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Facilitated oxygen transport in liquid membranes: review and new concepts

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Abstract

In this paper, an overview is given on membranes with oxygen facilitated transport properties to enrich the oxygen content in air. Special emphasis is paid to recent developments of oxygen carrier systems and carrier containing membranes. Concepts leading to a structural evolution of supported liquid membranes are discussed in view of ion as well as gas separation processes. As a new concept, micro-encapsulated liquid membranes are introduced, in which a mobile carrier operates in the interior of liquid droplets that are encapsulated and dispersed in a solid polymer matrix and routes to prepare the new membranes described.

Keywords: Liquid membranes; Oxygen enriched air; Polymeric membrane; Microencapsulation; Oxygen carrier systems

1. Introduction

In this article, an overview is given on the current status of liquid membranes for the production of oxygen enriched air. In the second part, we introduce preparation routes for a new class of membrane, the so-called micro-encapsulated liquid membrane, and show preliminary results.

The separation of gas mixtures is a major operation in the (petro)chemical industry, whereby the separation of oxygen/nitrogen presents one of the main applications. Oxygen enriched air is used in many industrial processes which do not require pure oxygen, e.g. combustion of natural gas, coal gasification and liquifying, as well as in the production of peroxides, in sewage treatment, in welding and in the glass production. Standard methods are cryogenic distillation and pressure swing adsorption [1]. Since these techniques are still highly energy intensive, the number of current applications is limited and a less costly process would be desirable. As an alternative approach, gas separation membranes for the production of oxygen enriched air have been developed over the last 30 years based on the selective oxygen permeability of polymeric membrane materials and later on carrier mediated transport in liquid membranes. Polymeric membranes systems, which have proven to be less cost intensive to operate, are presently still not suitable to produce highly oxygen enriched air, i.e. air with an oxygen content in excess of 50–60 vol.% and for commercial large scale production [2,3].

Improvement of polymeric membranes for gas separation can only be achieved by increasing both permeability and perm-selectivity. Polymeric membrane materials with relatively high selectivities used so far show generally low permeabilities, which is referred to as trade-off or ‘upper bound’ relationship for specific gas pairs [4]. For commercial production of oxygen enriched air, the upper bound relationship

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presents the major disadvantage in the utilisation of polymeric membranes. To improve single bulk material (polymer) properties, facilitated transport of a specific gas molecule through modified polymeric membranes or liquid membranes containing mobile carrier molecules has been investigated since the first paper of Scholander [5] in 1960.

Facilitated or carrier mediated transport is a coupled transport process that combines a (chemical) coupling reaction with a diffusion process. The solute has first to react with the carrier to form a solute-carrier complex, which then diffuses through the membrane to finally release the solute at the permeate side. The overall process can be considered as a passive transport since the solute molecule is transported from a high to a low chemical potential. In the case of polymeric membranes, the carrier can be chemically or physically bound to the solid matrix (*fixed carrier* system), whereby the solute hops from one site to the other. *Mobile carrier* molecules have been incorporated in liquid membranes, which consist of a solid polymer matrix (support) and a liquid phase containing the carrier molecules [6], see Fig. 1.

For both types of facilitated transport systems, mediated solute transport by fixed or mobile carriers, two modes of solute transport can be distinguished, see Fig. 1. This so-called dual-mode transport mechanism describes the combined total oxygen flux through the membrane. It was first proposed to explain the transport behaviour of gases, such as carbon dioxide in glassy polymers. The first mode refers to the solution-diffusion of the solute, e.g. oxygen and nitrogen, through the polymer matrix of the membrane. Characteristic for this mode is a low oxygen selectivity and a low transport rate (diffusivity), determined by a Henry-type sorption. The second mode concerns the facilitated transport provided by the carrier. It is highly sensitive for oxygen and can be described by a Langmuir-type adsorption. Due to the dual mechanism, the total flux is not proportional to the driving force. Therefore, even at very low concentrations of oxygen in the feed phase still appreciable oxygen fluxes can be obtained [7,8].

General advantages of facilitated transport membranes are improved selectivity, increased flux and, especially if compared with membrane contactors, the possibility to use expensive carriers. The specific pre-requisites, advantages and disadvantages connected to both types of carrier systems, the fixed and the mobile carrier, are listed in Table 1. So far, mainly conventional liquid membranes have been loaded with different mobile carrier systems to obtain facilitated transport properties [9]. Problems encountered are (evaporative) loss of solvent and carrier, temperature limitations, a too large membrane thickness and, therefore, too low permeabilities as well as a limited solubility of the carrier in the liquid medium. The low fluxes achieved have, until now, limited their application in industrial separation processes. In particular for oxygen carrier systems, a major problem is the instability of the carrier against irreversible oxidation. Improvements necessary for (large scale) commercial applications involve, therefore, the development

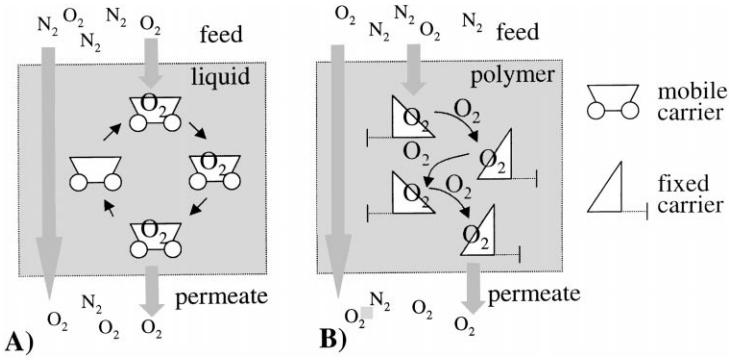

Fig. 1. Scheme for facilitated transport of gaseous molecules by a carrier (complex) through a membrane: (A) liquid membrane with a mobile carrier; (B) solid membrane with a fixed carrier.

