Brazilian Journal
of Chemical
Engineering

ISSN 0104-6632
Printed in Brazil
www.abeq.org.br/bjche

Vol. 24, No. 01, pp. 101 - 118, January - March, 2007

RECENT ACHIEVEMENTS IN FACILITATED TRANSPORT MEMBRANES FOR SEPARATION PROCESSES

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(Received: August 23, 2005 ; Accepted: October 10, 2006)

Abstract - Membrane separation processes have been extensively used for some important industrial separations, substituting traditional methods. However, some applications require the development of new membranes. In this work, we discuss recent progress achieved in this field, focusing on gas and liquid separation using facilitated transport membranes. The advantages of using a carrier species either in a liquid membrane or fixed in a polymer matrix to enhance both the flux and the selectivity of the transport are summarized. The most probable transport mechanisms in these membranes are presented and the improvements needed to spread this technology are also discussed. As examples, we discuss our very successful experiences in air fractioning, olefin/paraffin separation and sugar recovery using liquid and fixed carrier membranes.
Keywords: Facilitated transport; Liquid membrane; Fixed carrier membrane; Air fractioning; Propylene separation; Sugar separation.

INTRODUCTION

Membrane separation processes have been used for many applications in the chemical industry, given the compactness, simple and efficient operation and low energy consumption of membranes (Hagg, 1998). However, in some cases membrane use is limited by the opposite relation between permeability and selectivity, in such a way that membranes with high permeability also have low selectivity, and vice-versa, which is referred to as an "upper bound" relationship (Robeson, 1991). This can be explained by the fact that the tighter the polymer molecular spacing, the lower the diffusion coefficient through the material; hence, the lower the permeability. The separation efficiency, on the other hand, is increased.

The efficiency of these conventional membranes can be enhanced using facilitated transport. Facilitated transport membranes involve the use of a carrier, which interacts specifically and reversibly with one of the mixture components (reactive species). In these membranes, the reactive species is transported through other mechanism in addition to the ordinary sorption-diffusion, increasing its permeability. Since the carrier does not interfere with in the transport of the nonreactive species, selectivity also increases (Way and Noble, 1992).

Facilitated transport membranes have been used in many applications, for instance, in the removal of metallic ions such as copper, zinc, cobalt and nickel and of other elements such as gold, silver and lanthanides from metallurgic industry waste (Arous

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et al., 2004; de Gyves and de San Miguel, 1999) as well as in the recovery of many other components from industry effluents (Correia and de Carvalho, 2003). Biotechnological applications include separation of amino acids and proteins (Oxford, 2000), chiral separation using enzymes and surfactants as carrier (Jirage and Martin, 1999), separation of sugar mixtures (Duggan, 2004; Di Luccio et al., 2000), and other separations (Bartsch and Way, 1996). In the field of gas separation, facilitated transport membranes make possible the separation of several mixtures, otherwise considered very difficult, such as O_2/N_2 (Ferraz, 2003; Figoli et al., 2001), CO_2/CH_4 (Zhang et al., 2002) and paraffins/olefins (Kim et al., 2004; Duarte, 2004).

THEORETICAL BACKGROUND

Liquid Membranes

A liquid membrane (LM) can be defined as a thin liquid film separating two liquid or gaseous phases and controlling the mass transfer between these phases (Kemperman, 1995). The main advantage of this kind of membrane is the higher solubility and diffusivity coefficients of compounds in a liquid medium than in a solid one. Addition of a carrier agent increases even more the permeability of the membrane.

The permeation of a compound in a liquid membrane can be divided into the following steps: 1) sorption at the feed interface, 2) complexation reaction with the carrier, 3) diffusion of the species/carrier complex across the membrane, 4) decomplexation reaction at the permeate interface and 5) desorption of the species. After completing this cycle, the carrier diffuses back to the feed interface to complex more molecules.

Using a counter transport it is even possible to permeate one compound against its concentration gradient. This occurs when two ions with the same total charge are transported in opposite directions, because the complexation reaction that takes place in the membrane phase reduces the chemical potential of the permeating species (Neplenbroek, 1989).

Permeability of gaseous species in a liquid membrane is generally well described by the dual-sorption model, given by

$$P_i = kD_i + \frac{[C]_0 K_i D_c}{1 + K_i p_i} \quad (1)$$

where k and D_i are respectively the solubility and the diffusivity of species i in the membrane material, p_i is its partial pressure, D_C is the carrier diffusivity, K_i is the equilibrium constant of the binding of species i to the carrier and $[C]_0$ is the initial carrier concentration in the liquid membrane.

At low partial pressure, the solubility of the species in the liquid phase is highly increased by the presence of the carrier, so the facilitated parcel of the transport prevails. At higher partial pressures, all binding sites of the carrier will be occupied by the species, achieving saturation conditions.

A similar equation can be derived for the initial flux of neutral molecules through a liquid membrane where the transport is limited by diffusion (Chrisstoffels et al., 1996):

$$J_0 = \frac{D_m}{d_m} \frac{K_{ex}[A][C]}{1 + K_{ex}[A]} \quad (2)$$

where J_0 is the initial flux of compound A, D_m is the apparent diffusion coefficient, d_m is the membrane thickness, K_{ex} is the extraction coefficient, [A] is the concentration of component A in the departing aqueous phase and [C] is the total carrier concentration in the membrane phase.

When the components are in an aqueous phase, liquid membrane separation combines the solvent extraction process and solute recovery in a single step. The simplest liquid membranes consist in an organic phase that contains the carrier situated between two aqueous phases (Bartsch and Way, 1996). One aqueous phase contains the compounds to be separated (feed phase), while the other aqueous phase will receive the compounds that permeate the membrane (receiving phase).

In Figure 1 the most common apparatus for a liquid membrane study is shown. However, these configurations are almost exclusively used for preliminary tests, for xample, in the evaluation of possible carriers for a given separation, since they provide low interfacial area and low reproducibility of results due to poor mixing of the three phases.

