1. Validity and Mass Transfer Evaluation," *Ind. Eng. Chem. Res.*, 31, 877 (1992).
19. C. J. Tompkins, A. S. Michaels, and S. W. Peretti, "Removal of *p*-Nitrophenol from

- Aqueous Solution by Membrane-Supported Solvent Extraction," *J. Membr. Sci.*, **75**, 277 (1992).
20. T. Yano, P. Nuchnoi, N. Nishio, and S. Nagai, "Extraction of Volatile Fatty Acids from Spent Medium with a Supported Liquid Membrane," *Bioprodukt. Bioprocess*, pp. 281 (1986).
  21. C. H. Yun, R. Prasad, and K. K. Sirkar, "Membrane Solvent Extraction of Priority Organic Pollutants from Aqueous Waste Water," *Ind. Eng. Chem. Res.*, **31**, 1709 (1992).
  22. R. E. Terry, N. N. Li, and W. S. Ho, "Extraction of Phenolic Compounds and Organic Acids by Liquid Membranes," *J. Membr. Sci.*, **10**, 305 (1982).
  23. M. Protsch and R. Marr, *Proc. Int. Solv. Extr. Conf., Denver, Colorado*, 1983, p. 66.
  24. A. M. Neplenbroek, D. Bargeman, and C. A. Smolders, "Mechanism of Supported Liquid Membrane Degradation: Emulsion Formation," *J. Membr. Sci.*, **67**, 133 (1992).
  25. A. M. Neplenbroek, D. Bargeman, and C. A. Smolders, "Supported Liquid Membranes: Stabilization by Gelation," *Ibid.*, **67**, 149 (1992).
  26. A. M. Neplenbroek, D. Bargeman, and S. A. Smolders, "Supported Liquid Membranes: Instability Effects," *Ibid.*, **67**, 121 (1992).
  27. P. R. Danesi, "Separation of Metal Species by Supported Liquid Membrane," *Sep. Sci. Technol.*, **19**, 857 (1984-5).
  28. J. F. Dozol, J. Casas, and A. Sastre, "Stability of Flat Sheet Supported Liquid Membranes in the Transport of Nucleotides from Reprocessing Concentrate Solutions," *J. Membr. Sci.*, **82**, 237 (1993).
  29. R. Molinari, E. Drioli, and G. Pantano, "Stability and Effect of Diluent on the Transport of Metal across Supported Liquid Membranes for Cr(III), Cr(VI), and Cd(II) recovery," *Sep. Sci. Technol.*, **24**, 1015 (1989).
  30. A. J. B. Kemperman, "Stabilization of Supported Liquid Membranes," PhD Thesis, University of Twente, Netherlands, 1995.
  31. T. Shinbo, T. Yamaguchi, H. Yanagishita, K. Sakaki, D. Kitamoto, and M. Sugiura, "Supported Liquid Membranes for Enantioselective Transport of Amino Acid Mediated by Chiral Crown Ether—Effect of Membrane Solvent on Transport Rate and Membrane Stability," *J. Membr. Sci.*, **84**, 241 (1993).
  32. M. Tanigaki, M. Ueda, and W. Eguchi, "Facilitated Transport Zinc Chloride through Hollow Fiber Supported Liquid Membrane. Part 2: Membrane Stability," *Sep. Sci. Technol.*, **23**(10&11), 1161 (1988).
  33. H. Takeuchi, K. Takahashi, and W. Goto, "Some Observations on Stability of Supported Liquid Membranes," *J. Membr. Sci.*, **34**, 19 (1987).
  34. R. Chiarizia, "Stability of Supported Liquid Membranes Containing Long Chain Aliphatic Amines as Carriers," *Ibid.*, **55**, 65 (1991).
  35. G. Wong, V. C. Stent, and R. A. Stanley, *Supported Liquid Membranes for Peptide Separation*, ICOM, Heidelberg, Germany, August 30–September 3 (1993).
  36. Md. M. Hossain and R. A. Stanley, "Selective Transport of a Peptide from Its Mixture with an Amino Acid Using a Supported Liquid Membrane Process," *Sep. Sci. Technol.*, **30**, 3801 (1995).
  37. Md. M. Hossain and R. A. Stanley, "Selective Removal of Hydrophobic Peptides from Protein Hydrolysates in a Continuous Supported Liquid Membrane Process," *Ibid.*, **31**, 1443 (1996).
  38. D. Y. Takigawa, "The Effect of Porous Support Composition and Operating Parameters on the Performance of Supported Liquid Membranes," *Ibid.*, **27**(3), 325 (1992).

Received by editor November 5, 1996

Revision received March 1997