Table 1
The specific pre-requisites, advantages and disadvantages connected to mobile and fixed carrier systems with respect to their selective oxygen transport properties

	Mobile carrier (liquid)	Fixed carrier (polymer film)
Requirements	*Membrane*: low effective thickness *Liquid medium*: low viscosity, low volatility, high compatibility with polymeric material *Carrier*: high concentration in the liquid medium, high selectivity for O_2	*Membrane*: low thickness *Carrier*: high concentration in the polymer matrix, high selectivity for O_2, high carrier-oxygen binding constant
Advantages	*High selectivity* *High diffusivity* of the permeant molecule	*High selectivity*
Disadvantages	*Loss* of membrane solvent and carrier *Low carrier concentration* *Carrier inactivation* due to oxidation	*Inactivation* of the carrier after fixation in the solid state *Non-uniformity* in chemical reactivity of the fixed carrier *Defect formation* in the solid membrane *Low diffusivity* of the permeant molecule

of new membrane morphologies and stable carrier systems.

2. Background

In this section, an overview is given on facilitated oxygen transport in liquid membranes, whereby we will lay our main emphasis on oxygen/nitrogen separation.

The concept of a molecular carrier transport involving a reversible chemical combination between permanent and mobile species was pursued and developed by Osterhout and colleagues in the early 1930s, although the principle has been demonstrated much earlier by Pfeffer in 1910 and Freudlich and Gann in 1915 [10]. The model experiments of Osterhout (1940) using quiacol, a weak organic acid, as carrier for sodium and potassium ions, clearly established the concept in the biological literature.

Apparently, the first who studied the application of membranes with facilitated transport properties for gas separation were Ward and Robb [11]. The number of gases for which suitable carriers are currently available is small and most effort has been devoted to the clean up of acid gases. The first studies on facilitated transport systems for different gaseous permeants are reported in Table 2.

2.1. Stabilisation of supported liquid membranes (SLMs)

Despite their advantages, SLMs are, as mentioned above, not used at large scale in industry. The main

Table 2
First studies on facilitated transport systems for different gaseous permeants

Year	Gas	Carrier	Applications	References
1960	O_2	Haemoglobin, Fe, Co, Ru Porphyrins, Ir, Mn complexes	O_2 enrichment for medical use, combustion, sewage treatment, welding and glass production	Basset and Schultz [12]
1970	NO	Fe^{2+}		Ward [13]
1971	CO_2	CO_3^{2-}, ethanolamines	Biogas purification, enhanced oil recovery, life support systems	Enns [14]
1974	CO	Cu^{+}	Synthesis gas, purification	Steighelman and Hughes [15]
1977	H_2S	CO_3^{2-}	Gasified gas, desulphurisation	Matson et al. [16]
1981	Olefins	Ag^{+}, Cu^{+}	C_2H_4 recovery	Hughes et al. [17]

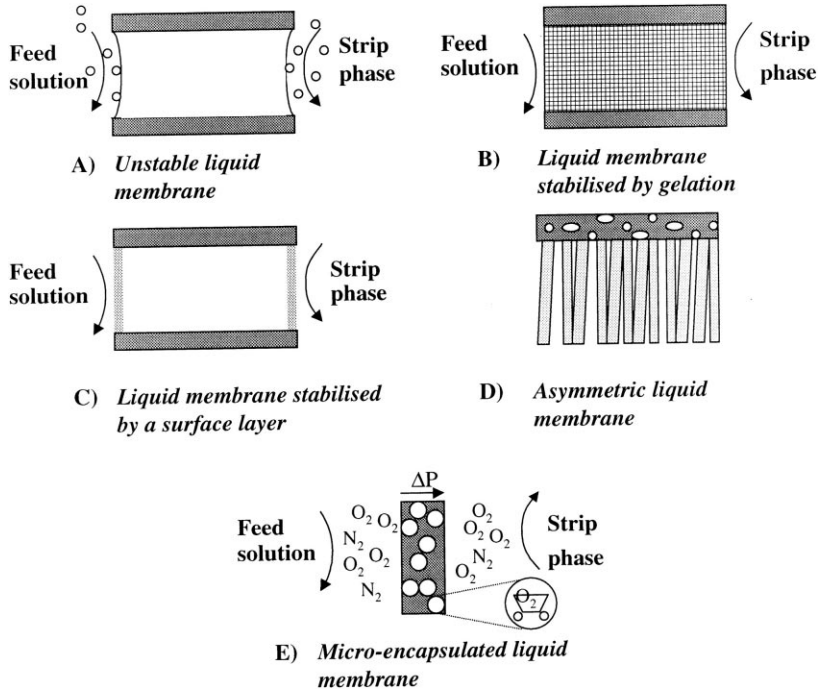

Fig. 2. Overview on stabilisation techniques for SLMs developed over the last 10 years.

reasons are besides low fluxes resulting from the substantial thickness (∼25 μm), the short membrane stability or lifetime, which is far too low to assure reliability. The instability of the SLMs is due to loss of solvent and/or carrier from the membrane (Fig. 2A) which influences the flux and selectivity of the membrane in a negative way.

In the last years, several methods have been developed to overcome the instability problems of SLMs which are depicted in Fig. 2.

