

# Supported liquid membranes: instability effects

A.M. Neplenbroek, D. Bargeman and C.A. Smolders

*University of Twente, Department of Chemical Technology, P.O. Box 217, Enschede (Netherlands)*

(Received July 13, 1990; accepted in revised form March 27, 1991)

## Abstract

The instability behaviour of several supported liquid membranes (SLMs) has been studied for a system in which nitrate ions are removed from an aqueous feed phase and concentrated in a stripping phase. The composition of the aqueous phases and of the membrane liquid has been determined after the aqueous phases had flowed parallel to the membranes for a period of six days. From the experimental data it can be concluded that SLM-failure results from the removal of LM-phase from the support. Contrary to literature data this is not caused by an osmotic pressure difference. It is shown that the membrane stability depends largely on the type of solvent and the molecular structure of the carrier. Furthermore the membrane stability increases with an increasing salt content in the stripping phase (at constant composition of the feed solution).

*Keywords:* coupled, facilitated transport; liquid membranes; supported liquid membranes; liquid membrane stability

## Introduction

The use of SLMs for the selective removal of ions from aqueous solutions is very promising because of the high selectivity and the relative high flux values which can be obtained. However, in practice only a few SLM-systems are being applied, since the stability of the membranes is insufficient and therefore the lifetime of the membranes unpredictable.

In spite of the fact that in the last few years the instability problem has time and again been mentioned [1,2], little systematic research has been done to find the causes of this instability.

At the same time there is a fair number of

observations on the consequences resulting from the instability problem. Two types of SLM instability effects can be distinguished. In the first place there is the problem of a decline in permeability as a function of time [3–10], which is generally ascribed to the loss of carrier from the membrane phase [3,4,11]. In the second place a “break down” of the system can be observed, which means that a direct transport between the two water phases is taking place [6,11–15]. The period of time after which such instability effects are observed can vary from some minutes to several months (in a very few cases). This depends particularly on the type of solvent [5,11] and on the support used [12,13,16,17]. It is remarkable that in Ref. [13,16,17] the use of Accurel<sup>®</sup> (microporous polypropylene from Enka) provides the most stable SLMs.

---

Correspondence to: D. Bargeman, University of Twente, Department of Chemical Technology, P.O. Box 217, Enschede, The Netherlands.

### *Causes of SLM-instability*

It is evident that the solubility of components from the LM-phase into the aqueous phases causes SLM-instability effects. Apart from this it is also possible that the LM-phase is pressed out of the pores of the support because of a pressure difference over the membrane. The maximum acceptable pressure difference which a membrane can resist is given by the Laplace equation. However, in practice it appears that even by preventing LM-components to dissolve into the aqueous phase and by an absence of a pressure difference over the membrane, instability effects do occur.

Two different research groups [18,19] describe the degradation mechanism of SLMs with the same model. They proposed a mechanism in which the degradation of the supported liquid membranes results from an osmotic pressure gradient.

Fabiani et al. [19] describe the determination of water transport through a liquid membrane as a result of an osmotic pressure gradient ( $\Delta\pi$ ) over the membrane. They found that the water transport increases with an increase in  $\Delta\pi$ . They concluded that the water flow through the membrane induces a repulsion of the LM-phase out of the pores of the support which causes the SLM to degenerate.

Danesi et al. [18] investigated the correlations between different physical variables and the stability of SLM-systems. The (salt) permeation and the water transport measurements showed that no water transport occurs when stable SLMs are used. Furthermore they concluded that when the LM-phase can dissolve a large quantity of water and when additionally an osmotic pressure difference is present, transport of water will take place. Apart from these observations stable SLM-systems are characterised by high interfacial tensions between the aqueous- and LM-phase, small

contact angles of drops of aqueous phase in contact with SLMs and a low solubility of water in the LM-phase.

The most important objection against the "osmotic pressure model" is that the results do not prove in any way that the LM-phase is expelled by an osmotic water flow. Another explanation which agrees with the phenomena observed is that the (osmotic) water flow is the result of the removal of the LM-phase from the support by a different primary cause.

Another article dealing with the causes of SLM-instability has recently been published by Takeuchi et al. [20]. In this article a study of the instability behaviour of SLMs with different solvents is given. They determined a so-called "water leakage" based on the leakage transport of ions through the membrane. From the results it was concluded that the stability varies notably with the solvent type and decreases roughly with decreasing interfacial tensions. Furthermore the instability increases with an increase of the flow velocity of the aqueous phases along the membrane and by an increasing hydrostatic pressure gradient over the membrane. The pressure differences applied are substantially smaller than the breakthrough pressures which are needed to expel the absorbed LM-phase from the pores and which can be calculated from the Laplace equation. An explanation for these phenomena was found in the replacement of the LM-phase by the water phase, in which the small pressure differences used facilitate the penetration of the water into the pores. However, the instability mechanism has not been formulated clearly and the relationship between SLM-stability and interfacial tensions is not unambiguous.

