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Supported liquid membranes modification with sulphonated poly(ether ether ketone)

Permeability, selectivity and stability

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Abstract

The development of a new type of composite membrane consisting of a microfiltration support membrane, an immobilised liquid membrane phase and a hydrophilic, charged polymer layer and its function as a supported liquid membrane (SLM) for copper selective transport are described. The ion-exchange layers function as stabilisation layers to improve the membrane lifetime and consist of sulphonated poly(ether ether ketone) (SPEEK). This polymer shows a high permeability for copper ions due to the presence of fixed negative charges and to its swelling capacity in an aqueous phase.

A method was developed to prepare composite membranes composed of the support membranes Celgard with one stabilisation layer on either the feed or strip side of the membrane or on both sides. Good adhesion of homogeneous, negatively charged, hydrophilic SPEEK layers to the hydrophobic macroporous support membranes could only be established when the support membranes were first hydrophilised with a concentrated sulphuric acid solution containing 5 wt% free SO_3.

The lifetime of the SLMs is significantly improved when one stabilisation layer is applied at the strip side or two layers at both sides of the SLM. A second advantage of this composite SLM is the increase in copper flux caused by a decrease in thickness of liquid membrane phase. However, when SPEEK penetrates entirely through some pores of the support membrane, ions diffuse non-specifically through the SPEEK matrix resulting in an undesired selectivity loss. This phenomenon occurs only when thin Celgard membranes are used as support membranes. © 1998 Elsevier Science B.V.

Keywords: Supported liquid membranes; Permeability; Selectivity; Stability; Ion-exchange membranes; Sulphonated poly(ether ether ketone)

1. Introduction

With respect to their fluxes and selectivities, supported liquid membranes (SLMs) have the potential to economically remove and recover valuable and toxic heavy metal ions from industrial effluents. However, the industrial use of SLMs is limited due to their instability and short lifetime. This instability is attributed to a loss of liquid membrane (LM) phase from the porous support into the surrounding aqueous phases. The loss of LM phase can be reduced by applying stabilisation layers attached to the SLMs. Studies of SLMs transporting nitrate [1,2] showed that poly(vi-

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nyl chloride) or polyamide could be used as stabilisation layer material. However, both types of polymers are not suited to stabilise SLMs transporting copper ions [3,4].

The aim of this study is to stabilise copper transporting SLMs by ion-exchange membranes made from negatively charged sulphonated poly(ether ether ketone) (SPEEK). Due to their negative fixed charges these layers are highly permeable for copper ions. However, an additional polymer layer in the SLM may increase the overall mass transport resistance and consequently decrease the flux. Sufficient swelling of the SPEEK layers by the aqueous solutions may also result in larger mesh-sizes counteracting the increase in membrane resistance. Also the water swollen material may show a negligible permeability for the components from the organic LM phase. This would imply that ultimately high copper fluxes can be maintained through these composite SLMs without a loss of the components from the LM phase into the aqueous phases.

2. Background

2.1. Ion-exchange membranes

Ion-exchange membranes are made from polymers carrying covalently bound cationic or anionic groups. The respective counter-ion can be exchanged by another ion having the same charge prefix. At low salt concentrations in the aqueous phases, ion-exchange membranes are only permeable for counter-ions, i.e. ions from an aqueous solution with an opposite charge as the ionic groups of the polymer. The higher the concentration of the fixed ions in the polymer is, the more co-ions, i.e. ions with the same charge as the fixed ions of the ion-exchange polymer, are excluded from the membrane matrix. This phenomenon is called Donnan exclusion [5].

From the Donnan equilibrium and for a fixed concentration of charged groups in the ion-exchange membranes C_{fixed}, a relation between the co-ion concentration in the membrane C_{CO}^m and in the adjacent salt solutions C_{CO} can be derived. For monovalent ions in a dilute aqueous solution, this relation can be expressed as [5–8]:

$$C_{CO}^m = \frac{C_{CO}^2}{C_{fixed}} \left(\frac{f_0}{f_m}\right)^2, \tag{1}$$

with f_0 the mean activity coefficient of salt in the solution and f_m the mean activity coefficient of salt in the membrane.

According to Eq. (1), Donnan exclusion is very effective, when the concentration of co-ions in the aqueous solution is low and that of fixed charges in the membrane is high. When the concentration of co-ions in the membrane and in the solution have the same order of magnitude, the co-ions in the solution are not excluded anymore from the membrane. The membrane loses then its preferential selectivity for the counter-ions. So, for selective permeation of counter-ions through the membrane, the concentration of the bulk salt solution should be lower than that of the fixed ions in the membrane or, in other words, the concentration of fixed ions in the membrane should be as high as possible. However, an increasing fixed ion concentration limits practical applicability of the material due to a decrease in mechanical strength [8].

2.2. Sulphonation of poly(ether ether ketone)

For the preparation of the cation-exchange membrane used in this study, the polymer poly(oxy-1,4-phenylene-oxy-1,4-phenylene-carbonyl-1,4-phenylene), also called poly(ether ether ketone) (PEEK), was sulphonated. Fig. 1 shows the chemical structure of PEEK, a semi-crystalline polymer possessing excellent thermal and chemical stabilities, and electrical and mechanical properties [9,10]. PEEK does not dissolve in organic solvents but in strong acids. Presumably, the difficulty in dissolving PEEK lies in overcoming the strong intercrystalline forces. The solubility of PEEK in strong acids can be attributed to protonation and in some cases chemical modification (e.g. sulphonation) of the polymer [10,11]. The solubility of SPEEK in different solvents depends on the degree of sulphona-
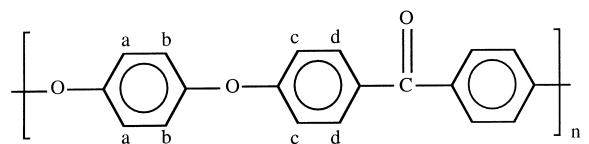