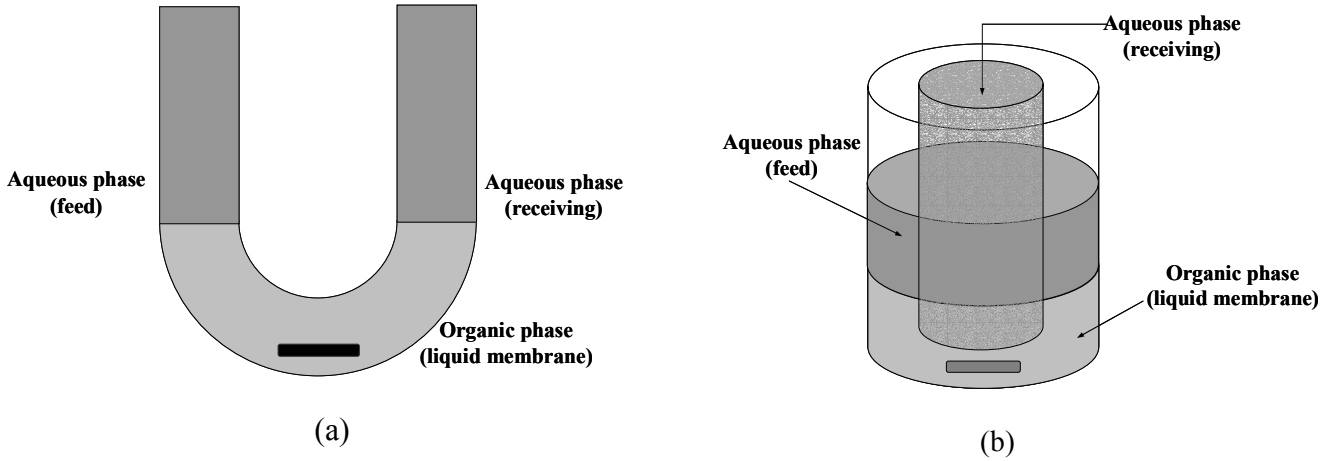


Figure 1: Simple configurations for liquid membranes.
(a) U tube (b) coaxial cylinders.

Emulsified liquid membranes (ELM) are being used to solve the problem of low interfacial area and reproducibility. In this system, a stable emulsion of the organic and receiving phase is prepared. A second emulsion is then prepared with the first emulsion and the feed phase. This configuration has the advantage of high interfacial area between the phases with the drawback of a typical batch process and the need to use other compounds to stabilize and break the emulsions (Bartsch and Way, 1996).

The supported liquid membrane (SLM) is the most attractive for industrial separations involving gaseous or liquid solutes. Figure 2 shows a supported liquid membrane (SLM), which consists of a microporous support containing a liquid phase impregnated with the carrier. Liquid is held inside the support pores by capillary forces, as described by the Laplace-Young equation, so caution must be taken so as not to exceed the maximum operation pressure.

Supported liquid membranes may be prepared using microporous membranes of various geometries. The hollow fiber geometry is particularly advantageous because it allows much higher module packing densities than the flat sheet plate and frame modules or the tubular membrane modules. Another advantage is that hollow fiber modules require low investment and operating costs due to the reduced equipment requirements (Majundar et al., 1988).

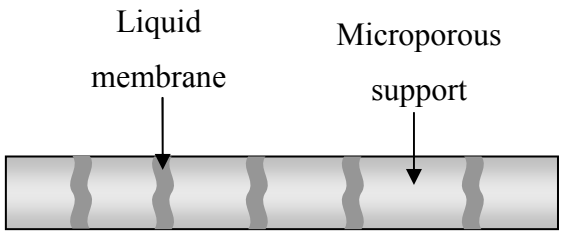


Figure 2: Supported liquid membrane.

Fixed Carrier Membranes

The development of fixed carrier membranes was proposed as an alternative to the utilization of liquid membranes. The fixed carrier membrane can be an ion-exchange membrane in which the carrier is anchored to a counter-ion found in the polymer backbone, and it can also be a solid polymer electrolyte. In this latter case, the membrane is a solid solution of polymer and salt, in which the salt cations interact with the electrons on a heteroatom or functional group in the polymer backbone.

The most accepted mechanism to explain permeant transport across a fixed carrier membrane is based on the transfer of permeant from chain to chain by hopping from site to site due to the

extensive thermal motions of the polymer matrix, as shown in Figure 3 (Duarte et al., 2002). In Figure 3(a), the permeant A molecule is bound to a site on the polymer backbone. The chains are rearranged due to thermal fluctuations and two reactive sites come close enough to exchange permeant between them, as shown in Figure 3(b). In Figure 3(c), a new configurational rearrangement joins together two other sites and the permeant jumps again. The nonoccupied first site can now react with a new permeant molecule.

The polymer should have low barriers to bond rotation to provide sufficient segmental motion of the chains. This requirement is achieved using a rubbery polymer or by a swelling agent. Besides this, the solute A can only be transported by the carrier if two sites are close enough. This result requires a carrier concentration limit, below which no facilitated transport can take place (Cussler et al., 1989; Noble, 1990; 1991; 1992; Pinnau and Toy, 2001).

Until now, only a few authors have proposed models to describe the transport through fixed carrier membranes. The dual sorption model is the most frequently used one, due to its simplicity. However, the dual sorption model does not provide a detailed description of the phenomena involved in the transport, as it takes into account neither the polymer matrix features nor the activated permeant diffusion between two sites.

In the next sections we will report on our experience and the main developments in three fields of separation: oxygen/nitrogen, paraffin/olefin and glucose/fructose.

