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Supported liquid membranes: stabilization by gelation

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Abstract

A new method has been developed to increase the stability of supported liquid membranes. By applying a homogeneous gel network in the pores of the support both the mechanical stability (against liquid displacement) and the long term permeability increase substantially. The flux decreases only slightly because of the open structure of the gel network. A second technique, by which a thin dense gel layer is applied to the feed side of the membrane, results in a specific suppression of the formation of emulsion droplets. The stability of the membrane increases by this treatment to values which are very promising.

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

Introduction

"A gel is a form of matter intermediate between a solid and a liquid. It consists of polymers or long-chain molecules cross-linked to create a tangled network and immersed in a liquid medium. The liquid prevents the polymer from collapsing into a compact mass; *the network prevents the liquid from flowing away*" [1].

The last part of this definition has been italicized because that's exactly what we need in order to stabilize supported liquid membranes (SLMs). The idea of "gelled" liquid membranes is not new. Already in 1967 Bloch et al. [2] published about the separation of metal ions by dialysis through so called "solvent membranes". This plasticised polymeric type of membrane contained an alkyl-phosphoric ester, which acted as extraction agent and as transport medium for the metal salts. One conclusion of this research was that the stability of this type of membrane had to be extended before the method is of practical value. Further research at the same institute for other systems was described in a number of papers [3–5]. However the conclusion remained that the lack of stability caused a major problem while furthermore the flux was too small [6].

The idea to apply homogeneously swollen polymeric films is also used by other researchers; this type of swollen films is often called "solvent polymeric membranes". Examples of transport studies for different systems, in which often a specific carrier is present, are described particularly by Sugiura et al. [7–10]. Relatively high polymer contents and rather thick membranes are necessary to obtain sufficient mechanical strength. This leads to long diffu-

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sion times of the carrier molecules through the membrane which results in a low permeability. The experimentally determined fluxes, which are in the order of magnitude of 10^{-11} mol/cm^2-sec, are a factor 100 lower than the fluxes through our type of SLMs of which the transport of nitrate ions and the fluxes obtained have been given before [11].

Swollen polymeric membranes, to which an active component is added, are also frequently used for the development of ion selective electrodes [12–14]. For these sensor systems it is sufficient that a minute quantity of one component out of a mixture permeates to a detector room. The mobility of the selective component through the film is of minor importance for most applications because these membranes only have an analytical purpose.

To enhance the flux through this type of membranes with relatively high polymer contents, and thus to make them suitable as selective transport medium, "composite solvent swollen membranes" are developed [15,16]. These membranes have a thin gel layer onto a microporous support and they are only suitable for the separation of gas mixtures which exhibit fast diffusion in the open pores. To get an effective transport of a component out of a liquid mixture using such a composite it is necessary that the feed or the stripping phase, which both have to be in contact with the membrane liquid, penetrates into the pores of the support. Because there is no convective flow in these pores, the mass transfer will be liquid diffusion controlled and the flux will be small again.

In our institute the idea rose to enhance the stability of SLMs by gelling the LM-phase *in* the pores of the support. In this case the inert support does not only immobilize the membrane liquid but also provides mechanical strength to the gel by functioning as a kind of a frame. Only a small amount of polymer in the gel is required, without the risk of deforming the membrane by the aqueous phases which flow parallel to the membrane surface. This can lead to such an open structured gel network that it may be expected that the diffusion rate of the carrier complex through this gelled phase is diminished only to a small extent.

Based on the definition of a gel, it might be expected that the LM-phase is fixed better in the support when a polymer network is present. By gelling the membrane liquid its macroscopic viscosity will increase and thus the resistance against liquid displacement out of the membrane pores will be enhanced. Especially the formation of emulsion droplets, which is the main cause of SLM-degradation [17], will be prevented and so the stability of the membrane will increase.

Except for a study of the influence of the gel network on the permeability and the long term stability behaviour, also the mechanical stability of the gelled SLMs has been tested in this article. Again *o*-nitrophenyloctylether (*o*-NPOE) was used as a solvent for the various experiments; this solvent was chosen at an early stage because of its capacity to form gel networks with small amounts of polymer, while in previous research [18] it appeared that, out of a selection of potential solvents, this solvent gave the most stable SLMs. Tetraoctylammonium bromide (TeOA) was mostly used as carrier, in a system in which nitrate ions were transported, but also experiments using trioctylmethylammonium chloride (TOMA) were carried out. PVC was used as gel forming polymer with *o*-NPOE as solvent; the influence of chemical crosslinking of this polymer in the network has also been studied.

Furthermore the influence of a gel network on the stability of SLMs with the least stable solvent (decanol) has been investigated. Poly(vinylisobutyleter) has been used as the polymer for the gelation of LM-phases with decanol; this polymer has been used for the preparation of a matrix for an ion selective electrode with decanol as solvent [19].

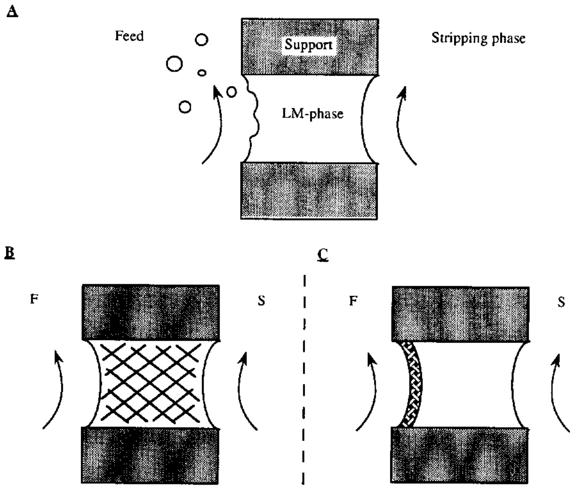

Fig. 1. Influence of a gel network on SLM-stability; A. without gel network: SLM-degradation by emulsion formation (due to local deformation of LM-phase in the pores of the support); B/C: SLM-stabilization by gelation; B: homogeneous gel network in LM-phase; C: one thin dense gel layer at the interface with the feed.