From these literature data it appears that until now a consistent model describing the degradation mechanism is missing. However, a breakthrough of the SLM technique such that it can be applied on a practical scale needs a

better understanding of the mechanism of SLM degradation. From the studies performed until now it is clear that this will be a difficult and complex investigation because of the large number of variables that are involved. Danesi et al. [18] illustrates this by calling it a "painful and often frustrating work".

In this paper a start is made with a systematic investigation of the instability factors. The strategy followed will be to make an inventory of instability effects first and then, on the basis of these results, to develop a theory which will be tested afterwards.

Based on the literature data mentioned above we studied the influence of the compositions of the aqueous phases and the membrane phase on SLM-instability. We also measured some physical properties of our system with the purpose to investigate the relevance of these properties to SLM stability. So the effect of solvent viscosity, the solubility of water in the LM-phase and the interfacial tensions between the LM-phase and the aqueous phases were determined in addition to actual nitrate enrichment measurements.

In order to approach the practical conditions and to get as much information as possible we modified our experiments compared to the permeation measurements normally described in literature. These modifications are:

- the feed volume is much larger than the volume of the stripping phase (as is the case in practical situations);
- the aqueous phases are flowing parallel to the membranes day and night;
- apart from the determination of the concentration of the permeating ions in the feed we also determine the concentration of counter ions in the feed;
- at the end of the experiment the membranes are analysed and the amount of carrier and solvent which has been removed from the membrane is determined.

## Experimental

The stability of a number of liquid membranes that are suitable for the removal of nitrate ions from water, has been studied. A description of the transport mechanism has been given earlier [21].

### *Materials*

#### *Carrier*

Two different lipophilic quaternary ammonium compounds are used as carriers: tetraoctyl ammonium bromide (TeOA; Fluka) and trioctylmethyl ammonium chloride (TOMA; Fluka). The first compound was used for studying the transport mechanism [21] while the second compound is frequently applied to the extraction of anions from an aqueous solution [22,23].

#### *Solvent*

The following 4 compounds have been used as solvents: decanol ("Gold Marke"; Aldrich), dibutylphthalate (DBP; Merck), dioctyladipate (DOA; Merck) and *o*-nitrophenyloctylether (*o*-NPOE; Fluka). These solvents have been chosen out of a series of solvents with an extremely low solubility in water of less than 0.01 w/w%; only in the case of decanol a more precise solubility value of 0.037 g/l is given in the literature [24]. These solvents have a low volatility, a viscosity lower than 20 cP and they are able to dissolve the carrier sufficiently (at least to an extent of 0.2 *M*).

All chemicals have been used without further purification.

#### *Support*

Flat sheet Accurel<sup>®</sup>, microporous polypropylene membranes (Enka) have been used as supports. The thickness of the supports was approximately 100  $\mu\text{m}$ , the porosity 69% and the average pore size was 0.1  $\mu\text{m}$ .

### *Membrane preparation*

The SLMs have been prepared by soaking the support for at least 15 min in a 0.2 M carrier solution in one of the solvents mentioned. Before using the membranes the attached liquid was removed from the surfaces of the support by wiping it with a tissue.

### *Methods*

#### *Viscosity measurements*

The kinematic viscosities of the solvents and the LM-phases were determined with an Ubbelohde viscometer. For the calculation of the dynamic viscosities we also measured the densities of the LM-phases with a digital density meter (Parr DMA 50). All measurements were performed at 25°C.

#### *Solubility of water in LM-phase*

Equal quantities of LM-phases (or solvent only) and feed or stripping phase were brought in contact intensively by shaking in a test tube during two hours. The mixture was at rest during three days, in order to establish an equilibrium and to let the phases separate, before samples were taken from the organic phase with an injection syringe. The water content of these samples was analysed according to the Karl-Fischer method.