Fig. 1. Chemical structure of poly(ether ether ketone) [9].

tion. For sulphonation degrees lower than 30%, SPEEK is, similarly to PEEK, only soluble in strong acids. Above 30% sulphonation, SPEEK is soluble in hot dimethylformamide (DMF), dimethylacetamide (DMAC) and dimethylsulphoxide (DMSO): above 40%, in the same solvents at room temperature: above 70%, in methanol and at 100% in hot water [9]. The sulphonation of PEEK in concentrated sulphuric acid is essentially free of degradation and cross-linking reactio'ns, provided that the acid concentration is kept below 100%. Cross-linking is presumably the result of sulphone formation, which should be negligible in aqueous H_2SO_4 (e.g. 95–98%). Water can decompose the postulated aryl pyrosulphonate intermediate that is required for sulphone formation. The sulphonation rate can be controlled by changing the reaction time, temperature and sulphuric acid concentration and can thereby provide a sulphonation range of 30–100% [10,11]. Sulphonation takes place at the positions ''a'' and ''b'' (Fig. 1). The positions ''c'' and ''d'' are deactivated for the electrophilic reaction by the electron-withdrawing carbonyl group [9].

SPEEK is heterogeneous with respect to the degree of sulphonation of individual polymer molecules. The extent of this heterogeneity is an important quantity to consider, as it influences the properties of SPEEK such as crystallinity and solubility [9,10]. Heterogeneity is a consequence of the random nature of the sulphonation. In addition, the significant time required for dissolution (more than 1 h) increases heterogeneity because this dissolution time depends on the molecular weight of the polymer chain and the accessibility of this chain. Accessibility describes whether a polymer chain in the interior of the PEEK granules is the last to dissolve in sulphuric acid resulting in shorter reaction times. This effect is less significant for longer reaction times at degrees of sulphonation beyond 20–30% [9,10]. Beside its heterogeneity, the physical and chemical properties of SPEEK also depend on the content of sulphonic groups and the type of counterions [9,10].

2.3. Ion-exchange membranes in liquid membrane processes

There is an increasing interest in using ion-exchange membranes in extraction processes [12–16]. Kojima et al. [12] used cation-exchange membranes (CEM) with sulphonic groups in a process to recover copper from leach solutions. The cation-exchange membrane concentrates a dilute copper leach solution at the interface with the extractant solution. Thereafter, copper ions can be extracted by a copper selective hydroxyoxime ligand and stripped by a sulphuric acid solution. Finally, an electrolysis step is used to precipitate copper on a cathode.

Several studies are published in which ion-exchange membranes are used in liquid membrane processes as a stabilisation layer to prevent the loss of extractant phase (LM phase) in aqueous phases [13–16]. Kedem and Bromberg [13] used cation-exchange membranes with sulphonic groups to keep the aqueous and extractant phases separated in a bulk liquid membrane configuration for the transport of copper ions and of silver ions. The cation-exchange membranes prevented the loss of organic extractant into the aqueous solution. When CEMs with thicknesses between 25 and 27 µm were used, the copper fluxes had the same order of magnitude as in an SLM device with analogous conditions, namely 2×10^{-9} mol/cm^2 s [13].

Wodzki and Sionkowski [14] also studied the transport of divalent ions in a hybrid liquid membrane system. The major difference between their permeation set-up and that of Kedem and Bromberg [13] is that the feed and strip phases were circulated between the permeation cells and reservoirs. This study [14] showed that zinc fluxes through this hybrid liquid membrane system stabilised with thick perfluorsulphonic cation-exchange membranes (280 µm) were similar to those through non-stabilised LM devices, namely 6.4×10^{-9} mol/cm^2 s [14]. Therefore, it can be concluded that transport through CEMs did not limit the overall transport rates, being in agreement with the experiments of Kedem and Bromberg [13]. Nonetheless, Wodzki and Sionkowski [14] only reported on the influence of the CEMs on the metal fluxes and not on the lifetime of the hybrid liquid membrane system. Kislik and Eyal [15,16] transported titanium with a similar hybrid liquid membrane system, as Kedem and Bromberg [13]. The major difference is that feed, strip and LM phases were circulated instead of stirred. Also in this hybrid liquid system, IEMs with thicknesses between 130 and 200 µm, prevented the loss of organic components of the LM phase into the aqueous phases without decreasing the fluxes [15,16].

The general conclusion of this section is that IEM has the potential to improve the lifetime of LM systems without decreasing the flux. The transport resistance of counter-ions remains low due to the high content of fixed charges in IEMs and to their reasonable degree of swelling in aqueous media. In the bulk liquid membrane devices and the hybrid liquid membrane systems described above [12–16], large amounts of LM phases are needed. However, SLM devices require much smaller amounts of LM phase. This means that SLM devices are particularly preferred over others in case of expensive extractants phases.

3. Experimental

The composite membranes described here consist of a microporous polymer membrane having an organic solvent and an organic carrier molecules immobilised in the pores. On top of the membranes ion-exchange polymer layers are applied to stabilise the membranes and increase their lifetime.