A gelled SLM is shown schematically in (Fig. 2B). This idea was first proposed by Bloch et al. [18] in the late 1960s and then further improved by Neplenbroek [19], whereby two gelation techniques were developed. In the first, a homogeneous gel network was formed in the pores of the support, increasing both the mechanical stability (against liquid displacement) and long-term permeability substantially. In the second technique, a thin dense gel layer was applied on the feed side and/or strip side of the membrane, avoiding loss of solvent and carrier without decreasing the flux and obtaining a significant reduction in permeability. The major disadvantage of the first technique was the low reproducibility, while the second method in which the gel layer is spread on the support surface is still not suitable for large scale applications. Another approach developed by Kemperman [20] is to apply a thin top-layer on the liquid membrane support (Fig. 2C), who used an interfacial polymerisation reaction. This technique is expected to give better reproducible membranes and is easier to scale up.

All the techniques used to increase the stability of the SLM, mentioned above, are essentially applied in the removal of (metal) ions from solution. The stability of liquid membranes used for the separation of gases is more complicated. Here, the addition of a top-layer on the macroporous support can negatively influence the permeability of gases through the membrane. Therefore, a careful choice of the layer material is important because it has to be impermeable to the solvent and should posses a high permeability for the gas molecules considered. In addition, the thickness of the top-layer as well as that of the whole liquid membrane has to be minimised.

The concept of micro-encapsulated liquid membrane was introduced for the first time by Bauer et al. [21]. They presented a method that provided a promising alternative to overcome the above-mentioned problems observed with conventional liquid membranes (Fig. 2D).

They developed an asymmetric liquid membrane obtained via a modified phase inversion process, with a very thin open cell type top-layer (100–500 nm), whereby individual cells were filled with a non-volatile solvent (oil) and the carrier molecules, allowing for high fluxes (more details in Section 3). A further advantage achieved was the prevention of carrier loss without applying a supplementary coating layers, since the polymer in the top-layer completely surrounds the carrier-containing liquid phase. The important disadvantage was the low long-term stability, due to loss of the solvent as well as oxidative decomposition of the carrier complexes.

Our work presents a continuation of the work carried out by Bauer. We are trying to overcome the limitation of the first micro-encapsulated liquid membrane by preparation of well-defined capsule-containing membranes (Fig. 2E). The function of these capsules is to avoid the loss of solvent and carrier. The oxygen flux through the membrane is expected to be still high due to the low membrane thickness ($<3\,\mu m$).

2.2. Overview of facilitated transport for the production of oxygen enriched air

In this section, we will report on the major developments in oxygen carrier systems. Since most of the publications are in the biochemical field, we will only highlight the progress made relevant to the application of these specific carriers in membranes with facilitated transport properties. Detailed information of the different carrier systems developed and their application in the production of oxygen enriched air are summarised in Tables 3 and 4.

Much of recent interest in facilitated oxygen transport in the field of chemical engineering has been stimulated by the experiments of Scholander [5] and Wittenberg [22] in 1960 and 1966, who worked on biological systems. They showed that haemoglobin (Hb) and myoglobin could accelerate the transport of oxygen across water films and arose the interest in the synthesis of oxygen specific carriers. The first to apply synthetic oxygen carriers were Basset and Schultz in 1970 [12], who used bis(histidine)cobalt(II) as a

Table 3
Traditional oxygen carrier systems

Name	Symbol	References
Bis(dimethylglyoximato) cobalt(II)/copper(II)/nickel(II)	Co $(DMG)_2$	[29]
Bis(2-amino-1-benzaldehyde)ethylenediamine		[30]
Cobaltodihistidine	Co $(\phi\ H)_2$	[12]
Cobalt(II) salt		[31]
Dinitrato-bis(*sym*-diethylenediamine) cobalt(II)	Co $(s\text{-}Et_2en)_2\ (NO_3)_2$	[32]
Fe or Co (dry-caves)		[24,33–35]
Haemoglobin	HbCO	[5,22,36]
Meso-tetra(α,α,α,α)-(pivalamidophenyl)porphinato cobalt(II)	Co(TpivPP)	[25,37–41]
[*N*,*N*′-bis(salicylidene)ethylenediamine] cobalt(II)	CoSalen	[30,42–49]
[*N*,*N*′-bis(salicylideneimino)di-*n*-propylamine] cobalt(II)	Co(SalPr)	[24,34,50]
[*N*,*N*′-bis(3-methoxysalycylidene)ethylenediamine] cobalt(II)	Co(MeOsalen)	[24,34,42]
[*N*,*N*′-bis(3-methoxysalycylidene)tetramethylethylenediamine] cobalt(II)	Co(3-MeOsaltmen)	[24,34,35,42]
N,*N*′-bis(3-salycylidene-amino)propylmethylamine		[48]
N,*N*′-ethylene-bis(3-methyl-7-phenylsalicylidendiminato) cobalt(II)	Co3	[48,51]
Peroxo-bis[*N*,*N*′-ethylene-bis(salicylideneiminato)dimethylformamide] cobalt(II)	Cosalen	[52]
α,α′,α″,α‴-Meso-tetrakis(*o*-aminophenyl)porphyne	CoMP	[53]
α,α′,α″,α‴-Meso-tetrakis(*o*-pivalamidophenyl)porphynato cobalt(II), 1-methylimidazole or laurylimidazole	(CoPIm)	[54–56]
α,α′,α″,α‴-Meso-tetrakis(*o*-pivalamidophenyl)porphyrin iron(II)	$(Fe^{III}P)$	[56]
N,*N*′-ethylene-bis(5-nitro-salicyliden-iminato) cobalt(II)	Co(5-NO_2-saltmen)	[21]

Table 4
Summary of oxygen permeability and selectivity in various membrane system with facilitated transport properties