#### *Interfacial tension measurements*

Interfacial tensions were measured by the Wilhelmy plate technique as described elsewhere [25]. The effect of the composition of the aqueous phase on the interfacial tension was investigated by measuring the interfacial tension values against double distilled water and also against a solution of 4.0 M NaCl. Before the measurements were executed the two liquids were equilibrated by bringing them in contact in a beaker during one night. The interfacial tension was determined from the "maximum pull" by moving the Wilhelmy plate

upwards through the interface. For the measurements ultraclean plates were used which were wetted completely by the heaviest, lower liquid phase. So the contact angle at the plate for the lower liquid was zero during the measurement. This means that for those systems in which the water phase was the lower phase a glassplate was used, while for the other systems a glassplate covered with a gold layer was used.

#### *Analytical methods*

The chloride and nitrate concentrations in the feed were determined by HPLC as described in Ref. [21]. The nitrate content in samples of the stripping phase was analysed spectrophotometrically at a wavelength of 420 nm. First the nitrate ion was reduced to nitrite with sulphuric acid and then complexed with sodium salicylate.

The concentration of the carrier in the membrane was quantitatively determined by the method described by Itoh et al. [22]. For this purpose the LM-phase from the membrane was dissolved in chlorobenzene. After an anion exchange step with the PAR<sup>-</sup> ion [4-(2-pyridylazo)resorcinol] in aqueous solution at pH 10, the concentration of the carrier-PAR complex was determined spectrometrically at a wavelength of 395 nm.

#### *Nitrate enrichment experiments*

Nitrate enrichment experiments were performed by flowing a feed aqueous phase with a volume of 4.1 litre and a sodium nitrate concentration of 0.004 M parallel to the membrane. An aqueous 0.5 M or 4.0 M sodium chloride solution with a volume of 0.13 litre was used as the stripping phase.

Preliminary measurements showed that for the SLMs with decanol and DBP as solvent the removal of LM-phase from the support was considerable. In these cases the aqueous phases were saturated with the LM solvent before

starting up the experiment to prevent the removal of the liquid membrane by solution effects. This was done by adding 0.5 ml organic solvent per litre to the water phase under stirring. An organic phase in contact with the water phase was constantly visible during the experiment because of this large excess. The experimental set up is given in Fig. 1.

To prevent hydrostatic pressure differences over the membrane during the experiment, the inlet-openings of the aqueous phases to the buffer vessel containing stripping phase and to the stock vessel containing feed were kept at the same level. The flow velocities of the aqueous phases along both sides of the membrane were also kept equal to a value of 5.5 ml/sec with the use of "tubing pumps" (Masterflex®). The measurements ran 24 hr per day in a thermostated room at 25°C. Feed-samples of 1 ml were taken regularly and analysed to obtain the chloride and nitrate content. Likewise the nitrate content of the stripping phase was determined spectrophotometrically to control the mass balance.

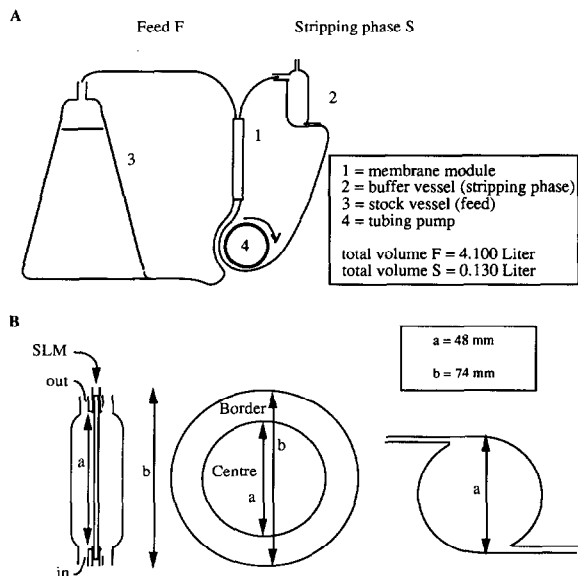


Fig. 1. (A) experimental set up; (B) dimensions of the membrane and membrane module.

From the decrease in nitrate content in the feed with respect to the initial concentration ( $-\Delta[\text{NO}_3^-]$ ) and the increase in chloride concentration in the feed ( $\Delta[\text{Cl}^-]$ ) during the experiment a counter transport factor  $CTF$  was calculated:

$$CTF = (-\Delta[\text{Cl}^-] / \Delta[\text{NO}_3^-])_{\text{Feed}} \quad (1)$$

This factor can be used as a measure for the direct (leakage) transport of chloride ions through the membrane.

Before starting the experiment the masses of the different membranes were determined. After 6 days the experiments were stopped and the centres and the borders were separated (by cutting the centres out of the membranes) and the carrier concentrations and the masses of these membrane parts were determined. The removal of solvent and carrier during the experiments both for the border part and for the centre part of the different membranes can be calculated from the changes in carrier concentrations and the masses determined.