Finally, apart from these homogeneously gelled SLMs also membranes were developed in which on one side of the membrane a thin gel layer with a dense structure was applied. The formation of emulsion droplets caused by the flow of the feed solution is specifically suppressed in this way. The stability of these membranes is investigated by simulating the long term permeability behaviour to study the effect of the layer in a short period of time. This means that the degradation process of the membrane has been accelerated on purpose.

The expected effect of both types of gel networks on the fixation of the LM-phase in the pores of a support is presented schematically in Fig. 1.

PVC-gels

For the improvement of the stability of SLMs suitable for the removal of components out of an aqueous solution, by means of gelation, a *hydrophobic* gel has to be prepared. For this purpose the choice of poly(vinylchloride) (PVC) is self-evident because we already obtain a gelled phase at low concentrations of this polymer (from 3% on, Ref. [20]). Furthermore this polymer is at present the most frequently used type in related systems like ion selective electrodes [12,21,22]. For these last mentioned applications, studies have been performed on the usefulness of other polymers like poly(urethane) [23], poly(methylmethacrylate), poly(styrene) and silicone rubber [14]. All these membranes were of poorer quality, as far as stability and sensitivity are concerned, than solvent membranes with PVC as polymer.

In spite of numerous investigations, the mechanism of formation and the structure of PVC-gels still have not been fully elucidated [20,24,26–28]. The most accepted hypothesis is that the gel crosslinking points are microcrystalline regions formed from occasional syndiotactic runs in a predominantly atactic polymer [26]. Mechanical properties of PVC-gels, like the storage modulus and the dynamic viscosity, are investigated in a.o. Refs. [20,24,25]. An important property of this type of gels is that the physical crosslinks formed are thermo-reversible.

Physically crosslinked gels can be formed by means of dissolving the polymer in the solvent at increased temperature. The gel network is formed when this solution is cooled. A different preparation method is to dissolve the polymer and the solvent in a suitable volatile second solvent. Gelation takes place by evaporating the volatile solvent. For the preparation of PVC-gels tetrahydrofuran (THF) is mostly used as volatile solvent.

In this paper we also describe experiments in which a gel network is created with a shorter mesh size by crosslinking the polymer not only physically but also chemically. For this purpose PVC with carboxylic acid groups was used as the starting material and a diamine as the crosslinking agent. The chemical coupling re-

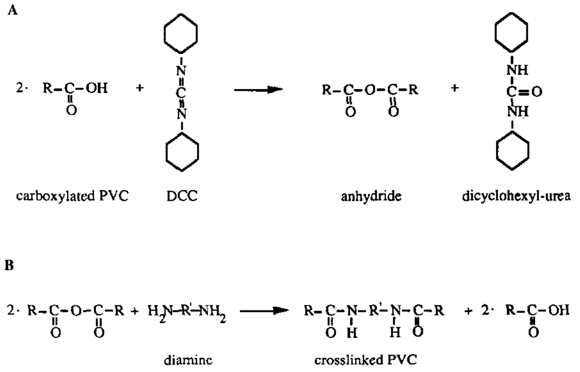

Fig. 2. Chemical coupling of carboxylated PVC; A: activation of carboxylated PVC by DCC, B: reaction of coupled polymeric chains with a diamine.

action, as given in Fig. 2, consists of 2 steps which are performed at room temperature. In the first step the carboxylic groups are "activated" by a di-imide compound (N,N'-dicyclohexylcarbodiimide; DCC). The mechanism of this activation reaction, in which an anhydride is formed, is described in more detail in Ref. [29]. In the next step the reaction with the diamine compound forms chemically stable bonds. This reaction runs analogous to the coupling of an amine to an anhydride as described in Ref. [30]. Because each PVC-chain (which can be branched) contains several carboxylic acid groups which can be coupled to other carboxylic acid groups, a crosslinked polymeric network will be formed.

Experimental

SLM-preparation

A. Homogeneously gelled liquid membranes

Two types of PVC were used for the preparation of the various homogeneously gelled SLMs: PVC-Fluka ("high molecular weight") and PVC-BASF ("Vinoflex 531"). The molecular weights of these polymers have been determined by gel permeation chromatography leading to MW values of 91,000 for PVC-Fluka and of MW=80,000 for PVC-BASF.

Accurel® (microporous polypropylene from Enka; batch "1E/PP"; thickness: 90 μm; porosity: 73%) and Celgard® (microporous polypropylene from Celanese; thickness: 25 μm; porosity: 45%) were used as supports.

For the preparation of the gelled membranes by using a temperature treatment, weighted amounts of LM-phase and polymer were put in a petri-dish. Homogeneous solutions were obtained by placing this mixture in an oven at 120°C for half an hour while stirring this once in a while. After the supports had been immersed in this solution for three minutes the membranes were taken out of the solution and the extra substance, sticking to the membrane surface, was removed outside the oven with a tissue. Especially the membranes with high polymer contents had to be treated rather quickly, because otherwise the membranes cooled down and gel formation occurred.

When preparing gelled SLMs according to the method of using a volatile solvent the LM-phase and polymer were dissolved in THF by stirring (ca. 5 ml THF was used on 1 ml of LM-phase). This solution was poured out in a petri-dish and then the support was immersed in the solution. The THF evaporated from the uncovered dish. After one night, when the THF was evaporated entirely, the gel substance attached to the membrane surface was removed with a tissue.

Gelled membranes without support were obtained by pouring out a solution of polymer, LM-phase and THF in a petri-dish and by evaporating the THF. After one night the films were pulled out of the dishes carefully. The thicknesses of these membranes were determined with a Mitutoyo digital thickness meter.

The membranes used for the experiments were always prepared at least three days before use.

Gelled membranes in which decanol was used as membrane solvent were prepared by the above mentioned method of using a volatile solvent. In this case poly (vinylisobutylether (Lutonal® IC K 110 BASF) was used as polymer and again THF as volatile solvent.