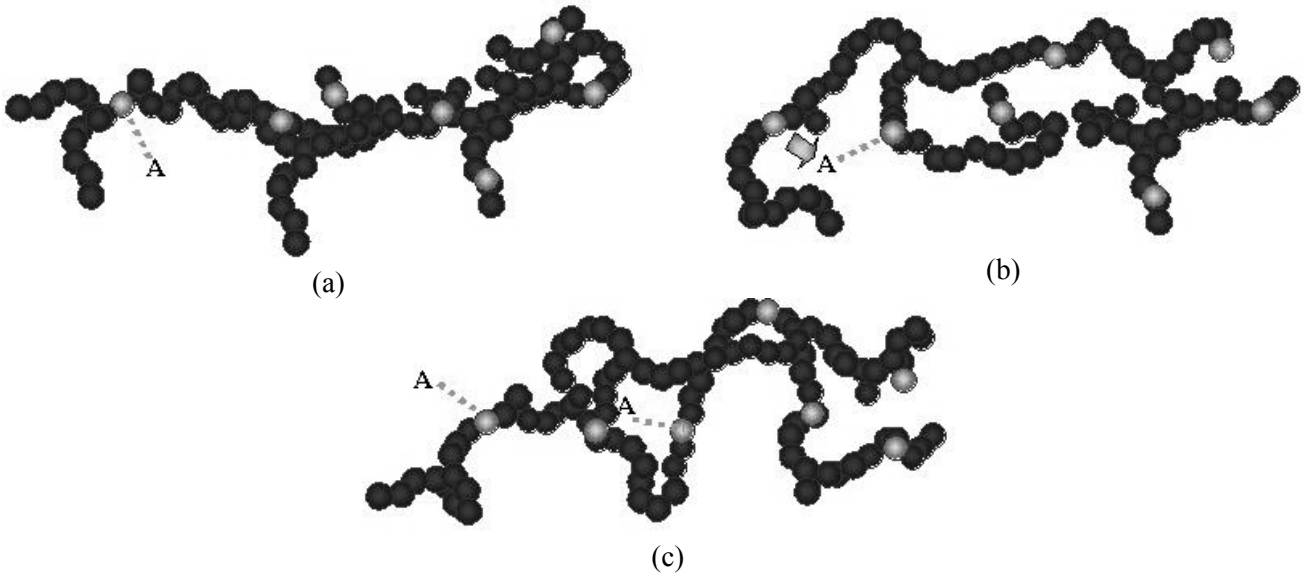


Figure 3: Facilitated transport mechanism of permeant A through fixed carrier membranes.

CASES STUDIES

1) Oxygen/Nitrogen Separation

Oxygen has traditionally been produced by cryogenic distillation of air, a technology that involves the cooling of air at very low temperatures, such as about – 200 ^{o}C. Recently, pressure swing adsorption technology (PSA) has also been used to produce high purity oxygen. However, both are highly energy-intensive processes in which energy costs correspond to more than 60% of total production costs (Baker et al., 1987; Castle, 2002). Therefore, there is a needfield for developing less expensive methods for oxygen-enriched air production.

Alternative methods for air fractionation have been studied and can be found in more than 400 patents, just to mention the USA patent database, 60% of which are related to noncryogenic methods (Castle, 2002). Of these, separation processes using membranes have been shown to be ideal substitutes for classical processes, mainly because of their mild operation conditions, resulting in very low energy consumption.

Economic analysis estimating producing costs of the oxygen by the three processes mentioned (cryogenic, PSA and membrane) shows that using a membrane with a permeability of 300 Barrer (1 Barrer = 10^{-10} cm^3. cm/cm^2. s. cmHg) and a selectivity of 20, it is possible to obtain 85%-pure oxygen competitivly (Matson and Lonsdale, 1987; Figoli et al., 2001).

Polymeric membranes have been studied for the last 40 years, but it is still not possible to obtain either highly oxygen-enriched air or high product flux using currently existing membrane, because materials with high permeability and selectivity are required.

Since oxygen and nitrogen have about the same molecular diameter, their diffusion coefficients are very similar. Thus, differences in membrane permeability, and hence a good selectivity, can only be achieved if the solubility of each gas in the membrane material is different (Baker et al., 1987).

Some strategies have been investigated in order to produce membranes that are more permeable and selective to oxygen. One of them is the introduction of functional groups that modify the polymer matrix, modifying its transport properties (Hayakawa et al., 1992; Aoki et al., 1996).

Another approach is the use of carbon molecular sieve (CMS) membranes, produced by pyrolysis of polymeric precursors (Ghosal and Koros, 2000). Although selectivities higher than 12 can be obtained, final permeability is often lower than that of the precursor.

Facilitated transport membranes are the most promising alternative. Tsumaki (1938) was the first to observe the ability of Schiff-base/cobalt complexes to reversibly bind molecular oxygen. Since then, many other compounds have been studied and employed as oxygen carriers. The pioneering work demonstrating facilitated transport in liquid membranes is attributed to Scholander (1960), who used a cellulose acetate microporous support impregnated with aqueous hemoglobin solution. He observed an oxygen flux about eight times higher than without hemoglobin. Later on, studying the same kind of membrane, Wittenberg (1966) proposed a mechanism for the facilitated diffusion of oxygen. A few years later, in 1970, Bassett and Schultz performed a similar experiment, but using a synthetic carrier, cobalt-histidine, instead of a natural one (Johnson et al., 1987).

Since then, a number of studies on the selective permeation of oxygen and nitrogen in facilitated transport membranes have been conducted. Several kinds of carriers can be found; most of them are cobalt Shiff-base or porphyrin complexes. Those are complexes where the cobalt ion is bonded to four electron-donating atoms, arranged in a planar assembly, having the metal at the center. An axial base, usually provided by a Lewis base, occupies the fifth coordinating atom. The sixth position is reserved for the oxygen binding.

Although liquid membranes (SLM) have very frequently been studied for oxygen separation, a comparatively higher number of works dealing with fixed carrier membranes (FCM) can be found in the literature. The main reason for this is the superior stability of the immobilized carrier. Despite that, liquid membranes are good alternatives due to their good transport properties. Figure 4 shows a comparison between SLM and FCM.

As can be seen, the performance of SLM in terms of permeability and selectivity is better than that obtained for CFM. The higher permeability exhibited by liquid membranes can be attributed to the fact that diffusion coefficients in liquids are about two orders of magnitude higher than those observed in solids.

Although facilitated transport membranes have demonstrated their potential for oxygen-enriched air production, much improvement is still needed. The main challenges in this field are as follows.

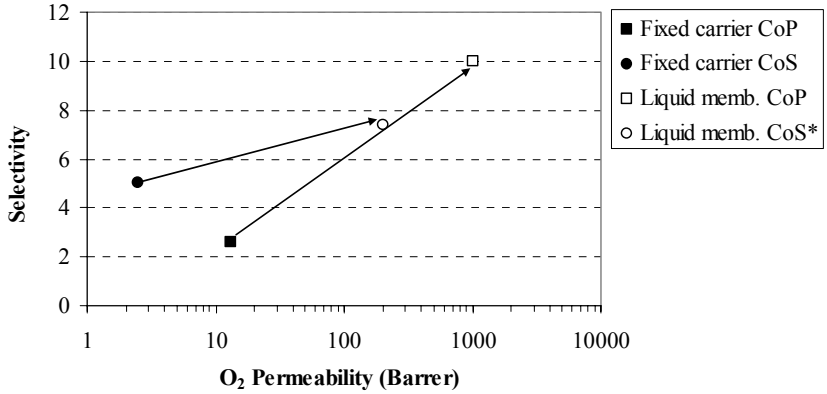


Figure 4: Comparison between Liquid membranes and Fixed carrier membranes containing cobalt salts. Experimental data: Liquid membranes = CoS* (Johnson et al., 1987), CoP (Chen et al., 1997), Fixed carrier membranes = CoS (Chen et al., 2000), CoP (Suzuki et al., 1996).