3.1. Materials

The following materials were used for the supported liquid membranes:
- *Carrier*: The copper carrier 5-nonylsalicylaldoxime oxime (ACORGA P50), molecular weight of 263 g/mol, supplied by ZENECA (ICI Specialties, Blackley, UK). The product 5-nonylsalicylaldoxime contained 95% oxime, 3% aldehyde and 2% nonylphenol.
- *Solvent*: Dodecane (Janssen 99%).
- *Support membranes*:
  1. Flat sheet Accurel, macroporous polypropene membranes (AKZO Faster A.G., Wuppertal, Germany, F-nr. 1502). The average thickness of the membranes was 100 μm (measured with a Mitutoyo digital thickness meter), the overall porosity was 69% (AKZO specification), the pore diameter varied between 0.17 and 0.28 μm with an average of 0.2 μm as determined with a Coulter Porometry.
  2. Flat sheet Celgard 2500, macroporous polypropene membranes (Hoechst A.G., Wiesbaden, Germany); the average thickness equaled 25 μm, the overall porosity 45%, as specified by the

supplier, the average pore size 0.05×0.19 μm (width $\times$ length), as specified by the supplier. An accurate determination of the pore size distribution with a Coulter Porometry II was not possible due to the slit shaped structure of the pores.
- *Stabilisation layer material*: poly(ether ether ketone) (PEEK VICTREX, speciality grade 450 PF with a molecular weight of 102 000 and a specific density of 1.34 kg/l), supplied by De Monchy (Rotterdam, The Netherlands).

The feed phases were composed of copper chloride dihydrate. For selectivity experiments also zinc chloride (Merck) was added to the feed solution. The standard concentration was 0.01 M salt. The strip phases were composed of 2 M hydrochloric acid (37% Merck). The water used was demineralised water using a Milli-Q Plux Water Purification System from Millipore.

3.2. Sulphonation of poly(ether ether ketone)

PEEK was dried in a vacuum oven at 70°C overnight. Thereafter, 20 g polymer was dissolved in 1 l concentrated sulphuric acid (Merck, 95–98%, extra pure) and vigorously stirred for 100 h at room temperature. Under continuous stirring, this mixture was then precipitated in 10 l ice-water. Over night, two layers were formed, a polymer rich and a polymer lean phase. The phases were separated and again 10 l distilled water was added to the polymer rich part. Stirring was stopped after 1 h and a separation into a polymer rich and lean phase took place during 1 h. This washing step was repeated until a neutral pH of the polymer lean part had been reached. The polymer rich part was filtered with a Büchner funnel. Thereafter, the polymer was neutralised in a 3 M sodium hydroxide solution and filtered again with a Büchner funnel. The SPEEK was ready to use after one night drying under nitrogen in an oven at 80°C.

3.3. Characterisation of sulphonated poly(ether ether ketone)

The sulphonation degree is defined as the percentage of sulphonated units and was determined by:
1. The ion-exchange capacity (IEC) which is a measure of the number of counter-ions exchange-

able in SPEEK. The IEC was determined by titration of the –SO$_3$H groups with sodium hydroxide (0.1 M).

2. The amount of sulphur present in SPEEK as determined by elemental analyses.

The degree of swelling of a polymer film depends on several factors, such as the type of polymer, the ion-exchange capacity, the degree of cross-linking and the homogeneity of the film [8]. After weighing a dry SPEEK film (cast from a 10 wt% solution of SPEEK in DMF), this film was submerged in a liquid until the mass did not increase anymore. The degree of swelling (DS) was determined from the difference in weight (W) between the dry and swollen SPEEK film according to

$$DS = \frac{(W_{swollen} - W_{dry})}{W_{dry}} 100\%. \qquad (2)$$

The swelling of SPEEK was studied in water, a solution of 0.01 M CuCl$_2$ representing a feed phase, a solution of 2 M HCl representing a strip phase and in a dodecane solution of 0.2 M carrier representing an LM phase.

3.4. Preparation of composite membranes

Several membrane configurations comprising of a SLM and one or two SPEEK layers were prepared to characterise permeability, long-term stability and selectivity. The membrane configurations are drawn schematically in Fig. 2. First the support membranes were pretreated with sulphuric acid to increase the hydrophilicity of the surface [17,18]. Pieces of Celgard or Accurel of 8×9 cm were cut and placed in a petri-dish floating on top of a sulphuric acid solution with 5 wt% free SO$_3$ (a mixture of fuming sulphuric acid and concentrated sulphuric acid, Merck) for 20 min. After this modification step two different procedures were followed.

In procedure 1 the sulphonation reaction was stopped by washing the support membranes first in hexane and thereafter in water. The membranes were dried in a vacuum oven at 30°C overnight. A 10 wt% SPEEK solution in dimethylformamide (DMF) was filtered through a metal filter with pores of 10 µm. Thereafter, a SPEEK film was cast on a glass plate with a knife of 0.10 mm thickness. The modified support membranes were placed on top of the SPEEK
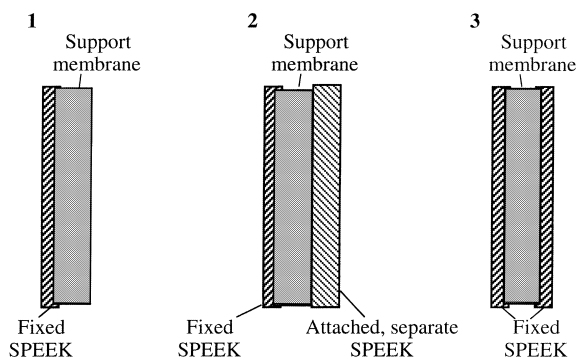

Fig. 2. Three types of composite membranes were used: (1) one fixed SPEEK layer at the support membrane, (2) one fixed SPEEK film and one SPEEK film sticked with a few droplets of LM phase to the support membrane, and (3) two fixed SPEEK layers at the support membrane.

film after approximately 5 min. Longer drying times of the cast SPEEK solution resulted in a bad adhesion of the hydrophilised SPEEK films to the hydrophobic support membranes. For short drying times pore-penetration of SPEEK may occur. To avoid pore-penetration, the alternative procedure 2 was tested; the surface of a dry SPEEK film was sprayed with DMF. After 2–5 min of penetration of the solvent into the film surface, the modified support membranes were placed on top of this film.