B. SLMs with an interfacial dense gel layer

To apply a dense gel layer at the interface of the membrane first a liquid SLM is prepared. This means that the support is soaked in the LM-phase so that the LM-phase can penetrate into the pores. The attached liquid is removed from the surfaces of the membrane with a tissue.

Separately the gel forming polymer and LM-phase are dissolved in THF by stirring (ca. 10 ml THF per gram of polymer). Activator and crosslinking agent, if any, are added to this solution. The gel layer is applied by wetting a tissue in the gel-forming solution and spreading a layer with this tissue as smoothly as possible over the membrane surface. The THF evaporates during this treatment.

The following polymers were used: PVC-Fluka ("high molecular weight") and PVC-carboxylated (Janssen-Chimica) with 0.3×10^{-3} equivalent carboxylic groups per gram polymer [31]. N,N′-dicyclohexylcarbodiimide (DCC) was used as activator and 1,12-diaminododecane (DDDA) and 1,4-phenyldiamine (PDA) were used as crosslinking agents.

The total amount of PVC put on the membrane surface was determined quantitatively by gel permeation chromatography after redissolving the gel mass of a part of the membrane in THF.

Permeability measurements

To determine the permeability of the various SLMs the permeation set up as described before has been used [11]. The SLMs were clamped in the module and a feed solution of 0.004 *M* $NaNO_3$ and a stripping phase of 4.0 *M* NaCl were circulated through the cell halves with a flow rate of 5.5 ml/sec. Under these conditions the transport is limited by diffusion of the carrier molecules through the membrane liquid [11]. The flux was calculated from the slope of the curve for the nitrate concentration in the feed as a function of time.

Mechanical stability (liquid displacement) measurements

A new method has been developed to determine the resistance of the gelled membranes against pressure differences. For these measurements the experimental set up represented in Fig. 3 has been used.

The membrane, supported by a screen (Millipore: xx 4504704), was clamped in a high pressure filter holder (Millipore: xx 4504700). A layer of aqueous solution of 4 *M* NaCl was put on top of the membrane. The module was placed in a beaker with demi-water. The support screen and thus the lower-surface of the membrane were in direct contact with the demi-water phase. The water was stirred vigorously. A N_2-pressure was put on the upper side of the membrane, after which the pressure difference over the membrane was increased stepwise. The breakthrough behaviour of the SLMs could be determined by determining the conductivity of

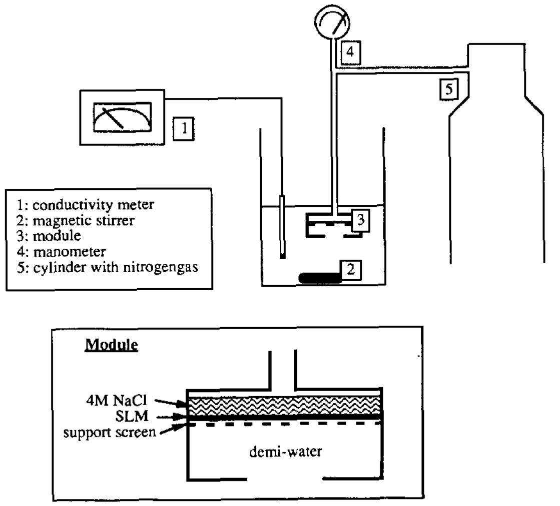

Fig. 3. Experimental set up to determine the mechanical stability of SLMs.

the demi-water phase as a function of the pressure difference.

LM-removal by emulsion formation

These experiments were carried out in the same way as described before [17] and thus the feed and stripping phase during these measurements were given exactly the same composition when passing through the cell halves during the measuring time.

Solvent removal; in these measurements no carrier was present in the membrane solvent. The amount of LM-phase removed from the support was calculated by determining the weight of the membranes before the experiment was started and by weighing the centres of the membranes after the measurements were finished.

Carrier removal; the amount of carrier removed from the central area of the membranes was determined spectrophotometrically as described in Ref. [18].

Long term permeability

Measurements using homogeneously gelled membranes and Celgard as support

These experiments were performed in the same way as described before [17], i.e. feed and stripping phases (with equal volumes of 130 ml) were refreshed every 3 or 4 days. The nitrate and chloride contents were measured as a function of time by analyzing samples, which were taken periodically from the feed, using HPLC. From the increase in chloride content in the feed, and the calculation of the counter transport factor as a function of time [18], the occurrence of direct chloride leakage from stripping phase to feed could be determined.

Measurements using homogeneously gelled membranes and Accurel as support

The performance of these experiments were nearly the same as for the experiments with Celgard as support, except for the large feed volume of 4.1 l (like in the concentrating experiments described earlier [18]) that was used and the aqueous phases that were replaced by fresh starting solutions every week. After ca. 12 weeks the presence of small gas bubbles became visible at the surface of the membranes. These bubbles were removed by tapping.

Simulating long term permeability (by accelerated degradation)

During these measurements the permeability of a membrane was determined in the usual way by analyzing samples, which were taken periodically from the feed. For this purpose a feed solution of 4×10^{-3} M $NaNO_3$ (130 ml) and a stripping phase of 4 M NaCl (130 ml) were passed parallel to the membrane surface with a flow rate of 5.5 ml/sec. The flux was measured. After ca. 5 hr the "degradation process conditions" were installed by replacing the feed solution by an aqueous solution of 10^{-4} M NaCl, which then was passed along the membrane. The next day the stripping phase was replaced by a fresh solution of 4 M NaCl and the feed by a 4×10^{-3} M $NaNO^3$ solution and the flux was determined again. The degradation process conditions were reestablished again after the flux measurement. This sequence of actions was repeated during 5 days.

Results and discussion

Influence of a gel network on permeability

PVC-Fluka could not be used to prepare homogeneously gelled SLMs through the temperature treatment, because of instability problems (discolouration) at 120°C. A lower temperature could not be used for polymer contents above 5 w/w%. These problems did not occur when using PVC-BASF. Gelled SLMs were prepared with a polymer content of up to 10% in the pores of Accurel membranes by the temperature treatment method. It appears that from 3% PVC upwards the cooled polymer–LM solution has an extremely high viscosity indicating that we are dealing with gel formation above this polymer concentration. The influence of the polymer concentration on the permeability is given in Fig. 4.