## Results and discussion

The carrier TOMA was soluble in all four solvents to at least 0.2 M, while TeOA only dissolved in decanol and *o*-NPOE up to this concentration.

### Nitrate concentration in the feed as a function of time

Figures 2(A) and 2(B) show the nitrate concentrations in the feed as a function of time, with a chloride concentration in the stripping phase of 0.5 M and 4.0 M respectively.

The special marks indicate the moment at which a counter transport factor larger than 1 is measured. This means that at this time a direct diffusion transport of chloride ions from the stripping phase to the feed phase occurs through leaks in the LM-phase. Because of these leaks the chloride concentration in the

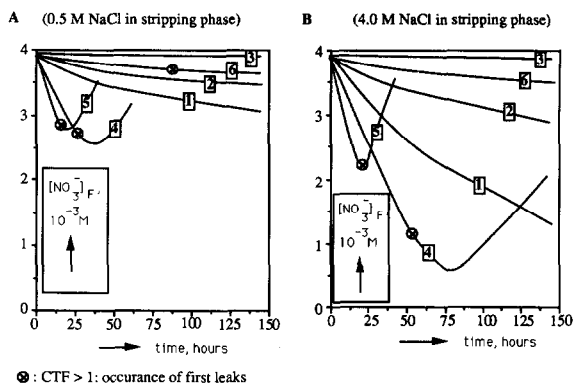


Fig. 2. Nitrate concentration in the feed as a function of time for the systems: (1) TeOA-*o*-NPOE; (2) TOMA-*o*-NPOE; (3) TOMA-DOA; (4) TeOA-decanol; (5) TOMA-decanol; and (6) TOMA-DBP. Feed: 0.004 M NaNO<sub>3</sub>; stripping phase: (A) 0.5 M NaCl and (B) 4.0 M NaCl.

feed can increase to such an extent that an accurate nitrate determination with HPLC is not possible any more.

#### Nitrate concentration in the stripping phase

To illustrate that we are dealing with a process in which nitrate ions are being concentrated some stripping phases were analysed. Because more nitrate is removed from the feed in the experiments with 4.0 M NaCl in the stripping phase than with 0.5 M NaCl, the nitrate content in 2 stripping phases with a composition of 4.0 M NaCl was determined. Based on the spreading in results of duplicated measurements the error in these spectrometric nitrate determinations are rather large and the errors have been estimated to  $\pm 10$  mM. These errors are caused by the presence of large amounts of chloride ions, which disturb the quantitative nitrate determination. Figure 3 shows the nitrate concentration in the stripping phase for the experiments with TeOA as carrier and decanol and *o*-NPOE as solvents (experiments 4 and 1 in Fig. 2B).

When comparing the change in nitrate concentration in the stripping phase (Fig. 3) with the decrease in nitrate concentration in the feed

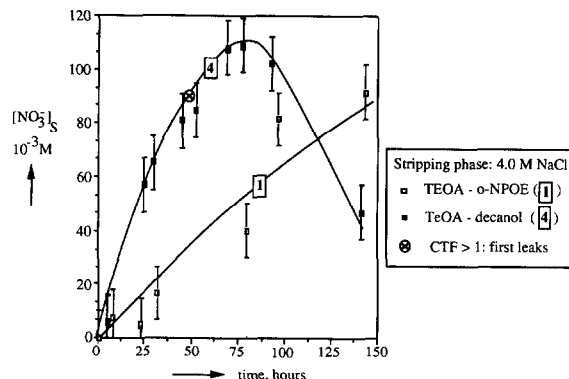


Fig. 3. Nitrate concentration in the stripping phase as a function of time.

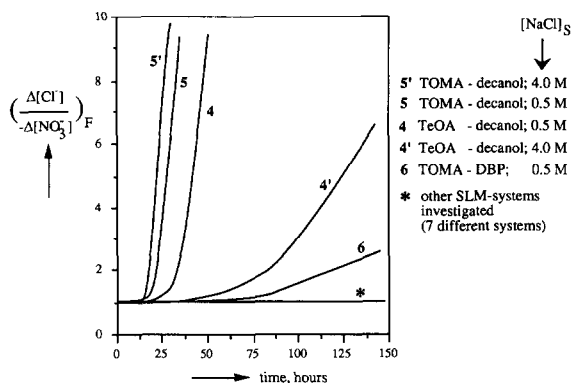


Fig. 4. Countertransport factor as a function of time.

for the same systems (Fig. 2) it appears that the increase in nitrate content in the stripping phase agrees quite well with the decrease in nitrate concentration in the feed multiplied by the volume ratio factor (31.5). The leakage behaviour of the membrane using decanol as solvent is illustrated also in this curve. It can be concluded that the nitrate that is removed from the feed is indeed concentrated in the stripping phase.