The different membrane configurations as shown in Fig. 2 were prepared as follows. The composite membranes with configuration 2 consisted of a membrane with configuration 1 made according to procedure 1 and a separate SPEEK film attached to the composite membrane with a few droplets of LM phase. For configuration 3 both sides of the support membranes were sulphonated in two successive steps. Composite membranes according to the above mentioned procedures were made. After one night drying under nitrogen, the composite membranes were removed from the glass plate, a new SPEEK film was cast and the previously prepared membranes were placed with the open porous side of the support membranes on top of this drying SPEEK film so that both sides contained a SPEEK layer. The composite membranes were dried under nitrogen for at least two nights. The pores of the support membrane were filled with LM phase by immersing the membrane overnight in the LM phase. The support membrane was always larger than the

SPEEK films so that capillary forces could pull the LM phase into the support membrane. When long-term experiments were carried out, these SLMs were clamped in the module and were preswollen in the aqueous feed or strip phase for one night.

3.5. Characterisation of composite membranes

The SLMs with a stabilisation layer were examined by scanning electron microscopy (SEM) to investigate the texture of the layer and the adhesion of the layer to the Accurel membrane. Cross-section samples were prepared by cryogenic breaking: the membranes were placed in an ethanol/water bath for about 5 min and subsequently broken in liquid nitrogen. Surface samples were prepared by glueing a small section of the membrane on a sample holder with conducting carbon. The samples were sputtered with gold to make them conductive using a Balzar Union SCD 040 sputtering apparatus (3 min, 0.1 mbar, 15 mA). SEM in investigations were carried with a JEOL 35 CF scanning electron microscope (acceleration voltage 20 kV).

Gas fluxes were determined of membranes with and without SPEEK layers to get an impression whether these layers contained macroscopic defects. Circular pieces of the samples were placed in a gas permeation cell, after which gas fluxes were measured with nitrogen and carbon dioxide at a transmembrane pressure difference of 1 bar. Gas flow was measured by a mass-flow meter of Brooks, Veenendaal, Netherlands.

3.6. Flux determination

The experimental set-up for the permeation experiments is illustrated in Fig. 3 [4,19]. The membrane module and the buffer vessels were made of glass and connected with silicone rubber tubes. After the macro-porous membrane with impregnated LM phase was placed in the module, the system was filled with the aqueous phases. The total volume of both the feed and the strip phase was 150 ml. The aqueous phases were flowing parallel to the membranes pumped by peristaltic pumps (Masterflex 7521–25, Cole-Parmer, Niles, Illinois, USA) at 25°C. The flow velocities of the aqueous phases were approximately 5.5 ml/s.
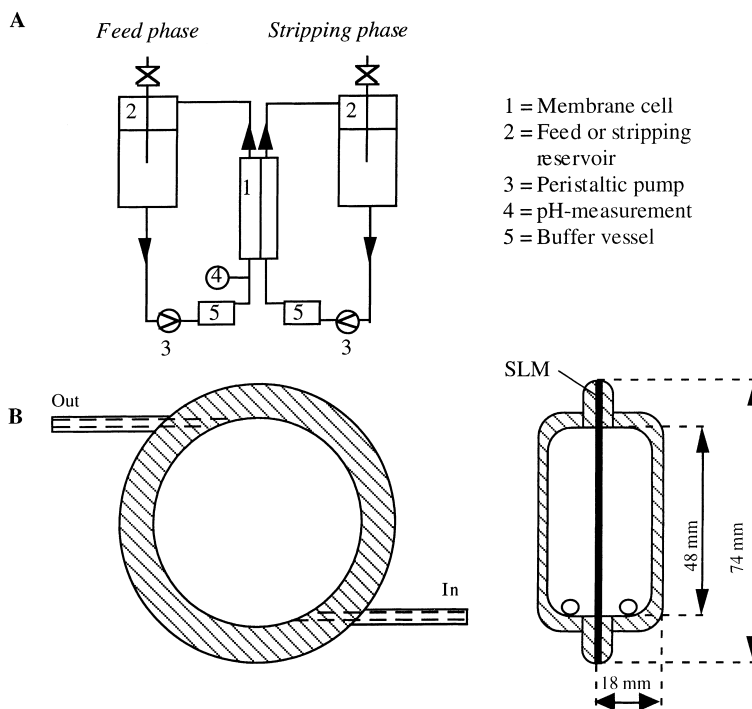

Fig. 3. (A) Experimental set-up for permeability measurements, and (B) Dimensions of the membrane module.

Buffer vessels were necessary to remove air bubbles from the aqueous phases and to minimise the pulsations caused by the pumps. The hydrodynamics of the modules are not well defined due to the shape of the module and, therefore, mass transfer coefficients in the liquid boundary layers could not be estimated. As the flat membranes were not supported by a screen, the flow pattern of the aqueous phases was influenced by slight movements of the membranes.

Periodically, samples were taken from the feed phase and possibly the strip phase. The concentration of metal ions was analysed by atomic absorption spectrometry (AAS, Spectra 10 Varian) and that of protons by pH-measurements (Metrohm). The chloride concentration in the feed phase was determined with HPLC (Waters IC-PAK^{TM} anion column).

A linear relationship of the initial part of the concentration versus time curves was obtained. From the slope of this relationship, the copper flux J can be calculated using Eq. (3):

$$J = \frac{V}{A}\left|\frac{dC}{dt}\right| \tag{3}$$

in which C is the concentration of copper ions, A the membrane area in contact with the aqueous phase (18.1 cm^2) the V and volume of the feed or strip phase (0.150 l). The modulus signs are introduced to avoid negative values for a flux.

Diffusion coefficients of copper through SPEEK films were measured in the permeation cell described above with a feed phase of 0.01 M CuCl$_2$ solution (150 ml, pH=1) and a stripping phase of 1 M HCl (150 ml, pH=1). From the concentration decrease in the feed, the flux was determined and the diffusion coefficient was calculated using Eq. (3).