The permeability at higher polymer content is studied also in order to get more insight in the influence of gel networks on the diffusion rate. However the preparation of these gelled SLMs via the temperature treatment gave problems. Also the PVC-BASF darkened at temperatures above 150°C, which are needed for dissolution. Furthermore the support shrunk at these high temperatures. Therefore the method using the volatile solvent THF has been used. SLMs were prepared using Accurel as support and PVC-Fluka up to 10% as polymer. At still higher polymer content it was not possible to remove the attached gel substance from the support with a tissue.

In order to get information on the permeability at very high polymer concentration, gelled membranes without a support were prepared, having polymer contents from 10% up to 70% PVC-Fluka, by pouring out the polymer solution and evaporating the THF. These unsupported membranes had to be relatively thick (250–300 μm) to be able to handle them. Still the SLMs (without support) containing 10 and 15% PVC had insufficient mechanical strength in the permeation module. They were dragged along immediately by the aqueous phases which flowed parallel to the membranes, so the flux could not be determined. Eventually it was possible to determine the permeability for a membrane with 15% PVC by preparing a 400 μm thick membrane, although some membrane deformation could be observed during this measurement.

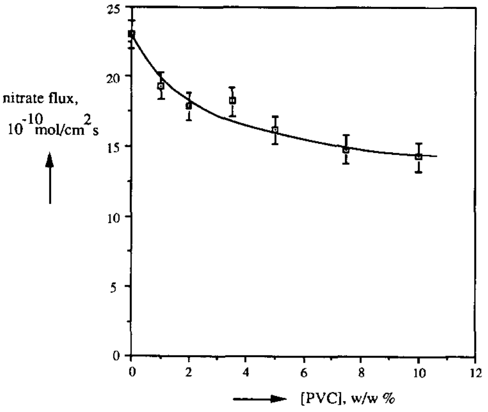

Fig. 4. Influence of a homogeneous gel network on SLM-permeability; solvent *o*-NPOE; carrier TeOA; support Accurel; polymer PVC-BASF; preparation 120°C (30 min).

For a mutual comparison of the permeabilities, the effective diffusion coefficients for the various SLMs have been calculated using the following formula:

$$D_{\text{eff}} = J d_{\text{eff}} / \Delta C$$

In this formula J is the measured nitrate-flux through the membrane and d_{eff} (the effective pathlength of the carrier through the membrane) is calculated without making a correction for the actual presence of the gel network; d_{eff} is equal to the measured membrane thickness when no support is present. When a support is present in the membrane this value is obtained by multiplying the membrane thickness with the tortuosity factor of the support. The support tortuosity, as given in Ref. [11], is calculated using the formula given by Mackie and Meares and for a porosity of 73% a value of 1.74 is calculated for this factor.

For the calculation of ΔC (the concentration gradient of carrier over the membrane) we have to be aware that the ΔC value to be used depends on the amount of carrier in chloride form at the stripping side ($0.96 \times 0.2\,M$ [11]), on the porosity of the support (0.73) and on the fraction of polymer in the gel network ($[PVC]$). The influence of the polymer content on the diffusion rate, determined in this way, is given in Fig. 5.

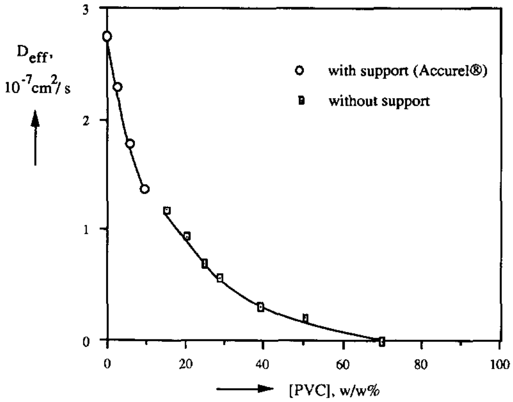

Fig. 5. Influence of polymer concentration on diffusion rate through gelled liquid membranes; solvent o-NPOE; carrier TeOA; preparation via THF evaporation.

Discussion

Figure 4 shows that, in spite of the increase of the macroscopic viscosity of the LM-phase with a very large factor when a gel network is present, the permeability decreases only to a small degree in case of low polymer concentrations. This can be explained by the open structure of the gel network so that the microscopic viscosity increases just slightly. This uncoupling of the macroscopic viscosity (which determines the mechanical strength of the membrane) and microscopic viscosity (which determines the diffusion rate through the membrane) can not be realized in liquid membranes without a gel network. The diffusion rate is inversely proportional to the viscosity of the LM-phase of these "conventional" SLMs.

By comparing Figs. 4 and 5 we observe the same trend in diffusivity for small PVC contents (up to 10%) although the decrease in permeability in Fig. 5 is a little larger than for the membranes which are gelled via temperature treatment using lower molecular weight PVC. It can be seen from Fig. 5 that the permeability decreases drastically for higher polymer contents to vanishingly small transport at 70% PVC. It is gratifying that the two curves, which are based on membranes with different thicknesses and differing in the presence of a support, link so well. It can be seen as a confirmation for the correctness of the calculation of the tortuosity factor for the support used.

The most important reason for the decline in the effective diffusion rate when increasing the polymer concentration is the increase in tortuosity factor. The carrier molecules have to cover a longer pathlength through the membrane around the polymer chains.

To compare our diffusion coefficients in gelled liquid membranes with a related system, the results of Oesch and Simon [22] are also plotted in Fig. 6. They performed experiments with an ion-selective electrode using o-NPOE as solvent and PVC as polymer. For polymer contents from 37 to 67 w/w% PVC the diffusion coefficients of a ligand through these solvent polymeric membranes were determined experimentally. For 0% PVC, D_{eff} was estimated according to the Stokes–Einstein equation.