Membrane Stability

The lack of mechanical stability is especially critical for liquid membranes. As the solution is maintained in the support pores by capillary forces, when the pressure exceeds a given critical value, the liquid phase is pushed out of the pores. Evaporation of the solvent also affects both flux and selectivity of the membrane. As the solvent evaporates, solution viscosity increases, reducing the diffusivity through the membrane. If evaporation occurs, complete loss of solvent will cause the gas to leak to the product side of the membrane by convective flow.

To enhance membrane stability, several procedures have been adopted. Air saturation with solvent vapor, for instance, decreases evaporation rates, extending the membrane lifetime (Jonhson et al. 1987). In the same work, Johnson et al. (1987) sandwiched the liquid membrane between two layers of a microporous Teflon membrane. This procedure ensured the creation of a stagnant layer of solvent vapor adjacent to the liquid membrane, minimizing its evaporation.

Another method to increase the stability of liquid membranes is gelation. It consists in creating either a gel network inside the support pores or a thin dense layer on the feed side of the membrane (Neplenbroek, 1989).

The presence of common compounds like CO_2 and water in the air has a deleterious effect on the stability of oxygen-enriching membranes. Even in usual concentration of 300 ppm, CO_2 can irreversibly poison the carrier molecule (Johnson et al., 1987). It is known that protic solvents such as water increase the carrier oxidation rate in a way not totally understood. Oxidation of the metal center responsible for oxygen binding has been reported in several works (Kawakami et al., 1982; Chen et al., 1997; Nishide et al., 1988) and it is doubtless the main cause of membrane instability.

In our work (Ferraz, 2003) we used myoglobin, a naturally occurring protein, as oxygen carrier in facilitated transport membranes. We demonstrated that the preparation of cobalt-substituted proteins (Co-Myoglobins) and recombinant proteins can markedly increase myoglobin stability. Together the two strategies should result in a myoglobin twenty times more stable than a native one.

Some relevant results found in our work using facilitated transport membranes for oxygen separation from air will be discussed in the following section.

Facilitated Transport Membranes Containing Myoglobin

Liquid membranes were prepared using a nylon microporous membrane support, impregnated by immersion in a myoglobin aqueous solution. Liquid phase is kept in the pores by capillary forces. The chart in Figure 5 shows the effect of the protein concentration on membrane permeability.

One can observe that permeability reaches a maximum at a myoglobin concentration of 50 g/L. This behavior is explained by the dual-mode transport mechanism, which attributes the total oxygen flux through the membrane to two terms. One contribution is due to the ordinary diffusion of oxygen through the liquid membrane, well described as a Henry-type sorption. The other refers to the highly specific oxygen transport by the carrier and can be described as a Langmuir–type adsorption (Way and Noble, 1992). Thus, at very low myoglobin concentrations, the second term becomes less significant. On the other hand, higher concentrations increase solution viscosity, lowering O_2/carrier diffusivity.

The behavior of membrane permeability as a function of transmembrane pressure is also explained by the dual-mode model and is illustrated in Figure 6 for a liquid membrane containing a 60 g/L myoglobin solution. For high pressures, all carrier molecules are saturated with oxygen and facilitated transport is less significant than diffusive transport. Conversely, at low pressures, almost all transport will be performed by the carrier. Nitrogen permeability, however, is not affected by the carrier at all, remaining constant at about 100 Barrer.

Myoglobin was also immobilized in a poly(vinylalcohol) membrane. Immobilization did not jeopardize protein functionality, as seen by the appearance of the membrane, which preserved the protein color. The transport properties of the fixed carrier membrane can be verified in Figure 7. An increase in permeability with a decrease in pressure, which characterizes the facilitated transport, was observed.

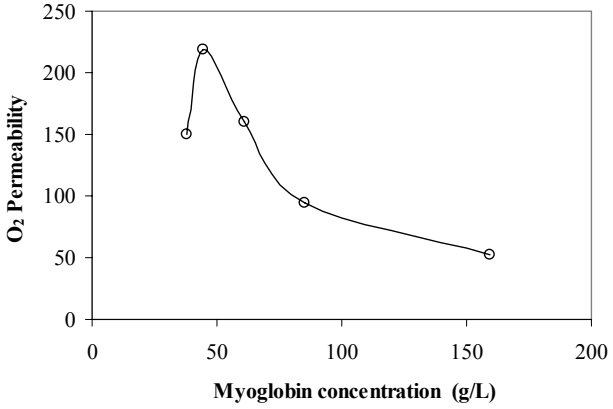


Figure 5: Effect of carrier concentration on membrane permeability.

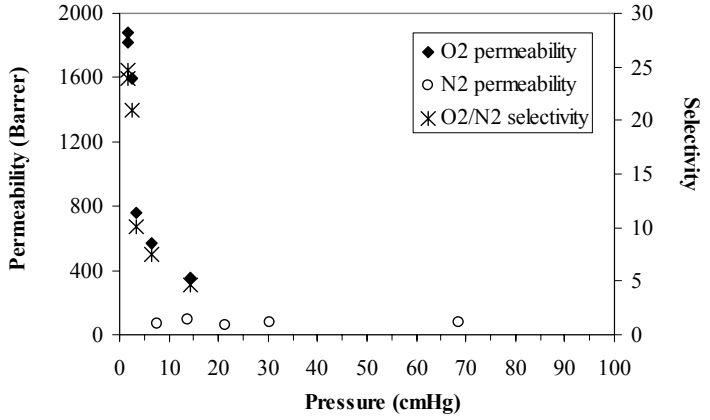


Figure 6: Permeability of a liquid membrane containing myoglobin as a function of the difference in pressure through the membrane.

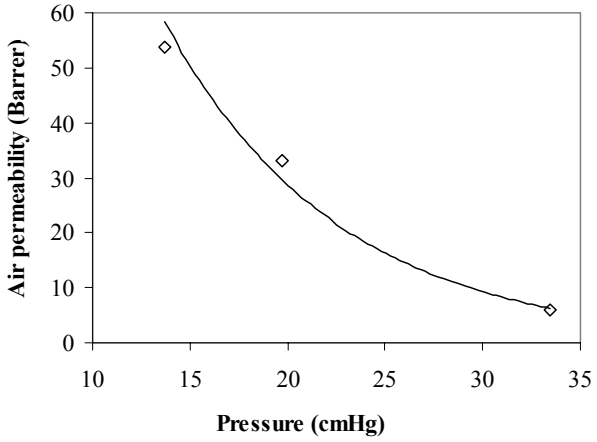


Figure 7: Permeability to oxygen of a PVA membrane containing myoglobin.