4. Results and discussion

This section first describes the results of the characterisation of SPEEK and the composite SLMs. Thereafter, the permeation experiments are discussed. For an implementation in industrial processes, SLMs have to meet three requirements, namely a high permeability, a high stability and a high selectivity. Therefore, the attention is focussed on these requirements.

Table 1
Ion-exchange capacity (IEC mmol/g polymer) and degree of sulphonation (DS mol%) for SPEEK samples determined by titration or element analyses

Method	IEC (mmol/g)	DS (mol%)
Titration	1.72	58
Element analyses	1.82	61

4.1. Characterisation of SPEEK

The degree of sulphonation was determined from the ion-exchange capacity of SPEEK and from the amount of sulphur present in SPEEK. Table 1 shows that the results of both techniques agree very well. The sulphonation degree of 60% corresponds with literature values for the same sulphonation procedure [10].

A certain percentage of aqueous swelling of SPEEK layers is required to minimise the mass transport resistance of the composite membranes and to increase the permeability of cations through these stabilisation layers. However, a too high degree of swelling may result in a polymer network that allows the components of the LM phase to permeate through the SPEEK layers into the surrounding aqueous phases. Especially, a high degree of swelling with the LM phase has to be avoided to maintain reasonable lifetimes of the SLMs. This high swelling was the major reason why poly(vinyl chloride) could not be used as stabilisation layer material [3]. Therefore, the swelling of SPEEK was determined in three hydrophilic and one hydrophobic solvent. Table 2 illustrates that the swelling behaviour of the polymer SPEEK fulfils the requirements. The swelling in hydrophilic solvents is much higher than in the hydrophobic LM phase, but not too high (maximum 20 wt%) to guarantee mechanical stability. The degree of swelling decreases with increasing ionic strength, or decreasing chemical potential of the aqueous solution.

Table 2
Degree of swelling (wt%) in four solvents (values are averaged over four samples and the experimental errors are lower than 30%)

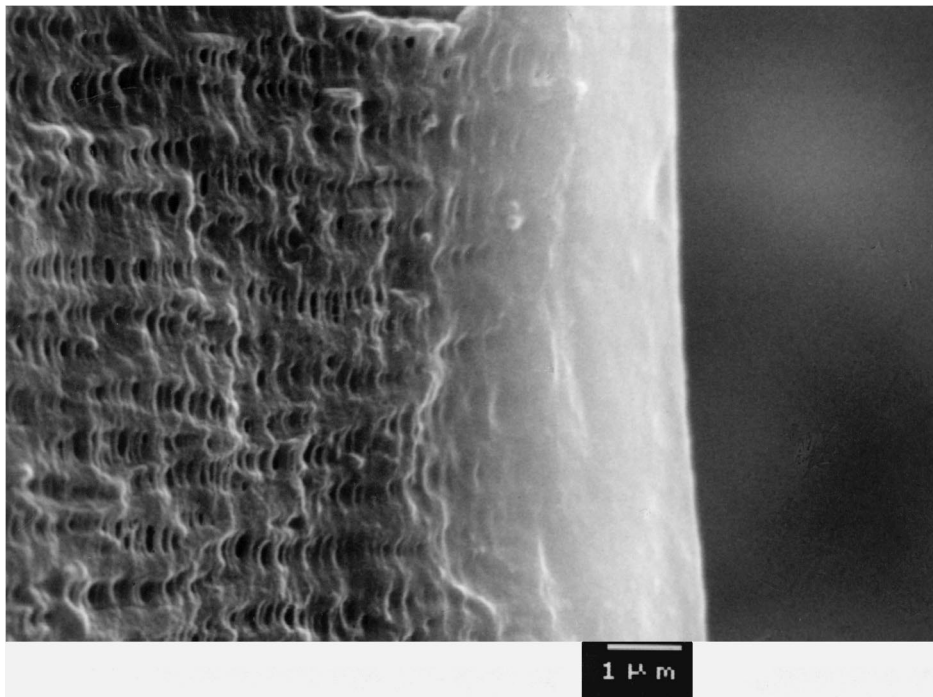| Solvent	Swelling (wt%)
Ultrapure water	20
Copper chloride (0.01 M)	15
Hydrochloric acid (2 M)	11
Carrier in dodecane (0.2 M)	3

Fig. 4. SEM photograph of a composite membrane composed of Celgard 2500 and SPEEK. Cross-section (10 000).

4.2. Characterisation of composite SLMs

SEM photographs give information on the morphology of the SPEEK top layer and the support membrane, on the thickness of the top layer, on the adhesion of the hydrophilic SPEEK to the hydrophobic support membrane and on the presence of macroscopic defects. Only limited conclusions can be drawn from SEM photographs since SEM photographs reflect only a small part of the actual membrane and they are made under dry conditions whereas flux measurements are carried out under wet conditions. A cross-section of a composite membrane made according to procedure 1 is shown in Fig. 4. It shows good adhesion of the SPEEK layer to the support membrane. The border between the two different materials is not distinct. This may indicate that SPEEK is present in the porous support membrane. The thickness of the SPEEK film is approximately 3 μm under dry conditions. A SEM photograph of the membrane surface showed a flat and homogeneous structure without defects.

Gas fluxes of carbon dioxide and nitrogen through composite membranes were measured to obtain information on macroscopic defects of the SPEEK layer. The composite membranes with a homogeneous SPEEK film were hardly permeable for these gases, but no gas selectivity could be measured between carbon dioxide and nitrogen. This indicates that the stabilisation layers were not gas tight and contained small defects. After operation of the composite membrane as SLM the gas fluxes increased, apparently due to growth of defects. However, the growth does not automatically include a loss in long-term stability in the liquid membrane application.