#### Counter transport factor (CTF)

Figure 4 shows the countertransport factors for the different SLM-systems as a function of time.

In Ref. [21] we found that the transport

mechanism prescribes an equimolar ion exchange between the carrier-nitrate complex and the chloride ion, which means that a counter transport factor of 1 should be expected. It appears that this value is being exceeded for 5 systems after some time. This means that a direct diffusive chloride transport from stripping phase to feed occurs through leaks in the LM-phase. For the other systems no leakage takes place.

### Removal of LM-phase

Immediately after finishing the experiments the masses of the membranes (centres and border area) were measured. In Table 1 the removal of LM-phase is given for the different membranes at the two different compositions of the stripping phase. For both the border and the centre area of the membrane the percentages of solvent and carrier that were removed are recorded. These data will be discussed in the general discussion.

### Visual observations

For a number of experiments, transport of water from the feed to the stripping phase could be observed after some time. This could be noticed by an increase of the volume of the stripping phase in the buffer vessels which resulted in an overflow. It was often accompanied by a slight bulging of the membranes to the feed-side. The membrane deformation is caused by the hydrostatic pressure difference due to the transport of water. This phenomenon was only noticed for those SLMs which showed chloride-leakages (on account of an increasing countertransport factor). The time at which the osmotic water transport was observed coincided with the moment at which the deviation of the counter transport factor value from 1 was measured.

From the transparency of the membrane it could also be seen that during the experiment LM-phase is removed from the support. This gives the opportunity to get a qualitative impression of the stability of the membrane. The membranes with an aromatic solvent (*o*-

TABLE 1

Removal of LM-phase for different SLMs and  $[\text{NaCl}]_s$  (after 6 days of nitrate enrichment experiments)

system	LM		$[\text{NaCl}]_s$		LM-removal (%)			
	solvent	carrier	0.5 M	4.0 M	centre part		border part	
					carrier ( $\pm 5\%$ )	solvent ( $\pm 2\%$ )	carrier ( $\pm 5\%$ )	solvent ( $\pm 2\%$ )
1	<i>o</i> -NPOE	TeOA	×		-7	-5.5	-13	+0.6
				×	-5	-4.5	-7	+0.2
2	<i>o</i> -NPOE	TOMA	×		-74	0.0	-28	-3.4
				×	-76	+1.3	-16	-2.2
3	DOA	TOMA	×		-80	-3.2	-24	-2.1
				×	-76	-4.4	-21	-7.1
4	decanol	TeOA	×		+4	-84	-63	-74
				×	+18	-76	-45	-60
5	decanol	TOMA	×		-77	-92	-54	-76
				×	-74	-92	-34	-62
6	DBP	TOMA	×		-84	-62	-66	-62
				×	-84	-30	-44	-36

TABLE 2

Physical properties of LM-systems

system	LM		viscosity (cP)	solubility of water in LM-phase		interfacial tension	
	solvent	carrier (0.2 M)		0.004 M NaNO <sub>3</sub> (%)	4.0 M NaCl (%)	water (10 <sup>-3</sup> N·m <sup>-1</sup> )	4.0 M NaCl (10 <sup>-3</sup> N·m <sup>-1</sup> )
1	<i>o</i> -NPOE	-	12.3	0.1	0.1	27.9	35.0
	<i>o</i> -NPOE	TeOA	21.0	0.6	0.7	16.4	17.3
2	<i>o</i> -NPOE	TOMA	17.1	1.3	1.1	5.0	7.3
	DOA	-	11.1	0.2	0.2	19.1	24.0
3	DOA	TOMA	15.2	2.2	1.7	2.0	6.2
	decanol	-	11.8	3.9	2.5	7.7	10.1
4	decanol	TeOA	20.4	3.6	2.5	8.8	11.4
5	decanol	TOMA	16.8	4.8	3.1	6.6	10.6
	DBP	-	15.8	0.4	0.3	19.1	23.5
6	DBP	TOMA	22.7	2.0	1.5	4.3	5.9

NPOE and DBP) provide a transparent membrane at the moment the LM-phase is added to the support. The SLMs with decanol and DOA as solvents are somewhat less transparent at the start. During the experiments the SLMs are generally becoming less transparent due to a partial removal of LM-phase out of the support. It was noticeable that always the border of the membrane was less turbid than the centre, indicating that more LM-phase is removed from the centre of the membrane than from the border.