2) Propane/Propylene Separation

The separation of olefins from paraffins is a challenge for membrane processes. In this section of the review, propylene/propane separation will be focused on due to its importance. According to Baker (2002), propane/propylene separation will become one of the major areas for application of membranes, if the appropriate membrane material is developed.

Propylene is largely used in the petrochemical industry as feedstock for the synthesis of polymers and chemicals. The propylene generation sources produce propane as well, and it is necessary to separate the propylene/propane in order to get pure propylene. This separation is currently carried out by energy-intensive cryogenic distillations. As propylene and propane have about the same boiling point, large towers and high reflux ratios are required to achieve good separation, which requires a large capital investment and entails high operation costs. For example, olefin purification, including propane/propylene separation, is the largest consumer of energy for distillation in the chemical industry, and about 1.2×10^{14} BTU of energy is used yearly to perform this separation (Eldridge, 1993). Therefore, more economical processes to separate propane and propylene have been investigated.

Polymer membranes can hardly distinguish between propane and propylene because these compounds have similar physical properties and about the same molecular size. Thus, the difference in solubility and in diffusivity shown by propane and propylene through the polymer matrix (sorption-diffusion mechanism) is not significant and separation is not generally efficient. The effectiveness of the polymer membranes can be increased by adding fixed carriers, which interact specifically and reversibly with the propylene molecules, to the polymer matrix.

Transition metal cations are the most commonly used carriers for propylene facilitated transport given their ability to form reversible complexes with molecules that have double bounds. The interaction that can occur between transition metal cations and the olefin double bonds has been known since the XIX century. Basically, all elements from groups VIB, VIIB, VIIIB and IB, in different oxidation states, are able to form complexes with the olefins (Winstein and Lucas, 1938; Bennett, 1962). In spite of the fact that all transition metals are able to act as complexing agents, Ag^+ is the most frequently used because the Ag^+-propylene complexes have a lower stability than the other olefin-metal transition complexes. The low stability allows the propylene to be released more easily on the permeate side.

Dewar, in 1951, and Muhs and Weiss, in 1962, tried to explain the nature of the bond in Ag^+-olefin complexes. These authors proposed that the complexation reaction involves a σ-bond formed by the overlap between the filled π-orbital of the olefin and the empty 5s-orbital of the Ag^+ and between a π-bond provided by the back-donation of electrons from filled d-orbitals of the silver and the empty antibonding π*-orbitals of the olefin. This mechanism is represented schematically in Figure 8 (adapted from Cotton et al., 1995). The arrows indicate the direction of electron transfer. The same mechanism is used to explain the complexation between the other transition metals and olefins, and it is cited by different authors (Coates et al., 1968; Huheey, 1993; Cotton et al., 1995; Cotton and Wilkinson, 1997).

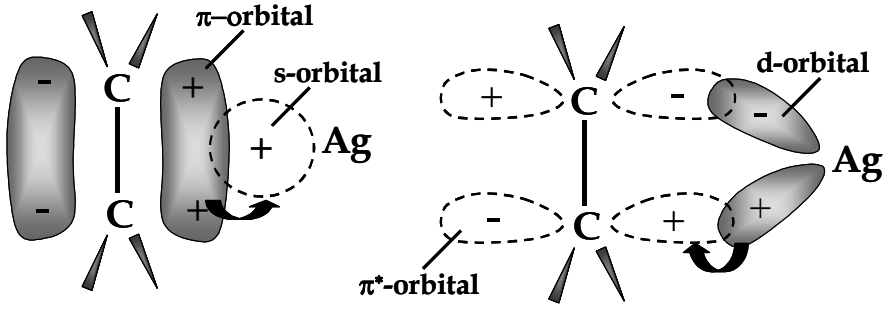


Figure 8: Schematic representation of Ag^+-propylene complexation.

Earlier work investigating membranes for olefin/paraffin separation was based on liquid membranes. Although these membranes show high performance for the separation, the carrier can be washed out of the membrane, which limits membrane lifetime. This situation changed in the 1980's, due to LeBlanc's work, which introduced the utilization of carrier fixed membranes for olefin/paraffin separation (LeBlanc, 1980).

In carrier fixed membranes for olefin/paraffin separation, the Ag^+ cation is held on the polymer backbone. The presence of electron donor groups such as oxygen, nitrogen, carbonyl and nitrile in the polymer backbone makes possible the coordination between these groups and the Ag^+ cation. Besides the Ag^+-polymer interaction, the Ag^+ cation can interact with the salt anion or with the olefin molecules. The forces related to these interactions are important and significantly change the olefin facilitated transport through the membrane. Thus, the separation performance will depend on the material that constitutes the membrane, on the silver salt used, and on the presence of a swelling agent (Yoon et al., 2000).

The performance of polymer membranes and polymer membranes containing fixed-site carriers (Ag^+) for propane/propylene separation can be compared in Figure 9, which shows propylene/propane selectivity as a function of propylene permeability (given in Barrer). In this figure, the membranes contain Ag^+ are divided into two groups: hydrophobic polymer-based membranes and hydrophilic polymer-based membranes. The hydrophilic polymer membranes containing fixed carrier were produced as dense films, which were deposited on a porous support, and permeability values were normalized for a superficial dense layer thickness equal to 1 mm. Analysis of the results reveals that in the polymer membranes without carriers there is an inverse relationship between permeability and selectivity. One way of circumventing the trade-off between permeability and selectivity is by using facilitated transport membranes.

Some results on the study of polyurethane (PU) membranes containing silver salts for propane/propylene separation will be presented next (Duarte, 2004). In this investigation, a methodology was developed to analyze the effect of adding transition metal salts to the PU matrix. Interactions between the ions and the polymer backbone and cation avaliability for the facilitated transport of propylene were evaluated.

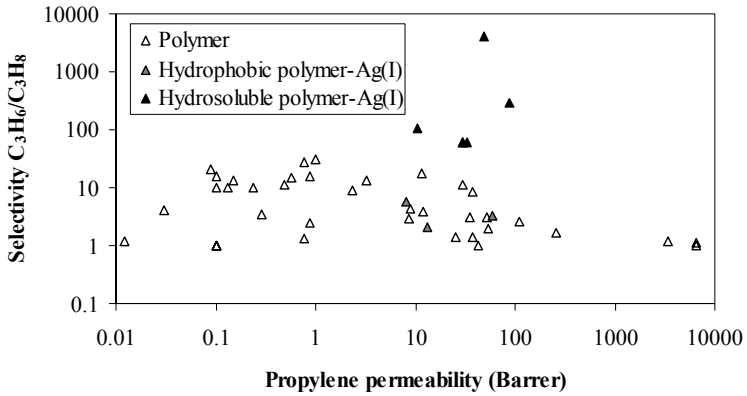


Figure 9: Propylene/propane selectivity as a function of propylene permeability for polymer membranes and for facilitated transport membranes.