Figure 6 shows clearly that the experimentally determined diffusion rates through gelled liquid membranes agree quite well with those of a comparable electrode system. An important difference between these two methods is that the diffusion rates through liquid membranes with low polymer contents (from 0% to

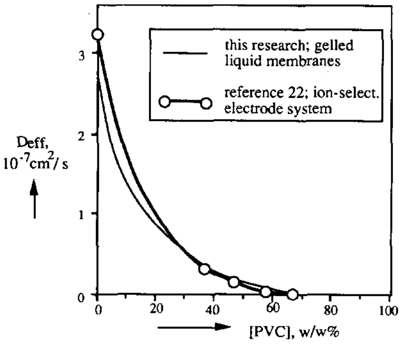

Fig. 6. Diffusion rates through gel networks; comparison between gelled liquid membranes and ion-selective electrode system (Ref. [22]).

30% PVC) can actually be determined by using a support and don't have to be estimated. Undoubtedly this method of using a support is also suitable for other systems in which the determination of diffusion coefficients at low polymer concentrations might give problems.

From the strong decrease in permeability at relatively high polymer contents it follows that, for economical reasons, in practical applications only small polymer concentrations (up to ± 10% PVC) in the membrane will be permissible. Our measurements confirm that such open gel networks can only be handled when they are fixed in the pores of a support. In this way relatively thin membranes with sufficient mechanical strength to withstand the flow of the aqueous phases can be prepared.

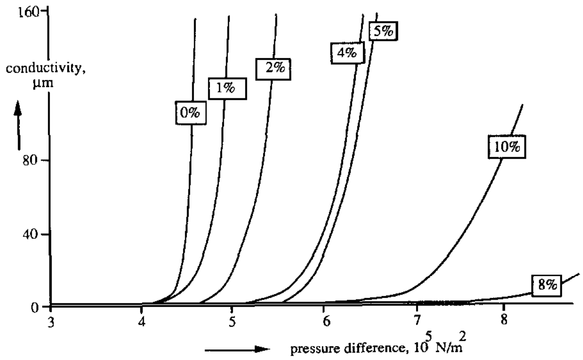

Fig. 7. Influence of a gel network (with different PVC-concentrations) on the mechanical stability of SLMs; solvent *o*-NPOE; carrier TeOA (0.2 *M*); support Accurel, polymer PVC-BASF; preparation dissolution at 120°C (30 min).

Influence of a gel network on mechanical stability (liquid displacement)

The mechanical stability of SLMs with Accurel as support, *o*-NPOE as solvent, TeOA as carrier and PVC-BASF as polymer has been studied. These membranes (with polymer contents up to 10%) were prepared via the method of PVC dissolution at 120°C.

A reproducible method for SLMs without PVC has been developed first. On this basis it was decided to test the membranes starting with a pressure difference of 3×10^5 N/m^2 and increasing the pressure difference every 5 min with 0.2×10^5 N/m^2. This increase in pressure was continued till the conductivity of the demiwater phase increased strongly (SLM-breakthrough). The breakthrough curves for the membranes with different polymer concentrations are plotted in Fig. 7.

From Fig. 7 it can be concluded that:

- An SLM without PVC shows a break through at a pressure difference of a little over 4×10^5 N/m^2. This value is in agreement with expectations. The break-through pressure can be calculated from the Laplace equation because we are dealing with the displacement of a liquid out of a capillary system:

$$\Delta P = 2\gamma_{\mathrm{w/LM}} \times \cos\Theta / r$$

At the moment of the removal of the liquid out of the pores, cos Θ equals 1 and the interfacial tension ($\gamma_{\mathrm{w/LM}}$) between the LM-phase and the aqueous phase is: 16.4×10^{-3} N/m [18], while the pore radius (r) is: 0.1 μm (data obtained from Enka). This gives a ΔP value of: 3.3×10^5 N/m^2, which agrees rather well with the experimentally determined value of 4.2×10^5 N/m^2.

- Considerably larger pressure differences are needed to remove the LM-phase when the LM-phase is gelled in the pores of the support. This pressure difference increases gradually when increasing the polymer content. The trend is unambiguous despite the fact that the reproducibility of the gels formed has not been verified. An explanation for this behaviour is that when increasing the macroscopic viscosity of the LM-phase (due to gel formation) the resistance against deformation of the LM-phase and thus the resistance against flow through the pores increases.

For the application of SLMs it means that the membranes have a higher resistance against pressure differences. In practice there are always small pressure differences present over the membrane, especially in the performance of the SLM-process in hollow fiber modules. Dworzak and Naser [32] e.g. measured the pressure drop in the lumen over the length of hollow fibers due to the frictional flow of liquid through the fibers. For an inner diameter of 1.8 mm and a length of 2 m. this pressure drop amounted to 0.7×10^5 N/m^2. Furthermore larger pressure differences (e.g. caused by faults in the apparatus) can be withstood better by gelling the LM-phase. The lifetime of the membranes will be extended by this increase in mechanical stability.

Influence of a gel network on removal of LM-phase from the support, due to emulsion formation

A more important contribution of the gel structure to the stability of liquid membranes results from the suppression of emulsion formation. This is investigated in the following experiments. Always two aqueous phases with identical compositions were flown parallel to the membrane surface (analogous to the experiments described to exclude osmotic pressure differences [17]) and the influence of this shearing flow on the composition of the membrane was studied.

Solvent removal

To study the effect of a gel network on the removal of solvent from a membrane, SLMs with decanol as solvent have been chosen because this compound gave the least stable membranes [18]. Furthermore Celgard is used as support, analogous to the same type of experiments as described in Ref. [17]. In Fig. 8 the removal of LM-phase resulting from the flow of aqueous phases with 0.5 *M* NaCl during 7 hr is given as a function of the concentration of poly(vinyl isobutyl-ether).