Facilitated transport by	Solvent or polymer	Carrier	Selectivity ($\alpha = P_{O_2}/P_{N_2}$); permeability (P) (Barrer)[a]	References
Mobile carrier	Hb-solution	Hb	–	[20,22,25,36]
Mobile carrier	Water	Co (ϕ H)$_2$	–	[12]
Mobile carrier	γ-Butyrolactone, dimethylsulfoxidedimethyl-acetamide, *N*-methylpyrrolidone	Co/Fe (dry-cave), Co(SalPr), Co(MeOsalen), Co(3-Me Osaltmen)	$\alpha = 10$–30 $P_{O_2} = 1000$ [23,30]; 260 [31] $P_{O_2} = 18$ [29]	[24,33–35]
Fixed carrier	Poly(butylmethacrylate)	(CoMP)	$\alpha = 3.2$–12 $P_{O_2} = 6$–14	[54,55]
Fixed carrier	Epoxy-diacrylate copolymer photografted onto cellulose	Cosalen	$\alpha = 50$	[52]
Fixed carrier	Poly[(octyl methacrylate)-co-(4-vinyl pyride), poly[(octyl methacrylate)-co-(1-vinylimidazole)	CoSalen	$\alpha = 2.3$–12 $P_{O_2} = 19.5$–31.2	[44]
Fixed carrier	Poly[(octyl methacrylate)-co-(1-vinylimidazole)	Co(TpivPP)	$\alpha = 6.1$–12 $P_{O_2} = 15$–40	[25,40]
Fixed carrier	Styrene-vinylbenzyl chloride, styrene-methacrylamidoethyl	Co (s-Et$_2$en)$_2$ (NO$_3$)$_2$	$\alpha = 10.3$–12.2 $P_{O_2} = 13.9$–39.9	[32]
Fixed carrier	Poly(butylmethacrylate)	(CoPIm)	$\alpha = 3.2$–12 $P_{O_2} = 6.4$–2.3	[54]
Fixed carrier	Styrene-butadiene-styrene	Cosalen	$\alpha = 3.4$ $P_{O_2} = 23.4$	[45]
Fixed carrier	Styrene-butadiene-styrene	Co3	$\alpha = 2.94$ $P_{O_2} = 62$	[51]
Fixed carrier	Poly(vinyl alcohol)/poly(*N*-salycylidene allyl amine) blend	Co(II)	$\alpha = 2.19$–8.50 $P_{O_2} = 215$–228	[57]
Fixed carrier	Polycarbonate membrane	CoSalen	$\alpha = 4.7$–7.9	[46]
Liquid carrier	4-Methylanisole	(CoPIm)	$\alpha = 20$–40	[56]
Fixed carrier	Polycarbonate	Co(SalPr)	$\alpha = 5$–7 $P_{O_2} = 1$–2	[50]
Encapsulated carrier in liquid	Polyethersulfone	Co(5-NO$_2$-saltmen)	$\alpha = 19.7$–15.6	[21]

[a] 1 Barrer=10^{-10} cm^3 (STP) cm cm^{-2} s^{-1} cmHg^{-1}.

complexing agent in an aqueous medium. Their best results gave an approximate doubling of the oxygen flux compared to water and a selectivity of 3.5.

The first main problem encountered in facilitated oxygen transport was the low oxygen selectivity and the instability of the carrier systems used, which tended to degrade rapidly. Due to the still significant thickness of even thin SLMs, the oxygen permeability observed was too low to be of commercial interest. A substantial increase in oxygen selectivity as well as improvement in the lifetime of the carrier system was obtained by Roman and Baker in 1982 [23,24]. In operating the membranes with a partial oxygen pressure on the product side, that was about 10 mmHg less than that of the feed stream, they obtained an O_2/N_2 selectivity of 30 and an O_2 permeability of 1×10^{-7} Barrer. The energy requirement amounted to only a fraction of the costs of the cryogenic processes. A detailed study on fixed cobalt porphyrin complex carriers has been performed by Nishide et al. [25,26] over the last 10 years. They reported that oxygen sorption and desorption to and from the fixed carrier complexes in their membranes is very rapid and reversible showing the form of a Langmuir isotherm. The oxygen permeability was enhanced by a decrease in the upstream oxygen pressure, $P(O_2)$, and the oxygen transport analysed by dual mode transport. The permselectivity $P(O_2)/P(N_2)$ reported was >10. Using in situ UV–VIS spectroscopy, they could show that in order to enhance the facilitated transport of oxygen in the membrane, the complexes formed have to posses both a strong oxygen-binding affinity and a fast oxygen-dissociation kinetics.

Key parameters for a successful application of the synthetic oxygen carriers are the stability and high affinity of the oxygen-carrier complexes and the control of the auto-oxidation processes. The carrier-oxygen complex formed should posses a strong affinity to oxygen molecules but should also be stable against auto-oxidation, which would otherwise destroy the carrier. In literature, mainly a variety of porphyrin-based carrier complexes has been reported and investigated for oxygen binding but almost no attention has been paid to newly developed self-assembled systems. For the latter, the synthetic effort is significantly reduced widening up the possibility for practical applications. Very recently research activities have been directed to using ion-pair interactions as a valuable tool to build up molecular assemblies. Easily obtainable building blocks, such as 5,10,15,20-tetrakis(*N*-alkylpyridinium-3-yl)porphyrins and calix [4] arens tetrasulfonated on the upper rim, have lately been investigated as starting materials for oxygen carriers to prepare cobalt(II) complexes [27].