Production and Characterization of PU Membranes Containing Silver Salts

The membranes were produced as dense films, to which different silver salts were added. The main advantage of fixed carrier membranes over liquid membranes is their increased mechanical stability, since there is no loss of carrier during operation. However, improvement in the chemical stability of the carrier still needs to be proven. A thermoplastic PU, which contains polyester as the flexible segment, was used as polymer matrix. The films were characterized structurally and the intensity of the interaction between the cations and the electron donor group in the polymer chains was evaluated by measurement of ionic conductivity under argon and propylene. Propylene and propane permeability was also measured at different pressures.

The results showed that the membrane structure changes according to the kind of salt used and this depends not only on the cation, but also on the anion type. The conductivity results also evidenced that the different salts interact in different ways with the PU chains. The conductivity values obtained at 25°C for the films produced with one of the silver salts are presented in Figure 10. As can be seen, the values for conductivity in propylene are higher than the ones obtained in argon. And in experiments carried out in propylene, conductivity increases with silver concentration. These observations confirmed the formation of an Ag^+-propylene complex.

Figure 11 shows the propane and propylene permeability values as a function of the concentration of the same silver salt as that in PU films, as previously discussed. The experiments were carried out at 1 bar and 25°C.

The permeability results show that the addition of the silver salt to the PU matrix produces two opposite effects in the propylene transport through the membranes. The negative effect is due to the decrease in chain mobility produced by the coordination between the PU chains and the ions that act as transient crosslinks. The lower chain mobility makes the movement of the propane and propylene molecules through the chains more difficult and their permeability values decrease. Besides, at high concentrations, crystalline regions are formed (as detected by X-ray), which also contributes to the decrease in permeability values, given that the crystalline phases are impermeable. On the other hand, the propylene molecules are able to form complexes with the Ag^+ cations, which facilitates the transport. This effect does not allow the propylene permeability to decrease significantly, as observed for the propane.

As a result of these effects, there is an increase in selectivity to propylene, as can be seen in Figure 12, which shows propylene/propane selectivity as a function of silver salt concentration in the PU films. These results evidence the occurrence of facilitated transport of the propylene molecules.

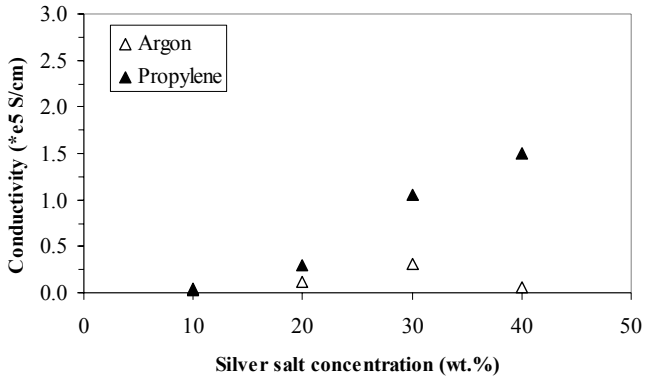


Figure 10: Conductivity under propylene and argon as a function of silver salt concentration (T = 25°C).

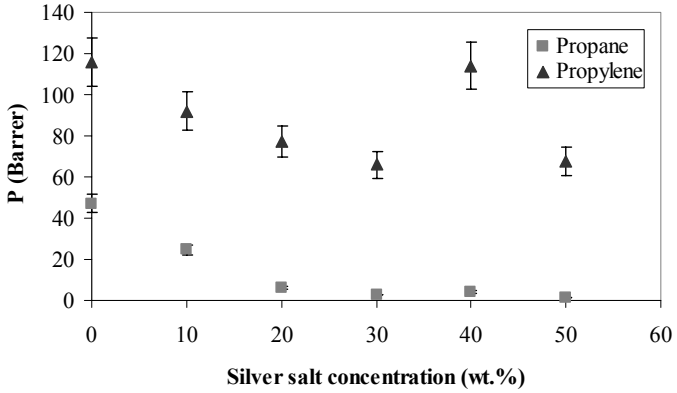


Figure 11: Propane and propylene permeability as a function of silver salt concentration (T = 25°C, Δp = 1 bar).

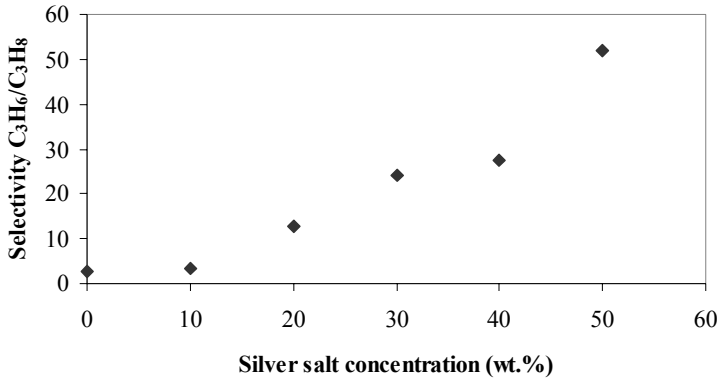


Figure 12: Propylene/propane selectivity as a function of silver salt concentration (T = 25°C, Δp = 1 bar).

3) Glucose/Fructose Separation

Sugar separation is often a relatively difficult and costly task. Chromatography is the method most frequently used for commercial sugar separation. This kind of process is currently applied to enrich the fructose content in high fructose corn syrup (HFCS), to separate maltotriose and other compounds from starch hydrolysate and to separate sucrose and other compounds from molasses (Kishihara et al., 1992). Such separations are batch processes and normally imply expensive installations, low productivity and low yields of the desired product. In order to accomplish continuous operation, high yield and productivity in chromatographic processes, a complex valve system (Lee and Lee, 1992) or a special column arrangement on a rotating disk that contains the connections (Kishihara, 1992) should be used. Although many improvements have been implemented in the past several years, the investment costs are still very high (Azevedo and Rodrigues, 2000).