4.3. Permeability

As hypothesised earlier, the additional ion-exchange layer does not necessarily increase the total membrane resistance. In contrast, the fluxes listed in Table 3 suggest that the fluxes through composite membranes with cast fixed SPEEK layers are higher for all configurations tested. Since a single SPEEK

Table 3
Copper fluxes for different membrane configurations made according to procedure 1 (errors are within 25%)

Configurations	Total membrane thickness (μm)	Copper flux (10^{-9} mol/cm^2 s)
NO stabilisation	25	4.46
Composite F	32	6.65
Composite S	32	5.00
Composite F+film S	45	4.56
Composite F+S	35	8.06

Conditions: a feed phase of 0.01 M CuCl$_2$, a strip phase of 2 M HCl, an LM phase of 0.2 M carrier in dodecane, a support of Celgard 2500. Thicknesses were measured with a Mitutoyo digital thickness meter. F refers to a SPEEK layer at the feed side and S one at the strip side.

film cast from a 10 wt% DMF solution on a glass plate has a thickness between 10 and 13 μm and of a composite membrane of 32 μm, the pore-penetration of SPEEK for the composite membranes with one SPEEK film varies from 3 to 6 μm. The thicknesses of the composite membranes could not be measured very accurately because of their strong curling. The thickness of the composite membrane with two fixed SPEEK films is very low, possibly caused by a more prominent pore-penetration of SPEEK. Due to the small thickness of the Celgard membranes, it is difficult to prepare composite membranes with Celgard in a reproducible way and, consequently, the deviation in the measured copper flux is high, namely 25%. This implies that the copper flux is only significantly higher for the composite SLM with two fixed stabilisation layers.

Below we will elaborate that pore-penetration of the ion-exchange material is responsible for the increase in flux by studying the mass transfer of copper ions through an SLM. The mass transfer depends on a number of variables, such as the copper concentration in the feed phase, the proton concentration in the strip phase, the composition of the liquid membrane phase, the flowing velocity of the aqueous phases and the thickness of the support membrane. It is neither that a SPEEK film affects the flow conditions nor the optimal proton concentration in the strip phase. The composition of the LM phase is kept constant in all experiments, namely 0.2 M carrier in dodecane. The influence of the copper concentration in the feed phase, the thickness and type of support membranes
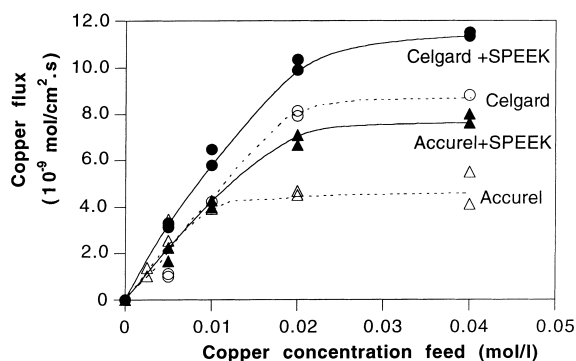

Fig. 5. Copper flux as a function of the copper concentration in the feed phase illustrating the effect of a SPEEK layer at the feed side of the SLM and the effect of the type of support membrane. Conditions: a feed phase of variable concentration CuCl$_2$, a strip phase of 2 M HCl, an LM phase of 0.2 M carrier in dodecane and support membranes Accurel and Celgard 2500.

and of the thickness of the SPEEK layer on the copper flux were studied to better understand the mass transfer through the composite SLMs.

The initial copper concentration in the feed phase has a significant influence on the copper flux, as shown in Fig. 5. At low copper ion concentrations, the flux increases linearly with the aqueous copper ion concentration. In this region, the transport is determined by the degree of saturation in the complexation reaction of copper ions and carrier molecules. At higher copper ion concentrations, the flux becomes independent of the aqueous copper concentration; all the effective carrier molecules at the feed-LM interface are complexed. In this region the ratelimiting step of the overall copper transport is the diffusion of copper-carrier complexes through the LM phase. For both support membranes, Accurel and Celgard, the plateau values of the stabilised membranes are higher and they are reached at higher copper ion concentration in presence of SPEEK, while the initial slopes of all curves are almost similar. This implies that there is no change in rate-limiting step when the membrane is stabilised by an additional layer.

To characterise the diffusive resistances of separate layers of the composite membrane, the diffusion coefficients of these media are compared in Table 4. This table shows that the diffusion of copper ions through the LM phase is a factor 6 lower than through the SPEEK film. This fact already suggests that a decrease of LM phase thickness may even increase the

Table 4
Diffusion coefficients D for copper in different phases

Medium	D_{Cu} (10^{-12} m^2/s)	References
Water	750.0	[20]
SPEEK	77.0	Experimental
LM phase	13.6	Experimental

Copper is present in ionic form in water and SPEEK phases and in complex form in the LM phase.

overall flux in contrast to the common anticipation of a flux decrease upon application of an additional layer.

This is also demonstrated in experiments where the thickness of the SPEEK layers were varied by using casting knives of thicknesses of 0.1, 0.2 and 0.3 mm. Accurel was chosen as support membrane and one SPEEK film was applied at the feed side. The copper fluxes were measured for initial copper concentration of 0.04 M in the feed. The differences in copper fluxes for these three different composite membranes were not significant and were within the reproducibility of the flux measurements demonstrating the fact that the additional layer does not decrease the flux.

The effect of the thickness of the support membrane was investigated by measuring copper fluxes through one or two Accurel support membranes. The accuracy of the copper flux measurements is lower when two support membranes are sticked together. This is due to the lower flux values and to the difficulties to prepare a reproducible interface between two support membranes. Table 5 shows that the copper flux decreases

with increasing thickness of Accurel. When an Accurel support is attached to a composite membrane of an Accurel membrane and a SPEEK layer, the total thickness increases with about a factor of 2, but the copper flux decreases with a factor more than 2. This supports the picture of pore-penetration of SPEEK; the thickness of the support membrane in the composite membrane will be lower than 100 μm and, consequently, the total thickness of the LM phase will be increased more than a factor 2.

