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Developments and Applications of Membranes in Chemical and Bioprocess Engineering

Richard England

Department of Chemical Engineering, University of Bath, Bath BA2 7AY, United Kingdom

Abstract: Membranes are increasingly being used in the chemical and bioprocess industries replacing more conventional separation techniques and as a means of producing high purity intermediates for further processing. Application of membranes in the water industry and waste treatment is also becoming increasingly important as water shortage and environmental problems need to be addressed. An outline of the materials used for the production of membranes and their applications are described. Some of the research into the development of more selective membranes for vapour separations and pervaporation is discussed. An example of the latest work on the development of ceramic hollow fibre membranes is also given.

Key words: Membranes, polymers, ceramics, selective extraction, pervaporation, diffusion dialysis

INTRODUCTION

As a method of separation, membrane processes are relatively new. Membrane filtration was not considered technically important as a process until about 35 years ago. From an economic point of view the present time is intermediate between the development of 1st generation processes e.g.,

- Microfiltration (MF),
- Ultrafiltration (UF),
- Nonofiltration (NF),
- Reverse Osmosis (RO),
- Electrodialysis (ED)
- Membrane Electrolysis (ME)
- Diffusion Dialysis (DD)
- Dialysis

and the second generation membrane processes

- Gas Separation (GS)
- Vapour Permeation (VP)
- Pervaporation (PV)
- Membrane Distillation (MD)
- Membrane Contactors (MC)
- Carrier Mediated Processes

where, a large number of studies are being carried out to improve the selectivity and efficiency of the processes. The range of applications is very wide and this study will concentrate on membranes and processes using pressure or concentration as the driving force. Membrane processes are characterized by the fact that the feed stream is divided into two streams, i.e., the retentate or concentrate stream and the permeate stream. This implies the product is either the retentate or the permeate. If the objective is concentration then usually the retentate is the

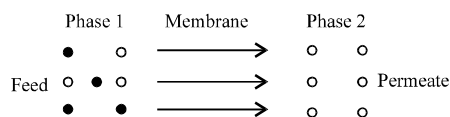


Fig. 1: Membrane separation process

product stream. However, in the case of purification, both the retentate or the permeate can yield the desired product depending upon the impurities to be removed.

The membrane is at the heart of every membrane separation process and can be considered as a permselective barrier or interface between two phases is shown in Fig. 1.

Phase 1 is usually considered as the feed or upstream side and phase two is considered the permeate or downstream side. Separation is achieved because the membrane has the ability to transport one component from the feed more readily than any other component. The performance or efficiency of a given membrane is determined by two parameters; the membrane's selectivity and the flow.

MATERIALS AND MATERIAL PROPERTIES

Membranes can be made from a wide range of materials, a classification can be made as biological and synthetic. Synthetic membranes can be further divided into a) organic (polymeric) and b) inorganic.

Polymers: Polymers are high molecular weight components built up from a number of basis units. The polymers used can be Homopolymers-where basis unit is the same e.g., polyethylene-basic unit is $-\text{CH}_2 = \text{CH}_2-$ Copolymers-where repeating units are different e.g., two

polymers A and B coupled together in various ways. The properties of random copolymers are strongly dependent on the molar ratios of A and B. Block copolymers are when the polymer chain is built up by linking blocks of each of the monomers. Graft copolymers are when the irregularities occur in the side chains rather than the main chain. These polymers are either linear or branched. It is possible to connect two or more chains by means of cross linking. The methods of production of membranes depends upon the application proposed for the membrane and this widely documented by Mulder (1997). Inorganic membranes are typically made from alumina, silica, glasses, stainless steel, titanium dioxide, zirconium dioxide etc. The membranes produced can be classified into porous and non-porous membranes. Porous membranes are subdivided into:

Microfiltration membranes possessing pores in the size range 10-0.1 μm ; Ultrafiltration membranes possessing pores in the size range 0.5 μm to 1 nm and Nanofiltration membranes with pore sizes <2 nm.

Nonporous membranes are usually classified according to their application i.e., gas and vapour separation membranes, pervaporation membranes and reverse osmosis membranes.

PRESSURE AS THE DRIVING FORCE

A number of membrane process use pressure as the driving force for separation. The main processes are discussed:

Membranes for microfiltration: Membranes are porous and typically symmetric. Thickness is approximately 10-200 μm with pore sizes ranging from 0.05 to 10 μm . The driving force for separation is pressure (<2 bar) and the separation principle is a sieving mechanism. The membrane can be prepared from wide range of materials including both organic and inorganic materials.