In the past few years, many alternative processes, such as adsorption using zeolites (Odawara, 1977, 1979; Neuzil, 1983; Cheng, 1992) and reverse osmosis (Kim, 1985), have been proposed to achieve sugar separation. Nevertheless, processes based on the chemical affinity of sugars or their ability to form complexes with some compounds seem to be the most promising for separation of many kinds of saccharides. These separation processes include electrodialysis (Langevin, 1996), ion exchange membranes (Shigemasa, 1990) and liquid membranes (Shinbo, 1986; Mohler and Czarnik, 1993; Kida, 1996; Smith, 1996; Paugam, 1996; Riggs and Smith, 1997; Karpa, 1997; Smith, 1999; Di Luccio, 2000).

A large number of studies have been investigating the interaction of saccharides with different compounds and their use in artificial membranes. Saccharides are molecules with a complex combination of polar and nonpolar regions, and their partition between organic and aqueous phases may be well correlated with their hydrophobic and hydrophilic areas. The transport of sugars in nature is usually controlled by noncovalent interactions, like hydrogen bonding. Thus, the aim of most saccharide recognition studies is then to develop artificial low molecular weight molecules that are able to bind to a specific sugar, distinguishing it from a mixture, and transport it as fast as possible through a membrane (Smith, 1999).

Zinc porphyrins are known to bind to a variety of diols, including many saccharides, such as glucosides and mannosides (Bonar-Law and Sanders, 1995; Mizutani et al., 1995). Resorcinarenes have also been reported to be able to extract some sugars (Tanaka et al., 1989). Their ability to extract sugars was explored for sugar transport in supported liquid membranes, with the advantage that they provide high stability to the SLM due to their highly lipophilic nature (Rhlalou et al., 2000; Tbeur et al., 2000). Some sugars show an affinity for alkaline earth metals and this ability has also been used to develop liquid membranes. Lipophilic alkaline earth metal complexes are obtained by mixing the metal hydroxide with phosphoric acid diesters. Barium salts seem to provide the highest fluxes and selectivity for pentoses over hexoses (Kasuga et al., 1998).

Interaction of sugars with anions in solutions has also been investigated, especially with borates (Langevin et al., 1996; Coteron et al., 1996). Boronic acids can form covalent complexes with diols and their derivatives, like saccharides (Babcock and Pizer, 1980). This ability to complex with sugars can vary greatly according to the chemical nature of the diol involved in the process. In anhydrous aprotic solvents boronic acids can condense with diol and their derivatives to form trigonal boronate esters. When water is present, the trigonal boronate ester is unstable and may hydrolyze or ionize to yield an anionic tetrahedral boronate. This process is reversible, which makes this kind of reaction very attractive for sugar separation applications (Smith, 1996).

The study of Shinbo and co-workers was the first to investigate the uphill transport of monosaccharides using liquid membranes and phenylboronic acid as carrier in the presence of a quaternary ammonium salt (trimethyloctylammonium chloride). They showed that the transport rate is higher for fructose than for galactose and glucose and proposed a mechanism based on the formation of a tetrahedral boronate ester. This property makes these compounds perfectly suitable for fructose extraction by facilitated transport, using the concept of liquid membranes, as presented in Figure 13.

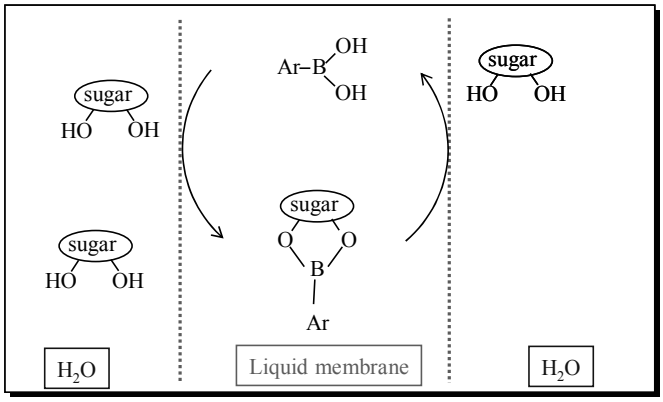


Figure 13: Most likely mechanism for sugar transport through liquid membranes using boronic acids as carriers (Riggs and Smith, 1997).

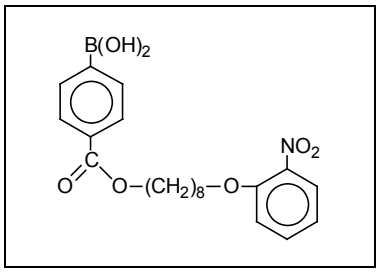
The major drawback of phenylboronic acid is its high solubility in water, which causes the carrier to leach out to the aqueous phase and the membrane to degradate, as well as changes in the complexation mechanism, making some separations unfeasible (Smith, 1996). The work of Shinbo was extended later by Karpa and co-workers (1997), confirming the complexation mechanisms proposed previously. They also show that changes in the lipophilicity of the boronic acid are required to increase sugar fluxes.

Many of the subsequent investigations involving boronic acids deal with modifications of the phenylboronic acid to improve its lipophilicity and thus membrane stability and also to manipulate its transport properties. Takeuchi and co-workers (1996) proposed to couple a quaternary ammonium salt to phenylboronic acid, elucidating some mechanisms in the extraction of fructose.

TheSmith group has made concentrated efforts to building new molecules derived from phenylboronic acid that show good sugar transport properties when used in SLM as well as elucidated transport and complexation mechanisms. Boronic acid **1** (Figure 14) was synthesized and showed selectivity for fructose up to 19 times higher than that for glucose, thus being suitable for fructose enrichment in a mixture of sugars (Paugam, 1996; Smith, 1999; Di Luccio, 2000). Riggs and Smith (1997) showed that a plasticized cellulose triacetate membrane containing trioctylmethylamonnium chloride may have a fructose flux ten times higher than a SLM with **1** as carrier, but with a great loss in selectivity. Diboronic acids have also been proposed for hexose separation using SLM, although with little improvement in flux (Gardiner et al., 1999). Molecular modeling has also been used as a tool for explaining differences in selectivity and fluxes for different combinations of carriers and saccharides (Draffin, 2003).

Sugar Separation Using Supported Liquid Membranes (SLM)

Tests were performed with flat-sheet (FS) and hollow-fiber-supported liquid (HFSLM) membranes using a phenylboronic acid derivative (Smith, 1996) as carrier, as depicted in Figure 14.



1

Figure 14: Structure of the carrier 4-[8-(2-nitrophenoxy) octyloxycarbonyl] benzeneboronic acid.

Microporous polypropylene membrane supports were impregnated with a solution of the carrier in 2-nitrophenyloctylether (NPOE). Results of transport experiments using FSSLM are presented in Table 1. One can verify that the membrane with 50 mM of boronic acid **1** did not show selectivity for fructose. However, when carrier concentration is increased, fructose flux also increases to the detriment of glucose flux, enhancing selectivity.