As illustrated in Fig. 5, the initial copper concentration in the feed phase affects the copper flux. Therefore, the influence of thickness of the support membrane on the flux was determined for two copper concentrations. For the low experimental concentration of 0.01 M CuCl$_2$, the overall transport is determined by the diffusion through the LM phase and by the complexation reactions. On the other hand for the higher value of 0.04 M CuCl$_2$, the transport is only limited by diffusion through the LM phase. As seen in Table 5, no significant difference in ratio for a varying copper concentration in the feed phase is determined. Thus, it can be stated that for both concentrations, the diffusion of carrier-copper complexes through the LM phase plays the major role in the overall transport.

The addition of a stabilisation layer made of SPEEK does not hinder transport. Instead, due to partial pore-penetration of SPEEK, the flux increases. Partial pore-penetration results in a thinner LM phase and in a higher flux, because the flux is inversely related to the thickness of the LM phase.

Table 5
Copper fluxes and flux ratios J_1/J_2 of the average (av.) copper fluxes through composite membranes of Accurel and a SPEEK film at the feed side

Configuration	CuCl$_2$ (M)	Copper flux (10^{-9} mol/cm^2 s)				J_1/J_2
		1 Support average		2 Supports average		
No SPEEK	0.01	3.91	3.94	1.41	2.06	1.9
		3.97		2.70		
	0.04	4.68	4.60	2.72	2.65	1.7
		4.51		2.57		
With SPEEK	0.01	4.26	4.12	1.60	1.38	3.0
		3.97		1.16		
	0.04	6.72	5.59	2.43	2.02	2.8
		4.46		1.60		

In the case of 2 supports, an extra Accurel membrane is attached to the composite membrane at the strip side with a few droplets of LM phase. Conditions: a strip phase of 2 M HCl, a LM phase of 0.2 M carrier in dodecane.

Table 6
Separation coefficients and copper fluxes for different membrane configurations made according to procedure 1

Configurations	Thickness (µm)	Copper flux (10^{-9} mol/cm^2 s)	$a=J_{Cu}/J_{Zn}$	
			Feed	Strip
No stabilisation	25	4.36	239	>10-00
Composite F	32	4.58	>1000	>10-00
	32	7.17[a]	n.d.	74
	38	1.75[a]	n.d.	94
	38	5.35[a]		5.6
Composite S	32	3.61	17	23
	32	3.02	39	38
	32	3.07	3.6	33
Composite F+attached SPEEK S	45	3.48	5.8	4.7
	45	2.10	9.1	18
Composite F+S	35	4.25	1.0	n.d.
	35	4.19	1.3	1.2
	50	5.75	1.0	n.d.
	50	7.59	1.2	n.d.

Conditions: a feed phase of 0.01 M CuCl$_2$ and 0.01 M ZnCl$_2$, a strip phase of 2 M HCl, a support membrane of Celgard 2500, and LM phase of 0.2 M carrier in dodecane. F refers to a SPEEK layer at the feed side and S at the strip side. Samples are taken from the feed or strip phase.
[a]Flux determined from copper concentration changes in the strip, n.d. not determined.

4.4. Selectivity copper/zinc

For a potential industrial application a SLM has to show a high selectivity for different ions. First, composite membranes made according to procedure 1 are tested and the data are presented in Table 6. This table shows a significant loss in selectivity for copper in presence of zinc. The deviation in fluxes is high, about 30%. Also the determination of the zinc flux is not very accurate, especially when the zinc concentration in the feed phase is used for the flux determination due to very high dilution factors needed for the analysis of zinc with AAS. This results in large differences between several of the feed and strip separation coefficients. Depending on the reliability, copper and zinc fluxes were sometimes determined with data from the feed and from the strip phase. We hypothesise that the higher zinc transport through these composite membranes is caused by non-selective diffusion through pores filled with SPEEK. Pore-penetration may be more prominent for a composite membrane with two fixed SPEEK films in which SPEEK can penetrate into the support from both sides. The diffusion coefficients for Cu^{2+} and for Zn^{2+} through SPEEK will be similar, as the differences in hydrated ionic radius and

electronegativity between both ions are very small [6,12].

To check the hypothesis of the loss of selectivity due to pore-penetration, the chloride and proton fluxes were determined for a non-stabilised SLM and the composite membranes with two fixed SPEEK layers and a thickness of 50 µm as shown in Table 6. There is no transport of chloride ions from the strip phase into the feed phase for the non-stabilised SLM. However, for the composite membranes with two fixed SPEEK layers and a thickness of 50 µm, the chloride fluxes have the same order of magnitude as the copper fluxes, namely 4.42×10^{-9} and 3.83×10^{-9} mol/cm^2 s. This implies that SPEEK bridges exist through the entire support allowing chloride transport from the strip phase with a high chloride concentration to the feed phase with a low concentration. This type of transport is only possible for high salt concentrations, when there is no effective Donnan exclusion of SPEEK anymore. SPEEK is then permeable for both cations and anions. Also the ratio between proton flux and copper flux increased from 2.0 for the non-stabilised SLM to 8.0 for the composite SLM. This also suggests that ions diffuse through pores filled with SPEEK without carrier molecules in an unfacilitated way.

Table 7
Separation coefficients and copper fluxes for different membrane configurations made according to procedure 2

Configurations	Thickness(μm)	Copper flux (10^{-9} mol/cm^2 s)		$a=J_{Cu}/J_{Zn}$	
		Feed	Strip	Feed	Strip
Composite F	38	4.39	4.29	>1000	35
Celgard 2500	36	4.36	4.36	>1000	>1000
Composite S	38	3.91	6.04	93	19
Celgard 2500	35	4.89	7.29	>1000	177
Composite F+S Celgard 2500	46	3.91	5.50	>1000	150
Composite F+S	124	3.26	3.48	10	>1000
Accurel	124	2.48	2.75	>1000	>1000

Conditions as described in Table 6, support membranes are Celgard and Accurel.