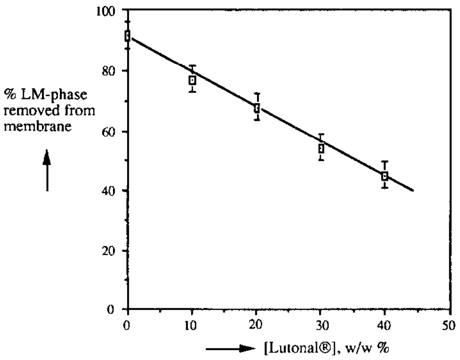

Fig. 8. Influence of polymer content in homogeneous gel network on removal of decanol from SLM; solvent decanol; carrier: none; polymer poly(vinyl isobutyl ether); support Celgard; preparation method via THF evaporation; composition aqueous phases 0.5 *M* NaCl; water flow velocity 5.5 ml/sec; period 7 hr.

This figure shows that by gelling the LM-phase the removal of decanol out of the membrane due to the formation of emulsion droplets is diminished. But the gel network must have a relatively high polymer content to result in a considerable reduction of the quantity of removed LM-phase when a "bad" solvent (decanol) is used.

Carrier removal

To study the effect of a gel network on the removal of carrier from a membrane due to the formation of emulsion droplets, SLMs with *o*-NPOE as solvent and TeOA as carrier have been chosen because the instability behaviour of this type of membranes has been studied rather intensively [17]. Membranes with a dense gel layer at the interfaces were used during these experiments to prevent, as specifically as possible, the formation of emulsion droplets at the interface. Relatively high polymer concentrations can be used without reducing the flux appreciably because these gel layers are very thin in relation to the total thickness of the membrane. These experiments have an orientational character and they form the basis for the long term permeability measurements which will be discussed in the next section.

The membranes were provided with thin gel layers at both interfaces because identical aqueous phases (with a low salt concentration) were passed at both sides of the membrane. Accurel was chosen as support and gel layers with 40% polymer and 60% LM-phase were applied. It appeared, from the GPC-determination, that in all cases the amount of PVC, which was brought on the membranes, was smaller than 2% of the total amount of LM-phase. This means that, for a total membrane thickness of 90 μm, the gel layers (with a polymer content of 40%) were thinner than 2 μm.

Apart from gel layers with PVC-Fluka and carboxylated PVC as polymer the influence of the presence of the activator DCC in combination with carboxylated PVC has been investigated. The quantity of DCC (1 equivalent) is based on the amount of carboxylic groups present in the solution. The presence of DCC results in an crosslinking of the polymer indicated by the increase of the viscosity of the solution upon addition of the DCC to the solution of carboxylated PVC in THF. After ±10 min the solution is not fluid any more (despite the presence of THF) and consequently not manageable any longer. Therefore it was necessary to apply the gel layer within a few minutes after adding the DCC to the polymer solution.

The relative amounts of carrier removed from the membrane are given in Table 1 when aqueous phases with 10^{-4} M NaCl passed during 7.5 hr with a flow rate of 5.5 ml/sec parallel to the membrane.

TABLE 1

Influence of the presence of gel layers on the removal of carrier from the membrane; solvent *o*-NPOE; carrier TeOA; polymer concentration in gel layer 40%; thickness gel layers <2 μm; support Accurel; composition aqueous phases 10^{-4} M NaCl; water flow rate 5.5 ml/sec; period 7.5 hr

Type of polymer in gel layers	Carrier removed from SLM (%)
No gel layer	37
PVC-Fluka	30
PVC-carboxylated	25
PVC-carboxylated + 1 equivalent DCC	21

Table 1 shows that the removal of carrier out of the membrane is diminished substantially by the presence of a gel network on the surface of the membrane. It can be concluded that the gel network is indeed able to suppress the deformation of the LM-interface by the aqueous phases, so that less LM-phase can be emulsified.

The results also show that this effect is larger for PVC with carboxylic groups, with or without DCC, than for normal PVC. This can be explained by the fact that extra crosslinks due to hydrogen bonding are present between the polymer chains in case of carboxylic groups and by the formation of anhydride bonds when DCC is present, both leading to a network with a shorter mesh size. Special attention will be paid to gel layers based on carboxylated PVC in the following section (in which the long term permeability of this type of membranes is simulated), especially because this polymer can be crosslinked chemically.

Influence of a gel network on long term permeability

The most important stability parameter for SLMs is the long term permeability behaviour. This parameter is investigated in the following experiments for both homogeneously gelled SLMs and membranes with thin dense gel layers at the interface. For the homogeneously gelled SLMs a distinction has been made between membranes using Accurel or Celgard as support. For the membranes with a dense gel layer only Accurel is used as support and the determination of the actual long term permeability has been simulated.

Homogeneously gelled membranes using Celgard as support

First the influence of the presence of a homogeneous gel network on the chloride-leakage behaviour of SLMs is studied. Celgard is used as support in these experiments in order to be able to perform the measurements in a short period of time. Apart from stable systems with *o*-NPOE as solvent, membranes with decanol as solvent are also investigated in order to study the principle of the effect of a gel network.

The gel networks contained only small amounts of polymer (5%) in order to reduce the flux as little as possible. The path of the flux as a function of time for the membranes with *o*-NPOE as solvent and without gel network has already been treated in Ref. [17]. The flux of the membranes with a gel network showed a similar behaviour. However, the starting values of the permeabilities are roughly 20% lower as compared with the membranes without a gel network.

The first moments at which chloride ion leakage through the membranes was observed (counter transport factor (CTF) larger than 1) are presented in Table 2.

From Table 2 it follows that for all systems investigated the presence of a gel network in the membrane results in a considerable increase of the resistance against SLM-failure. These positive effects of a gel network can be explained by the fact that the removal of LM-phase due to emulsion formation is reduced.