The increase in flux with carrier concentration is also reported by other authors. Reusch and Cussler (1972) showed that flux is expected to increase with carrier concentration as long as the transport is diffusion-limited. This behavior was also observed for the HF geometry (Figure 15).

Flux also increased with feed concentration in both geometries (Table 1 and Figure 16), which reinforces the idea that transport is governed by diffusion rather than by reaction kinetics. Thus, flux is dependent on the chemical potential gradient of the solute between the two aqueous phases and increases when gradient.

Table 1: Results from FSSLM transport experiments using boronic acid

Membrane	Feed conc.(mM)[1]	Glucose Flux[2]	Fructose Flux[2]	Sel. Fru/Glu[3]
1 (50 mM BA)	**100**	15.0 (17.6)[4]	9.46 (8.57)	0.63 (0.48)
2 (50 mM BA)	**300**	19.6 (46.5)	15.6 (37.5)	0.79 (0.81)
3 (250 mM BA)	**100**	3.7 (2.1)	51.4 (20.4)	14.0 (9.81)
4 (250 mM BA)	**300**	6.6 (3.5)	55.3 (10.7)	8.3 (3.0)

1) Feed solutions: equimolar concentration of glucose and fructose in phosphate buffer 0.1M, pH 7.4; strip solutions: same buffer without the sugars
2) 10^{-8} mol/m^2.s
3) flux fructose/flux glucose
4) Values in parentheses represent the flux after washing the membrane for 20 h.

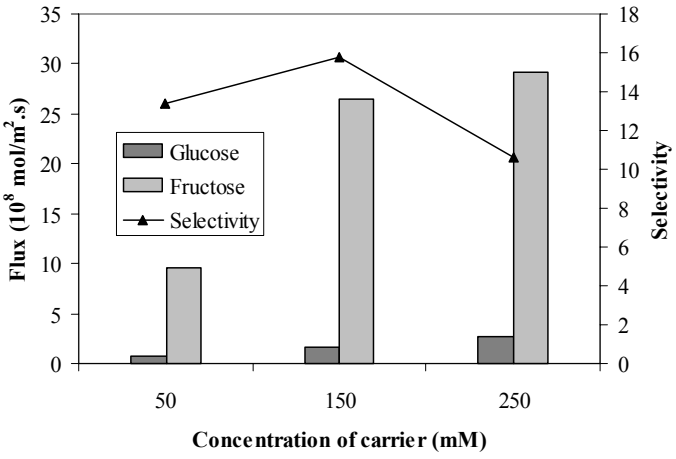


Figure 15: Effect of carrier concentration on fluxes and selectivity. HFSLM using 0.3M of each sugar in feed phase.

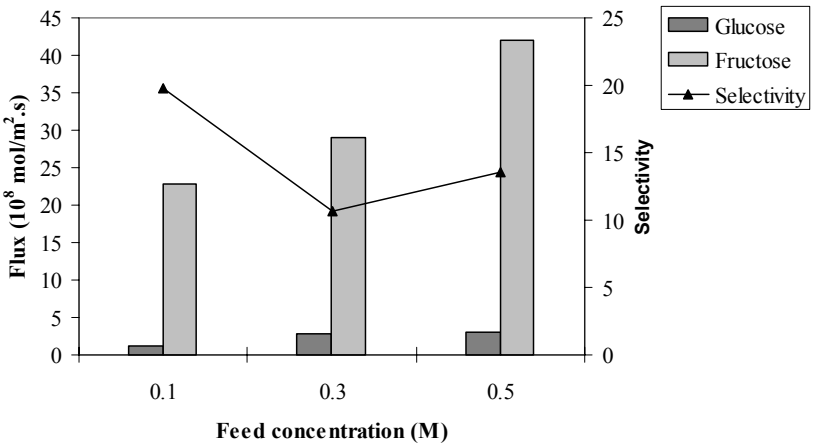


Figure 16: Effect of feed concentration on fluxes and selectivity. HFSLM with 250 mM of boronic acid **1** and feed phase consisting of an equimolar solution of both sugars.

In the experiments using HFSLM, even at low boronic acid concentrations the transport using this geometry was fructose selective. We attribute this result to increased membrane stability. In the hollow fiber system the disturbance caused at the membrane surface by the flow is lower than in the flat sheet cell, preserving membrane stability during the experiment. Previous researches have shown that the shear stress at the membrane surface disturbs the stability of the aqueous/organic interface, inducing emulsion formation and gradually removing the organic solution from the support pores (Kemperman, 1995).

CONCLUSIONS

Membrane processes are an alternative to the traditional energy-intensive processes for some difficult separations. Existing membranes have low selectivity for use in economically feasible process. Thus, facilitated transport membranes have been used in many applications to increase permeability and selectivity simultaneously.

Liquid membranes have been investigated in many studies, given that solubility and diffusivity coefficients of compounds in a liquid medium are higher than those in a solid one. The disadvantage of this type of membrane is the lack of stability due to the loss of solvent and carrier.

On the other hand, a comparatively larger number of studies dealing with carrier fixed membranes can be found in the literature. The main reason for this is the greater stability of the immobilized carrier. Despite this feature, the matrix must have sufficient segmental motion of the chains, and there is a minimum carrier concentration, below which no facilitated transport occurs.

Facilitated transport membranes, described herein, can produce oxygen-enriched air in an efficient way with a permeability of 1,600 Barrer and an O_2/N_2 selectivity of 21. This performance is better than that of other carriers reported in the literature, under the same operational conditions.

For the propane/propylene separation, the permeability experiments showed that the presence of silver salt in the PU films decreases the propane and the propylene permeability. However, the propylene permeability is favored by the complex formation with the Ag^+ cations. Thus, the facilitated transport was evidenced and high propylene/propane selectivity values up to 50 were obtained.

Use of facilitated transport membranes is also a very promising technique for fructose separation from a mixture of sugars. Boronic acid derivatives seem to be the best carriers to accomplish this separation, with high selectivity for fructose. The flat sheet system produced fructose/glucose selectivities of up to 14, while in the hollow fiber system, a fructose/glucose selectivity of 20 was observed.

Although the potential facilitated of transport membranes has been they need much improvement. One of the problems be overcome is the lack of carrier stability.

ACKNOWLEDGEMENTS

The authors would like to acknowledge the financial support received from the Brazilian agencies CNPq, CAPES and FAPERJ.

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