#### Physical properties

The viscosities, water solubilities in the LM-phase and the interfacial tensions of the different organic (LM) phases against aqueous phases are given in Table 2.

#### Viscosity

The results of the viscosity measurements (given in Table 2) show that the viscosities of the different organic phases are of the same order of magnitude. As could be expected the viscosity increases when carrier is added to the organic phase; TeOA has a larger effect on the viscosity increase than TOMA.

#### Solubility of water in the LM-phase

Table 2 shows that in general the solubility of water in the organic phase increases when carrier is present. This is probably caused by the hydration of the carrier molecules. The higher increase in water solubility with TOMA than with TeOA can be explained by the larger interaction that can occur between water and TOMA-molecules than between water and TeOA-molecules. Because of the presence of one methyl group in the TOMA-molecule, the hydrophilic N<sup>+</sup>-part can be approached better by water than in case of the TeOA-molecule with 4 relatively long alkyl chains.

#### Interfacial tension

The experimental results given in Table 2 also show that the presence of carrier molecules in the organic phase generally leads to a reduction in the interfacial tension against water because of the surface activity of the quaternary ammonium salts. The fact that TOMA lowers the interfacial tension more than TeOA, can be explained again by the larger interaction between water and TOMA than between water and TeOA as a result of the geometric structure of the carriers.



## General discussion

From the different results it can be concluded that there are large differences in the stability of the SLMs depending on the composition of the membranes and somewhat on the composition of the aqueous phases. In agreement with observations in literature mentioned before, the instability effects can not be explained by the molecular solubility of LM-components into the water phase.

In view of the relatively small differences in viscosities of the different organic phases and the large differences in SLM-stabilities it is also concluded that there is no direct relation between the stability and the viscosity of the membrane phase. This means that the flow of the organic phase through the pores of the support, which depends on the viscosity of the liquid, is not the major factor which determines the stability of the SLMs.

There is some connection between the interfacial tensions and the instability effects. In general the LM-phases which have the highest interfacial tensions provide the most stable SLMs. But this relation is not unambiguous. These observations are in agreement with the conclusions of Takeuchi et al. [20] who could not formulate an explicit instability mechanism based on interfacial tensions.

### *SLM-failure*

The results given in Table 1 clearly show that a large amount of solvent is removed after 6 days, especially from the SLMs having decanol and DBP as solvent and which show leakage of chloride ions within a couple of days (Fig. 4). The other membranes, which did not fail, show appreciably less solvent removal. Apparently SLM-failure is induced by LM-removal and the extent of LM-removal appears to be determined predominantly by the choice of the solvent.

The fact that SLM-failure is the outcome of

LM-removal is not so hard to understand when we realize that the LM-phase, which is removed from the pores, is replaced by the aqueous phase. A complete removal of LM-phase from one of the pores will short-circuit the feed and the stripping phase. Once there is a continuous water path in the membrane this will lead to chloride leakage into the feed due to ion diffusion and to water transport through the membrane into the stripping phase as a consequence of the osmotic pressure difference between the two aqueous phases. But, from the point of view of the first observation of leakage, it appears that the transport of water is a consequence of SLM-instability and not the cause of LM-removal.

The values of the solubility of water in the LM-phase show that there is no correlation between this property and the stability of SLMs. In view of these results the mechanism (as suggested in Refs. [18,19]) of LM-repulsion due to a transport of water as a consequence of the solubility of water in the LM-phase combined with an osmotic pressure difference can be seriously doubted. In any case it is necessary to have a continuous pathway for the aqueous phase in the LM-phase in order to create an effective osmotic pressure difference that could remove the LM-phase out of the pores based on convective, frictional effects. The quantities of water which dissolve into the LM-phase are so low that this is not very probable.

It is interesting to note from the results given in Figs. 2 and 3 that even when the counter transport factor deviates from one (and hence the membrane is leaking) the process of nitrate removal generally continues for some time before the nitrate concentration in the feed increases again by back diffusion from the stripping phase. This means that we are dealing with just a restricted breakthrough of the membrane, while the largest part of the membrane is still intact and keeps on functioning.