TABLE 2

Influence of a homogeneous gel network on permeation stability; support Celgard; 0.2 *M* carrier; preparation method via THF evaporation; feed 0.004 *M* $NaNO_3$ stripping phase 4.0 *M* NaCl

LM	Polymer	SLM-failure (CTF > 1)
Decanol–TeOA	none	2 hours
ibid.	5% Lutonal® 110 (polyvinyl isobutyl ether)	> 8 hours
o-NPOE–TOMA	none	7 days
ibid.	5% PVC	> 20 days
o-NPOE–TeOA	none	4 days
ibid.	5% PVC	11 days

It is remarkable that for the gelled SLMs with decanol as solvent no rapid chloride leakage is taking place in spite of the fact that relatively much LM-phase is being removed (see Fig. 8). Obviously the remaining part of LM-phase in the pores of the support has such a structure, due to the presence of the polymer, that channeling of the membrane is prevented. A possible explanation is that the transport of LM-phase from the pores which are situated deeper in the membrane to the interface of the membrane, where LM-removal takes place in the form of emulsion droplets, is hindered. Because this essential step in the degradation process is delayed the moment of chloride leakage is postponed.

Homogeneously gelled liquid membranes using Accurel as support

To get information on *real* long term permeabilities obtainable with SLMs, the stabilities of some stable membranes were determined. Hence *o*-NPOE was used as solvent, TeOA as carrier and Accurel as support. During these time consuming investigations the influence of the polymer content on the moment of SLM-failure (chloride leakage) and on the flux as a function of time was studied.

In order to approach the practical conditions more closely, concentrating experiments with large feed volumes (4.1 l) were performed. The gelled membranes were prepared in the same way, via the temperature treatment, as the membranes of which the experimentally determined fluxes are given in Fig. 4. The counter transport factor is given as a function of time for 4 membranes with different PVC concentrations in Fig. 9. After 18 weeks the experiments were terminated.

Figure 9 shows that the membrane without gel network starts to leak chloride ions after 13 weeks, while all three gelled membranes remain intact during 18 weeks. Analogous to the results of the long term permeability experi-

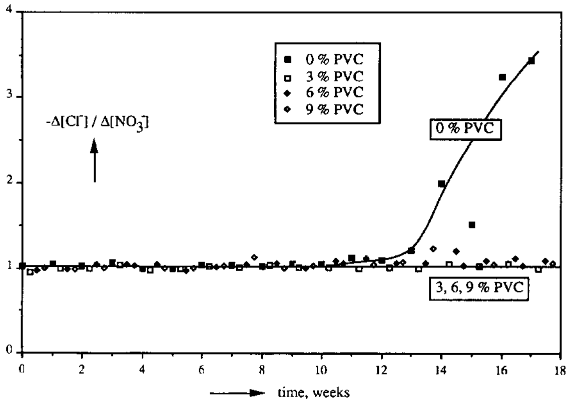

Fig. 9. Counter transport factor (CTF) as a function of time for homogeneously gelled SLMs with different amounts of PVC; solvent *o*-NPOE; carrier TeOA; support Accurel; gel-forming polymer PVC-BASF; preparation method 120°C (30 min); feed 0.004 *M* $NaNO_3$ (4.1 l); stripping phase 4.0 *M* NaCl (130 ml); feed and stripping phase weekly refreshed.

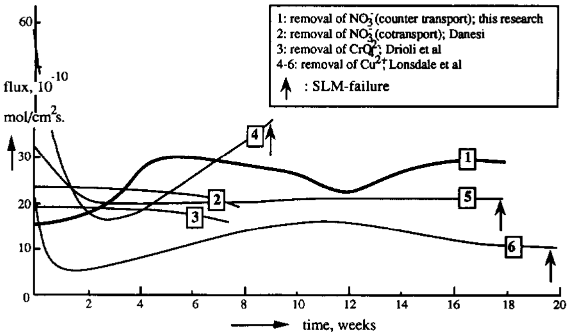

Fig. 10. Ion flux as a function of time for long term permeability measurements; (1) this research: 9% PVC; conditions as in Fig. 9; removal of air bubbles after 12 weeks; (2–6): data from literature; (2) Ref. [33]; (3) Ref. [34]; (4–6) Ref. [35].

ments using Celgard as support (Table 2) it can be concluded that because of the presence of a gel network in the membrane less LM-phase is removed via the formation of emulsion droplets, leading to a substantial increase in stability.

The course of the flux as a function of time for one of the gelled membranes (with 9% PVC) is given in Fig. 10. The other three SLMs showed a similar behaviour and are therefore not plotted. The best long term permeability results, known from literature, are also plotted in this figure to compare our results with other measurements.

Figure 10 shows that the flux of the membrane with 9% PVC first increases as a function of time. This must be caused by the decrease in thickness of the membrane, through which the effective pathlength for the diffusion of the carrier molecules diminishes and consequently the flux increases. After 6 weeks the flux shows a gradual decrease due to the adsorption of air bubbles onto the membrane surface which decrease the contacting area. Removal of these air bubbles (after 12 weeks) leads to an increase in flux again.

Such effects of adhesion of air bubbles and LM-removal by emulsion formation leading to SLM-failure might also be underlying the course of the permeation curves for the other systems taken from literature. Comparing these curves with the results of the gelled membrane it can be concluded that the gelled membrane shows a favourable stability. SLM-failure (chloride leakage) is prevented by applying the gel network, while the permeability remains relatively high because of the open structure of the gel network in the pores of the support.

Simulation of long term permeability measurements for SLMs with a dense interfacial gel layer

In addition to previous experiments, in which the influence of dense gel layers at the membrane interface on the removal of carrier is studied, the long term permeability of such membranes will be discussed in this paragraph. The influence of the presence of the thin interfacial gel layer on the flux will also be determined in these experiments.

Based on previous results, it could be expected that such measurements would require a very long test time. Therefore it was decided to *simulate* the measurement of the long term permeability behaviour. It means that the degradation process of the membrane is accelerated on purpose. This is realized by flowing an aqueous phase with a very low salt content (10^{-4} *M* NaCl) along the feed side of the membrane instead of a 4×10^{-3} *M* $NaNO_3$ solution. In Ref. [17] it is demonstrated that the membrane degrades much faster for lower salt content in the aqueous phases. Alternatingly the usual feed of 4×10^{-3} *M* $NaNO_3$ is passed through the measuring cell in order to determine the permeability of the membrane (and consequently the stability) as a function of time.