3. Micro-encapsulated membranes

The concept of micro-encapsulated membranes, as already mentioned above, was introduced by Bauer et al. [21]. They developed an asymmetric membrane by a dry/wet phase inversion process whereby a carrier solution was encapsulated in a closed-cell morphology within the ultrathin selective top-layer of only 0.1–0.5 μm thickness. The porous support layer gave good mechanical properties to the membrane in order to withstand mechanical stress from high pressures, which in turn could affect the thin top-layer. The carrier used was *N*,*N*′-ethylene-bis(5-nitro-salicyliden-iminato) cobalt(II) with dimethylpyridine (DMAP) as axial base. The main targets of the membrane developed were to achieve high fluxes and to avoid any loss of carrier without applying additional coating layers. The selectivity (O_2/N_2) measured with a gas permeation set up was initially 16, which is 3.5 times higher than that of the polymeric material (polyethersulfone) used but showed no long-term stability. The high selectivity observed dropped over a period of time much shorter than the desired lifetime of the membrane to the value of the hosting polymer. Unfortunately, the reproducibility of the top-layer structure and, thus, the encapsulation was not easy to obtain. In any case, this approach does not allow for a controlled tailoring of the capsule containing membrane layer. Droplet size and concentration as well as type of polymer and solvent are not readily to adjust or exchange, respectively.

In this paper, a new route to prepare micro-encapsulated liquid membranes (see also Fig. 2E) is introduced. Carrier molecules that can reversibly and selectively bind oxygen molecules are first encapsulated together with a suitable solvent and the capsules dispersed in a polymer matrix to obtain a homogeneous carrier-containing liquid membrane (Fig. 3). In this way, carrier and solvent should be more protected against losses resulting in better long-term

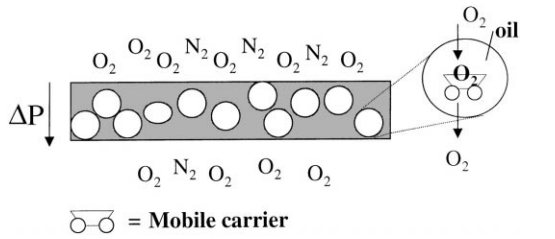

Fig. 3. Scheme for carrier-mediated transport in a micro-encapsulated liquid membrane.

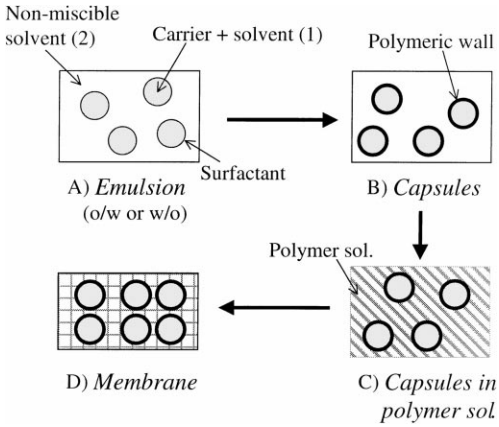

Fig. 4. Steps in the formation of a micro-encapsulated liquid membrane.

stabilities. To ensure high permeabilities, the membrane thickness should be ideally $<1\,\mu m$. In this section, we will mainly focus on preparation routes for micro-encapsulated membranes. The main stages in the formation of micro-encapsulated membranes are shown schematically in Fig. 4.

In general, micro-capsules can be formed using conventional encapsulation techniques. The underlying principal is that first droplets of one solvent will be dispersed in another solvent by mechanical agitation (Fig. 4A) to which a polymer has been added to form a stable polymeric wall around the droplets (Fig. 4B). To prepare membranes the capsules can then be dispersed in a polymeric solution (Fig. 4C) from which the membrane is cast (Fig. 4D). This approach combines classical membrane formation by solvent evaporation from a polymeric solution with encapsulation techniques.

The choice of the emulsion type, oil-in-water (o/w) or water-in-oil (w/o), and thus, the nature of the internal phase of the capsules as well as the choice of the wall formation technique depends on the solubility of the carrier molecules. In case they are soluble in organic solvents, water will form the continuous phase. The specific requirements for the preparation of micro-encapsulated membranes for oxygen enriched air by facilitated transport are summarised in Table 5.

There are a number of methods described in the literature to prepare liquid containing capsules via emulsions; these include coacervation, solvent evaporation and interfacial or in situ polymerisation [28]. Furthermore, polymerisable or cross-linkable surfactants or copolymers can in principle be employed to entrap the disperse phase. The coacervation technique involves the preparation of o/w emulsion droplets onto which the polymer that is dissolved in the continuous water-phase can be forced to adsorb by increasing temperature and/or by the addition of salt to the continuous phase. Polymers used should show in aqueous solution, a lower consolute point as, e.g. polyvinylalcohol (PVA) or polyethyleneglycol. In a following step, the phase-separated polymer chains around the droplets have to be cross-linked to form a water-insoluble capsule wall.

Interfacial polymerisation as, e.g. the formation of polyamide involves the polymerisation reaction of a water and an oil soluble monomer at the water–oil

Table 5
Summary of the specific requirements for the preparation of micro-encapsulated membranes for oxygen enriched air by facilitated transport

Compound	Property
Solvent 1	Should *dissolve 'high' concentrations of carrier* (o/w or w/o), *non viscous* solvent (o/w), *high boiling point* (o/w)
Solvent 2	continuous phase (o/w or w/o)
Capsule wall forming polymer	*permeable to oxygen* (o/w or w/o), *insoluble* in solvent 2
Membrane forming polymer	*permeable to oxygen, compatible with capsule* forming polymer and/or capsule solution

interface. Most of the conventional interfacial polymerisation techniques affect the internal phase. An exception form polymerisation reactions in the dispersed phase, whereby the in situ formed polymer becomes insoluble in the dispersed phase upon growing and finally migrates to the interface, or the spontaneous polymerisation of, e.g. *n*-alkyl cyanoacrylate at the water–oil interface [57]. Polymerisation or cross-linking of surfactants and/or copolymers in the interfacial film is a relatively new field. Approaches made so far deal mostly with a co-polymerisation of the surfactant and the dispersed phase [58].