When procedure 1 is used to prepare composite membranes, the surface modified support membrane (Accurel or Celgard) is placed on top of a very liquid SPEEK-DMF film (after 5 min) and the viscous SPEEK solution may penetrate into the pores. To avoid porepenetration procedure 2 was used: a dried solid SPEEK FILM (24 h) was rewetted with DMF by spraying and after 5 min the modified support was placed on the rewetted SPEEK film. However, the spraying procedure was not optimised and did not result in a homogeneously swollen SPEEK film surface. The adhesion of the SPEEK film to the modified support membrane was moderate and the composite membranes were strongly curled. Results of these membranes are presented in Table 7.

When data of Table 7 and Table 6 are compared, the copper fluxes through both types of membranes are similar. This means that the bad adhesion of the SPEEK layers to the support membrane does not influence the transport resistance. Notwithstanding the bad reproducibility in the determination of the separation coefficients, the values of these coefficients are significantly higher in Table 7 than Table 6. This demonstrates that a penetration of SPEEK through entire pores causes the loss in selectivity.

4.5. Long-term stability

The influence of SPEEK layers on the stability of SLMs was studied in long-term experiments. At the moment of replacing the feed phases, the percentage copper ions remaining in the feed phase was less than 2% of the original copper ion concentration. Fig. 6 shows that the unstabilised membrane shows no flux after already 50 h operation time. Also membranes
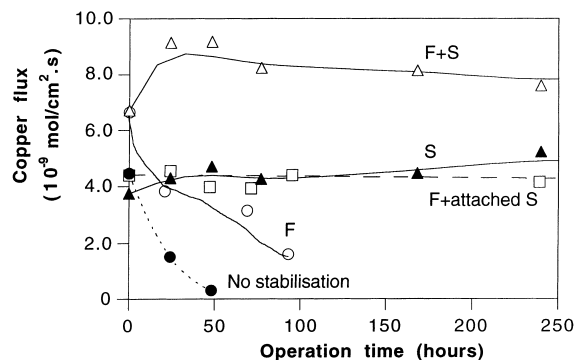

Fig. 6. Copper flux as a function of the operation time for different configurations of SLM with SPEEK. Configurations and conditions are the same as in Table 3. The feed phase was replaced before every flux measurement. F refers to a layer at the feed side, S at the strip side. The deviation in fluxes is lower than 25%.

with a stabilisation layer on the feed side do not show improved lifetime. However, the lifetime of SLMs is significantly improved when SPEEK layers were applied at the strip side as well as at both sides of the SLM. The permeation experiments of the SLM with a SPEEK layer at the strip side and at both sides were stopped after 2000 h. The fluxes for the composite membranes with two stabilisation layers are exceptionally high and apparently due to SPEEK penetration into the pores. The SPEEK forms non-selective bridges between the two aqueous phases and consequently, these membranes showed a low copper/ zinc selectivity. One may argue that also the membrane with the stabilisation layer at the strip side shows pore penetration and hence a constant flux in time, but the argument can be negated since the instable membrane with the stabilisation layer at the feed side and the stable membrane with the stabilisa-

tion layer at the permeate side were prepared according to exactly the same procedure. Ultimately, the problem of pore-penetration can be avoided when composite membranes are prepared according to procedure 2.

The fact that stabilisation at the feed does not affect the membrane lifetime but stabilisation at the strip side does agree with the study of the SLM degradation mechanism [22]. The carrier has a higher solubility in the acidic strip phase as RH or RH_2^+ than in the feed phase as CuR_2 [21–23]. An explanation for the initial increase in copper flux for the composites with two preswollen SPEEK films is lacking.

When the copper transporting SLMs presented in Fig. 6 are compared with the nitrate transporting SLMs of Neplenbroek et al. [1] and that of Kemperman et al. [2], it is demonstrated that the degradation mechanism of SLMs strongly depends on the system. For their systems with a feed phase of 0.004 M sodium nitrate and a strip phase of 4.0 M sodium chloride, a stabilisation layer at the feed side was sufficient to improve the stability. In the system described in this paper, stabilisation is required at the strip side. According to Neplenbroek et al. [1], emulsion droplets composed of the carrier tetraoctylammonium bromide and the solvent orthonitrophenyloctylether are the source for SLM degradation. Emulsion droplet formation is favoured at the SLM interface with a low aqueous salt concentration, i.e. the feed side. Kemperman et al. [2] used the carrier trioctylmethylammonium chloride in orthonitrophenyloctylether. A stabilisation layer at the feed side was sufficient to improve the lifetime of his SLMs, because this carrier has higher solubility in the feed phase than in the strip phase.

5. Conclusions

This study describes the preparation of stabilised composite SLMs, transporting copper ions, with improved lifetimes using sulphonated poly(ether ether ketone) (SPEEK) as material for the stabilisation layers. This polymer shows a high permeability for copper ions due to the presence of fixed negative charges and to its swelling capacity in aqueous phases. Composite membranes are prepared by first casting a SPEEK solution in DMF on a glass plate and, thereafter, bringing a support membrane on top of it. Composite membranes were made with a good adhesion of homogeneous, negatively charged, hydrophilic SPEEK layers to the hydrophobic macroporous support membranes, when the support membranes were first hydrophilised with a sulphuric acid treatment.

It is shown that the lifetime of the SLMs is significantly improved when one stabilisation layer is applied at the strip side or two at both sides of the SLM. A second advantage of this composite SLM is the increase in copper flux caused by a decrease in thickness of LM phase. However, when SPEEK bridges through the entire support, ions are not only transported through the LM phase complexed with carrier molecules but also in ionic form by SPEEK. Consequently, the selectivity of this SLM for copper in presence of zinc is lost. This phenomenon only occurs for the thin Celgard supports.

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