The *real* long term permeability can be predicted with these results when it is assumed that the instability effects of the different membranes, e.g. the loss of carrier from the LM-phase, are being reflected by the nitrate flux level in a proportional fashion. The stability of a certain membrane can then be estimated by comparing the observed simulated long term permeability with that of a membrane without gel network for which the *real* long term permeability is known.

A 4 *M* NaCl-solution was constantly passed along the membrane at the stripping side. From earlier work [17] we know that the membrane does not degrade at that salt concentration by the formation of emulsion droplets. Therefore the membranes were provided with only one dense interfacial gel layer which was always in contact with the feed solution. In addition to the preliminary measurements especially the influence of chemically crosslinked gel networks is studied now. Two types of crosslinking agents and different concentrations of activator DCC were used. Carboxylated PVC is always used as polymer in these measurements and the polymer content in the applied gel layer was 40%.

The influence of the crosslinking agent on the gel network becomes clear when studying the viscosity of the solutions. As described before the solution of carboxylated PVC in THF solidifies by adding DCC to the solution. After a few days, however, the gel becomes fluid again. A solution of carboxylated PVC in THF to which in addition to DCC also diamine is added also solidifies after some time. But this gel remains solid during at least one month. This means that the anhydride crosslinks formed by adding only DCC are not stable (against hydrolysis) while a chemically stable network is indeed being formed by adding diamine.

In Fig. 11 the flux is plotted as a function of the "degradation time" (that is the time that the 10^{-4} *M* NaCl solution was in contact with the membrane surface at the feed side) for five different membranes.

Figure 11 shows that the flux of the membrane without gel network decreases considerably in a period of 80 hr, under the conditions given. On the contrary this flux reduction is smaller for the membranes with a gel network so that it can be concluded that the gel network is able to suppress the degradation of the membrane that is caused by the formation of emulsion droplets. Furthermore from the results it

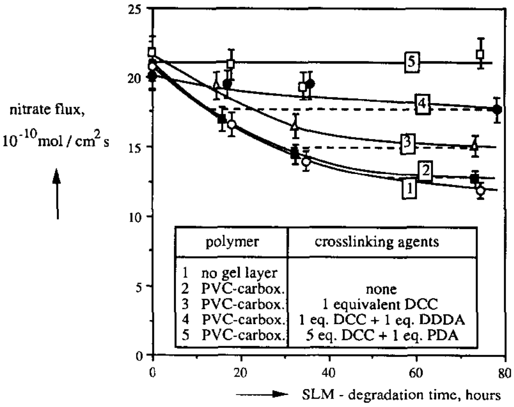

Fig. 11. Influence of the presence of one gel layer on simulated long term permeability; solvent *o*-NPOE; carrier TeOA; polymer concentration in gel layer 40%; thickness of gel layer <2 μm; support Accurel; feed solution: alternating 10^{-4} *M* NaCl/4×10^{-3} *M* $NaNO_3$; stripping phase 4 *M* NaCl; water flow rate 5.5 ml/sec.

can be concluded that the most stable membranes are formed by a gel network with a short mesh size which is built with chemically stable crosslinks.

When comparing the initial flux values it appears that the presence of the gel network has no measurable influence on the permeability of the membrane. This means that the thickness of the applied gel layer is very thin in relation to the total thickness of the membrane.

Quite a remarkable effect seen in this figure is that the flux reduces as a function of time at the start of the experiment, while in Fig. 10 (in which also Accurel was used as support) the flux increases substantially during the first period. Obviously the loss of solvent in the present situation is much smaller. These results confirm the conclusion of Ref. [17] (Table 3) that the average size of the removed emulsion droplets decreases with decreasing salt content in the aqueous phases in contact with the membrane surface (10^{-4} M instead of 4×10^{-3} M in standard long term measurements). The effect of flux reduction (through loss of carrier) dominates the small effect of the decreasing membrane thickness, because the small emulsion droplets that break away contain a relatively high amount of carrier.

So called "proportionality factors" were used to predict the *real* long term stabilities. These factors, which are a quantitative measure for the stability of a gelled membrane as compared to the membrane without a gel layer, are calculated by using the horizontal, dashed lines in Fig. 11. When the proportionality factors found in these series of experiments can be transferred to the practical permeation conditions (in which the removed ions are concentrated in the stripping phase) then we obtain the values as given in Table 3. The result of previous measurements in which it was found that a membrane without gel network remained intact during 13 weeks (see Fig. 9) is used for these calculations.

TABLE 3

Predicted long term stabilities of SLMs with one dense gel layer; the numbers 1 to 5 of membranes correspond to those in Fig. 11

SLM	Proportionality factor	Predicted long term stability
1 (no gel layer)	–	13 weeks (experimentally determined)
2	1.4	18 weeks
3	2.7	35 weeks
4	6.2	81 weeks
5	∞	∞

From this table it can be concluded that applying a thin dense crosslinked gel layer at the feed side of the membrane opens new perspectives.

For the sake of completeness it is stated here that results mentioned are a selection of all experiments performed. It is clear that in order to apply a perfect gel layer on the membrane in a reproducible way further research is needed.

Conclusions

Only gelled liquid membranes with low polymer concentration are interesting for practical application because the diffusion rate of carrier molecules in a gel network decreases drastically with increasing polymer content. Such loosely gelled membranes can only be handled when they are immobilized in an inert support because of the mechanical stability.

From the measurements it follows that the resistance of the membrane against a pressure difference increases by applying a homogeneous gel network (with a polymer content smaller than 10%) in the pores of a support. Furthermore the long term stability increases substantially while the permeability decreases only to a small degree because of the open gel structure.

A second type of gelled membranes, in which a thin crosslinked gel layer with a higher polymer content (40%) is applied at the feed side of the membranes, very effectively suppresses SLM-degradation caused by emulsion formation. This treatment has no negative influence on the flux because the thickness of the dense gel layer is small. From experiments in which the determination of the long term permeability is simulated, it appears that this type of asymmetrically gelled membranes have predicted stabilities which look very interesting for practical applications (far over one year).

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