Since in most of the classical preparation routes, surfactants are not necessarily used to reduce the interfacial tension and to stabilise the emulsion droplets against aggregation and coalescence phenomena, capsules in the size range of 1–10 μm are normally obtained. For the preparation of the micro-encapsulated membranes, the classical encapsulation routes have, therefore, not only to be modified with respect to the requirements summarised in Table 5 but also with respect to the droplet size.

3.1. Micro-encapsulated membranes via coacervation: preliminary results

As a first approach, we investigated and modified the coacervation technique used in conventional encapsulation processes to prepare liquid containing microcapsules which can then be dispersed in a polymer solution for the preparation of the final membrane (see Figs. 4 and 5). As has already been mentioned, the main pre-requisites for the new membranes that act as constraints in developing and modifying encapsulation routes are that (i) the capsules have to be in the submicrometer size range to obtain membranes thicknesses $<1\,\mu m$ and that (ii) the polymers used to form the capsule walls and the membrane matrix should posses a high or moderate oxygen permeability, respectively (see Table 5).

In the classical coacervation route, organic compounds are encapsulated by first dispersing the apolar phase as droplets in aqueous media and then to force an added polymer to phase separate onto the droplet surface by addition of a phase inducer, a salt such as sodium sulphate, or/and by increasing the temperature. In order to form a (rigid) shell, the coacervation step is followed by a cross-linking reaction of the droplet surrounding polymers. Thus, the capsule wall-forming polymer needs to show a lower consolute point (cloud point) in aqueous solutions and to be suitable for cross-linking. An ideal and often used polymer for the encapsulation process that is suitable for coacervation and cross-linking is PVA [59]. However, PVA is not ideal in our case because it posses a very low permeability for oxygen, being 1.9×10^{-3} Barrer in its dry state. The oxygen permeability of humidified cross-linked PVA has still to be determined.

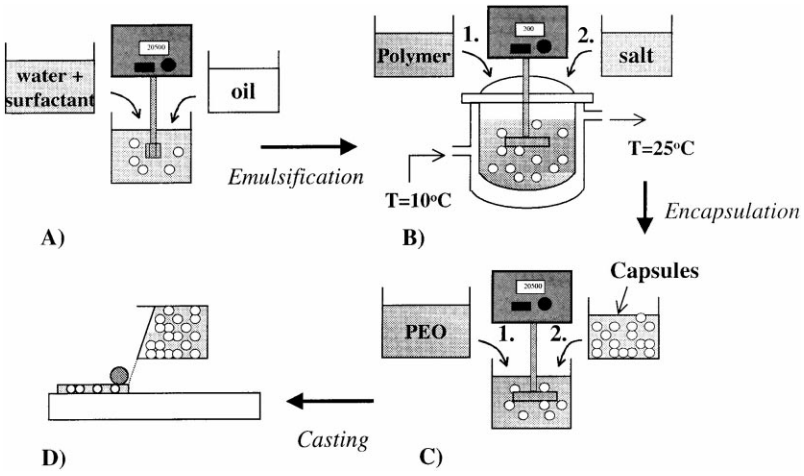

Fig. 5. Preparation route for micro-encapsulated membranes based on coacervation.

In order to prepare the micro-encapsulated membranes by coacervation, we investigated the use of non-ionic surfactants to reduce the interfacial tension and to produce and stabilise submicrometer sized emulsion droplets and thus capsules, as well as the use of polyethyleneoxide (PEO) as wall forming polymer. This comprises a profound characterisation of the surfactants and polymer used with respect to emulsification and coacervation processes. PEO shows in water a lower consolute point and permeabilities measured for oxygen and nitrogen lay in the order of 600 and 200 Barrer, respectively. In this section, the formation of the micro-encapsulated membranes will be summarised, the preparation of the capsules will be discussed in detail in a forthcoming article [60].

3.2. Preliminary results

The preparation route, developed so far, consists of three basic steps (see Fig. 5): emulsification, encapsulation and casting. Finding the optimal conditions for the first two steps (Fig. 5A and B) comprises a careful characterisation of the droplet size and distribution as a function of oil content, surfactant type and concentration as well as stirring conditions (stirring rate and time) and a detailed analysis of the coacervation conditions. For the latter process, cloud points of aqueous solutions containing surfactants (ethoxylated nonylphenols with 6–10 ethylenoxide groups, Arkopal 60–100, Hoechst), PEO with molecular weights of 3×10^5 and 5×10^6 g/mol and salt (Na_2SO_4) were measured to determine the optimal concentration range for the coacervation process.

3.3. Emulsion formation

We find that suitable conditions to obtain submicrometer w/o emulsion droplets that can be used as precursors in the encapsulation process were to use 4 wt.% Arkopal 100 and 8 wt.% of the oil (*ortho*-nitrophenyloctylether) to prepare the emulsions (Fig. 5A) at a stirring rate of 20×500 rpm and an agitation time of 10 min using an Ultra-Turrax T25 (IKA Labortechnik, Germany) with an extra fine dispersing tool (S25), based on a rotor/stator principal. The emulsion droplets have been characterised by means of light scattering/diffraction experiments using a Microtrac X-100 apparatus (Honeywell, USA) [61]. The oil droplets formed possessed diameters of 200–300 nm and a narrow size distribution.