### Permeability

It is conceivable that the permeation behaviour, as represented in Fig. 2, will be influenced to a large extent by the ease of removal of the carrier from the membrane. The quantity of carrier removed from the membrane is determined especially by the structure of the carrier. It follows from Table 1 that the carrier TeOA (with a symmetrical structure) is removed from the membranes to a much smaller extent than TOMA.

From Fig. 2 it also appears that the nitrate fluxes are generally larger for a stripping phase of 4 M NaCl than for 0.5 M. On the one hand this is caused by an increased level of desorption of nitrate ions into the stripping phase (resulting in an increase in driving force for transport), while on the other hand the influence of the composition of the stripping phase on the SLM-stability also determines these differences. As can be seen in Table 1 always more carrier is removed from the membrane when 0.5 M NaCl is used in comparison with a strip concentration of 4.0 M NaCl. This effect also causes lower fluxes for the 0.5 M NaCl stripping phases.

It is remarkable (see Table 1) that the composition of the stripping phase has no special effect on the removal of solvent from the membrane. Only in case of decanol and DBP as solvents somewhat more solvent has been removed from the SLMs when a stripping phase of 0.5 M NaCl is used compared to a stripping phase with 4.0 M NaCl. Once again this is in contradiction with the mechanism in which osmotic pressure differences are believed to be the reason for the instability effects. Such a model predicts greater instability effects for a larger osmotic pressure difference over the membrane. The results however show that the opposite is true. Generally the SLMs are more stable when using a stripping phase with 4 M NaCl than with 0.5 M NaCl. Because of these results the influence of the composition of the

aqueous phases on the stability of the SLMs is studied further [26].

Table 1 also shows that generally both solvent and carrier are removed from the border area to a lower extent than from the central area. An explanation for this difference might be that the LM-phase is removed from the central area and is partly replenished by LM-phase from the border by lateral diffusion through the pores of the support.

Finally, as will be shown in a following paper [26], there are strong indications that the instability is caused by the formation of emulsions. While performing the determination of the solubility of water in the organic phases the formation of stable emulsions have been observed for several systems. The ease with which these emulsions were formed coincides to a large extent with the instability effects observed for the different SLM-systems. In Ref. [26] this hypothesis is tested for the description of the degradation mechanism.

### Conclusions

An onset to a systematic investigation of the instability mechanism of SLMs was performed by collecting information about instability effects of different SLMs. From the results of the experiments one can conclude that SLM-failure is induced to a great extent by solvent removal from the support and by the removal of the carrier from the membrane-phase. The first mentioned effect is determined predominantly by the type of solvent used whereas the second effect largely depends on the molecular structure of the carrier.

The instability effects are generally larger when a stripping phase of 0.5 M NaCl flows parallel to the membrane than when 4.0 M NaCl is used. Furthermore the removal of LM-phase from the central part of the membrane is generally larger than from the border area which is not in contact with the aqueous phases.

There is no direct relation between the instability effects of the liquid membranes and the viscosity of the LM-phases. There is some connection with the solubility of water in the organic phase and with the interfacial tension between water and the LM-phases but these relations are not unambiguous. The instability effects observed are in disagreement with the model of LM-repulsion due to an osmotic pressure difference over the membrane.

### Acknowledgement

The authors wish to thank Z. Borneman and P. Schwering for the experimental help and the stimulating discussions. This work was financially supported by the Dutch Ministry of Economic Affairs, within the Dutch research program on membranes.