3.4. Capsule formation

In order to form a polymer wall around the emulsion droplets, the emulsion was first transferred into a reactor (Fig. 5B) and a concentrated aqueous PEO ($M_w = 3 \times 10^5$ g/mol) solution added under stirring. The reactor was then cooled to 10°C and a solution of Na_2SO_4 in water added under stirring. The concentration of surfactant, polymer and salt were adjusted in a way that the cloud point of the resulting aqueous phase (continuous phase) was around room temperature. After homogenisation, the temperature of the reactor was increased to 25°C to induce phase separation and precipitation of PEO onto the emulsion droplets. It is convenient to have the cloud point around room temperature for two reasons. The first is the easier handling of the emulsions once the polymer has been adsorbed. If $T < T_{\text{cloud point}}$, PEO becomes again soluble in the aqueous phase and will desorb from the droplet surface. The second reason is connected to the increased instability of (metal ion containing) oxygen carrier complexes at high temperatures. To adjust the cloud point temperature at 20°C, we used a PEO concentration of 1 wt.% in the continuous phase and a PEO/Na_2SO_4 ratio of 1:4. Polymer surrounded droplets formed under these conditions were of 0.5 μm in diameter (see Fig. 7). Fig. 6 shows an optical

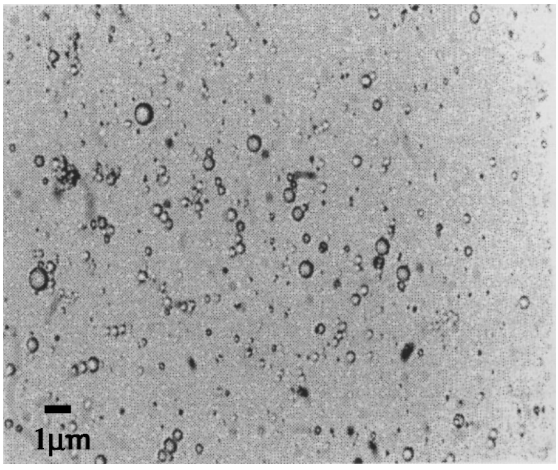

Fig. 6. Micrograph of polymer covered emulsion droplets obtained by light microscopy.

micrograph for isolated polymer covered oil droplets of 1 μm.

In conventional encapsulation routes, the step that follows coacervation is cross-linking of the adsorbed polymer chains to form a water insoluble (rigid) shell. PEO does not posses any functional side groups and can, therefore, not be easily cross-linked using, e.g. multifunctional isocyanates or aldehydes. Any attempts we made to cross-link PEO under moderate conditions such as catalysed radical formation using water soluble peroxides (ammonium persulphate, APS) and/or UV irradiation have not been successful. Capsules with a cross-linked polymer shell have so far only partially been formed with γ-irradiation.

3.5. Membrane formation

Since cross-linking of PEO has not yet been accomplished, we were not able to isolate the polymer surrounded oil droplets. As a first attempt, the droplet suspension obtained after coacervation was used directly to cast the membrane. The suspension was added to a solution of 5 wt.% PEO ($M_w = 1 \times 10^6$ g/mol) (Fig. 5C). After homogenisation, the dispersion obtained was cast on a glass plate (Fig. 5D) and membranes formed by means of solvent evaporation in a nitrogen atmosphere, whereby the oil (capsule) content varied from 11 to 30 wt.% The polymeric films obtained were white in appearance and quite porous. Scanning electron microscopy performed with a JSM-T220A microscope (JEOL, Japan) revealed that the films obtained contained a large number of clusters of oil droplets (capsules). The individual capsules displayed an average diameter of 0.5 μm and a narrow size distribution, indicating that the size of the polymer surrounded oil droplets did not change during casting and membrane formation.

Fig. 7 displays a scanning electron micrograph of a membrane prepared by dispersing the emulsion after coacervation in a 5 wt.% solution of PVA (88%, $M_w = 8.8 \times 10^4$) used to reduce the porosity of the polymer matrix. The picture shows regions of aggregated droplets within pockets formed by the polymer matrix.

From the results obtained so far, it is clear that more effort has to be put into the casting of the membranes. Other polymers that can be employed as matrix material have to be evaluated in order to maintain the singly dispersed state of the oil droplets during the membrane formation and drying process. Besides the coacervation technique, also the other techniques, mentioned above, will be investigated with respect to their applicability in the preparation of micro-encapsulated membranes.

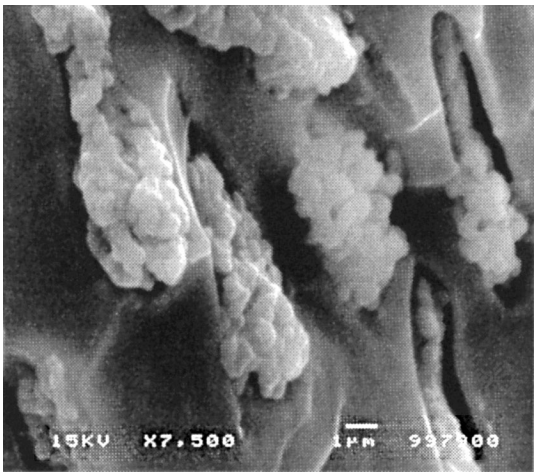

Fig. 7. SEM picture of the cross section of a membrane loaded with the capsules. The picture shows regions of aggregated droplets within a pocket formed by the polymer matrix.

4. Conclusion and outlook

Commercial membrane systems developed for the production of oxygen enriched air are not yet mature enough to be used for large-scale industrial applications requiring oxygen contents of 60–70 vol.%. Existing polymeric membranes show, due to the upper bound relationship between permeability and selectivity, a selectivity which is too low to obtain the required oxygen purity in a commercially feasible single stage process. Of the materials studied so far, none shows selectivity in excess of 10 and permeabilities higher than 10^3 Barrer, yielding oxygen purities not higher than 50% in a single stage process.

Membranes desired to compete with conventional techniques should provide an O_2/N_2 selectivity higher than 20 and fluxes higher than 1.5×10^{-2} m^3 m^{-2} h^{-1} bar^{-1} operating in single stage at a hydrostatic pressures of <10 bar and temperatures between 0 and 40°C. To ensure long-term stabilities,

the membrane lifetime should be longer than 1 year. In order to pass the selectivity-permeability trade-off, carrier mediated systems have been developed, and many research activities have been devoted in recent years to improve the performance of carrier-containing SLMs. However, the main problems still to be faced are low fluxes due to the substantial thickness of the liquid membrane, its instability with respect to carrier and solvent loss and the short lifetime of the oxygen carrier systems. There is, therefore, still a need for better carrier systems which are less sensitive to auto-oxidation processes and posses at the same time a high affinity for oxygen as well as stable new membranes with well-defined morphologies and thin active layers ($<1\,\mu$m).

The micro-encapsulated membrane first introduced by Bauer and further elaborated in this paper presents a new approach to overcome instability problems and low oxygen permeabilities observed in SLM systems used so far, but needs further development. The structure of the thin selective top-layer of the asymmetric membrane prepared by Bauer using wet/dry phase inversion is however difficult to control and does not allow for specific tailoring to avoid solvent losses and to optimise the oxygen transport properties of the composite membrane. The preparation of micro-encapsulated membranes proposed in this paper via dispersing of sub-micrometer sized capsules that contain the carrier loaded liquid phase homogeneously in a polymer matrix opens up more possibilities and a better control on the membrane morphology on the nanoscale compared with wet/dry phase inversion processes. In our case, it should be much easier to account for different carrier solvents and polymer matrix material and to adjust the amount of capsules in the matrix. To show the feasibility of this approach, we calculated the O_2/N_2 selectivity for different polymer matrixes and carrier phase permeabilities as a function of the capsule concentration. As a first approach, we used the formula of Petropoulos [62] based on the Maxwell model to determine the permeability and selectivity in heterogeneous (composite) systems. The overall permeability of component i (P_i), which is oxygen (nitrogen) in our case, is given by

$$P_i = \frac{1}{(1-\Phi_c^{1/3})/P_{p,i} + \frac{3}{2}\Phi_c^{1/3}/(P_{p,i}(1-\Phi_c) + \frac{3}{2}\Phi_c P_{c,i})}$$

$P_{p,i}$ represents the permeability of component i in the pure polymer, $P_{c,i}$ the permeability of component i in the capsules and Φ_c the capsule volume fraction in the membrane, whereby all permeabilities are given in Barrer. The basic assumptions made are that (i) the membrane consists only of two phases, the dispersed capsules and the polymer matrix and that (ii) both phases do not influence each other, assuring independent permeabilities.

Fig. 8 shows O_2/N_2 selectivities calculated for two different permeabilities of oxygen in the carrier-loaded capsules of 260 Barrer (Fig. 8A) and 1000 Barrer (Fig. 8B). For the permeability of nitrogen in the solvent inside the capsules, the value of 10 Barrer (e.g. γ-butyrolactone) was used in the capsules in both cases. For a better comparison, we calculated the selectivities for polymer matrixes of low (PVA: $P(O_2) = 0.0019$ Barrer, $P(N_2) = 0.00057$ Barrer), intermediate (polymethylpentene (PMP): $P(O_2) = 37.2$ Barrer, $P(N_2) = 8.9$ Barrer) and high (PEO:

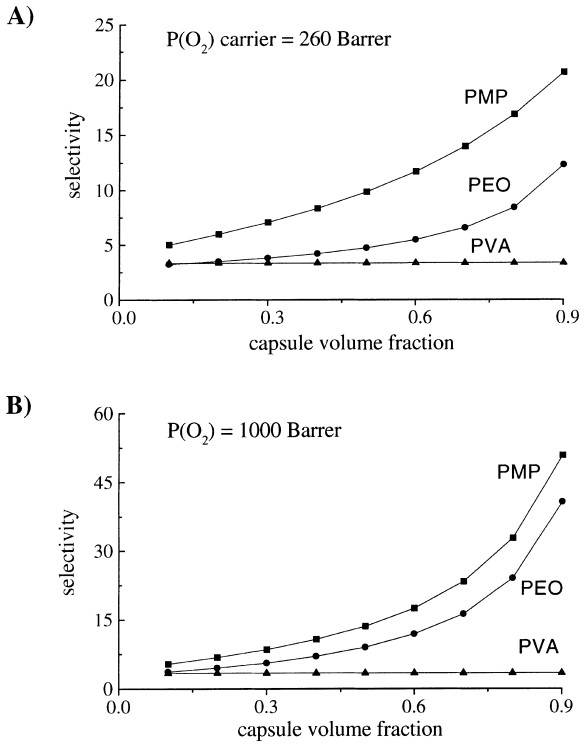

Fig. 8. Predicted micro-encapsulated membrane performance, for different carrier oxygen permeability, using Maxwell equation.

$P(O_2) = 600$ Barrer, $P(N_2) = 200$ Barrer) oxygen permeability. All three polymers posses comparable selectivities of $\alpha = 3$–4. A dramatic increase in the selectivity at higher capsule volume fractions is observed for both PMP and PEO as matrix material. The selectivity for membrane matrices of PVA, which is a barrier material for oxygen, stays unaffectedly constant at value below 4. Maximal values of the selectivity for PMP as matrix are as high as 20 and 50 for the two different carrier phase permeabilities, respectively. The selectivity in the capsule/PEO matrix composite system increases once the permeability inside the capsules is higher than in the polymer matrix. Once the specific carrier characteristics are determined, the model of Maxwell can be used to calculate the optimal conditions.

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