### References

- 1 C. Gavach, Ion transport in liquid membranes, Proceedings of the 4th summer school in membrane science, Sept. 13-18, Chester, England, (1987).
- 2 L.L. Tavlarides, J.H. Bae and C.K. Lee, Solvent extraction, membranes, and ion exchange in hydrometallurgical dilute metals separation, Sep. Sci. Technol., 22 (1987) 581.
- 3 T. Shimidzu and H. Okushita, Carrier-mediated selective transport of  $Ga^{3+}$  from  $Ga^{3+}/Al^{3+}$  binary solutions and  $Cu^{2+}$  from  $Cu^{2+}/Zn^{2+}$  binary solutions through alkylated cupferron-impregnated membrane, J. Membrane Sci., 27 (1986) 349.
- 4 L. Fernandez, J. Aparicio and M. Muhammed, Coupled zinc transport through a bis(2-ethylhexyl)-phosphoric acid solid-supported liquid membrane from aqueous perchlorate media, J. Membrane Sci., 27 (1986) 77.
- 5 R. Bloch, A. Finkelstein, O. Kedem and D. Vofsi, Metal-ion separation by dialysis through solvent membranes, Ind. Eng. Chem., Process Des. Dev., 6 (1967) 231.
- 6 M. Nakano, K. Takahashi and H. Takeuchi, A method for continuous operation of supported liquid membranes, J. Chem. Eng. Jpn., 20 (1987) 326.
- 7 M. Teramoto, H. Matsuyama, H. Takaya and S. Asano, Development of spiral-type supported liquid membrane module for separation and concentration of metal ions, Sep. Sci. Technol., 22 (1987) 2175.
- 8 O. Loiacono, E. Drioli and R. Molinari, Metal ion separation and concentration with supported liquid membranes, J. Membrane Sci., 28 (1986) 123.
- 9 M. Teramoto and H. Tanimoto, Mechanism of copper permeation through hollow fiber liquid membranes, Sep. Sci. Technol., 18 (1983) 871.
- 10 P.R. Danesi, Separation of metal species by supported liquid membranes, Sep. Sci. Technol., 19 (1984) 857.
- 11 J.D. Lamb, R.L. Bruening, R.M. Izatt, Y. Hirashima, P.-K. Tse and J.J. Christensen, Characterization of a supported liquid membrane for macrocycle-mediated selective cation transport, J. Membrane Sci., 37 (1988) 13.
- 12 A.C. Muscatello, J.D. Navratil, M.E. Killion and M.Y. Price, Supported extractant membranes for americium and plutonium recovery, Sep. Sci. Technol., 22 (1987) 843.
- 13 M. Tromp, M. Burgard and M.J.F. Leroy, Extraction of gold and silver cyanide complexes through supported liquid membranes containing macrocyclic extractants, J. Membrane Sci., 38 (1988) 295.
- 14 L.A. Ulrick, K.D. Lokkesmoe and M.M. Kreevoy, Mechanism of anion pumping through a synthetic liquid membrane, J. Phys. Chem., 86 (1982) 3651.
- 15 B.M. Johnson, R.W. Baker, S.L. Matson, K.L. Smith, I.C. Roman, M.E. Tuttle and H.K. Lonsdale, Liquid membranes for the production of oxygen-enriched air. II. Facilitated-transport membranes, J. Membrane Sci., 31 (1987) 31.
- 16 G. Parkinson, H. Short and S. McQueen, Liquid membranes, Chem. Eng., 22/8 (1983) 22.
- 17 M.E. Duffey, D.F. Evans and E.L. Cussler, Simultaneous diffusion of ions and ion pairs across liquid membranes, J. Membrane Sci., 3 (1978) 1.
- 18 P.R. Danesi, L. Reichley-Yinger and P.G. Rickert, Lifetime of supported liquid membranes: the influence of interfacial properties, chemical composition and water transport on the longterm stability of the membranes, J. Membrane Sci., 31 (1987) 117.
- 19 C. Fabiani, M. Merigiola, G. Scibona and A.M. Castagnola, Degradation of supported liquid membranes under an osmotic pressure gradient, J. Membrane Sci., 30 (1987) 97.
- 20 H. Takeuchi, K. Takahashi and W. Goto, Some observations on the stability of supported liquid membranes, J. Membrane Sci., 34 (1987) 19.
- 21 A.M. Neplenbroek, D. Bargeman and C.A. Smolders, Nitrate removal using supported liquid membranes: transport mechanism, J. Membrane Sci., 67 (1992) 107.

- 22 I. Itoh, H. Kobayashi and K. Ueno, Liquid ion-exchange extraction study of hexacyanoferrate (III) with trioctylmethylammonium chloride (Aliquat-336), *Anal. Chim. Acta.*, 105 (1979) 383.
- 23 T. Sato, Y. Takeuchi and K. Sato, The extraction of hexavalent metals (chromium, molybdenum, tungsten) from alkaline solutions by long-chain alkyl quaternary ammonium compounds, *Proceedings of the International Solvent Extraction Conference, München, 1986, Dechema, Frankfurt a. Main, II-153.*
- 24 K. Kinoshita, H. Ishikaura and K. Shinoda, Solubility of alcohols in water determined by surface tension measurements, *Bull. Chem. Soc. Japan*, 31 (1958) 1081.
- 25 H.S. van Damme, A.H. Hogt and J. Feijen, Surface mobility and structural transitions of poly(n-alkyl methacrylates) probed by dynamic contact angle measurements, *J. Colloid Interface Sci.*, 114 (1986) 167.
- 26 A.M. Neplenbroek, D. Bargeman and C.A. Smolders, Mechanism of supported liquid membrane degradation: emulsion formation, *J. Membrane Sci.*, 67 (1992) 133.