Techniques employed using organic polymers include:

- Sintering
- Stretching
- Trac-etching
- Phase inversion

Techniques employed using inorganic materials include:

- Sintering
- Sol/gel process
- Anodic oxidation

Industrial applications include cold sterilization of beverages and pharmaceuticals, cell harvesting,

clarification of fruit juice, wine and beer (Gan *et al.*, 2001), preparation of ultra pure water in semiconductor industry, metal recovery (colloidal oxides or hydroxides), waste-water treatment and separation of oil-water emulsions

Membranes for ultrafiltration: Ultrafiltration membranes usually have an asymmetric structure with a dense top layer. The membrane thickness is ≈ 150 μm although some ceramics are monolithic. Pore sizes of the membranes range from 0.05 μm to 1 nm.

Most UF membranes are prepared from polymeric material e.g.,

- Polysulphone/poly(ethersulphone)/sulphonated polysulphone
- Poly(vinylidene fluoride)
- Polyacrylonitrile (and related block co-polymers)
- Cellulosics (cellulose acetate)
- Polyimide/poly (ether amide)
- Aliphatic polyimides
- Polyetheretherketone

In addition inorganic materials e.g., alumina and zirconia are increasingly being used following the development of methods for producing ceramic membranes. The separation principle is a sieving mechanism using pressures between 1-10 bar as the driving force. Main applications of ultrafiltration are in the dairy industry (milk, whey and cheese making), food treatment (starch and proteins), pharmaceutical industry (antibiotics, enzymes, pyrogens), water treatment, textile industry and the metallurgical industries (oil-water emulsions, electropaint recovery). An example of the application of ultrafiltration membranes is in the development of the process for the simultaneous gelatinisation, liquefaction and saccharification (SGLS) of starches in a hollow fibre membrane reactor (Sarbatly and England, 2004; Sarbatly, 2005). They studied the production of glucose from tapioca starch solution ($w = 10\%$) in a hollow fibre reactor system using low trans-membrane pressure drops. The permeate stream was a glucose solution of purity $>99\%$ and concentration 25 g L^{-1} within 30 min from enzyme addition. At steady state operation the concentration of glucose was 64 g L^{-1} and a purity $>99.9\%$ as determined by HPLC. Increasing the trans-membrane pressure from 0.25 to 1 bar reduced the residence time to 5.8 h but also reduced the steady state concentration of glucose permeate to 28 g L^{-1} with no reduction in purity. The system was operated over 10 h with no reduction in flux after approximately 3 h.

The system was also operated as a batch system with recycle of the permeate stream to investigate if fouling of

the membrane due to intermediates build-up occurred and to determine maximum glucose yield. Operating over 48 h with a trans-membrane pressure drop of 0.5 bar a steady state concentration of glucose of 72 g L⁻¹ was obtained and no reduction in flux. This indicates that the glucose yield is approximately 70%. This process has considerable potential for integration into processes requiring glucose as feedstock e.g., the production of xanthan gum and other fermentations.

Nanofiltration and reverse osmosis: Nanofiltration and reverse osmosis are used when low molecular weight solutes such as inorganic salts or small organic molecules e.g., glucose are to be separated from a solvent. Nanofiltration membranes occupy the boundary between ultrafiltration and reverse osmosis membranes in terms of pore size. High pressure (P) has to be used to overcome the osmotic pressure (π). (Osmotic pressure of seawater is approximately 25 bar). The membrane is permeable to the solvent but not the solute.

Flux J_w is given by:

$$J_w = A (\Delta P - \Delta \pi) \quad (1)$$

In practice the membrane may be slightly permeable to the solute and hence real osmotic pressure across membrane is not $\Delta \pi$ but $\sigma \Delta \pi$ where σ is the reflection coefficient of the membrane to that particular solute. Hence,

$$J_w = A (\Delta P - \sigma \Delta \pi) \quad (2)$$

The water permeability coefficient A is a constant for a given membrane and is

$$A = (D_w c_w V_w) / (RT \Delta x) \quad (3)$$

Where, A is area, D_w is diffusion coefficient, x is membrane thickness. Solute flux can be described by:

$$J_s = B \Delta c_s \quad (4)$$

where:

b = Solute permeability coefficient

The selectivity of a membrane for a given solute is expressed by the retention coefficient or rejection coefficient R

$$R = (c_f - c_p) / c_f = 1 - c_p / c_f \quad (5)$$

where, c_f and c_p are concentration of feed and permeate respectively.

Hence as pressure increases selectivity also increases because solute concentration in permeate decreases.

Nanofiltration membranes are usually composite membranes with a top layer thickness of ~ 1 μ m and a supporting sublayer ~ 150 μ m, pore size is <2 nm. The driving force is pressure in the range of 10-25 bar and the separation principle is the solution-diffusion mechanism. The membrane material is often polymeric e.g., polyamide, however it is now possible to use ceramics e.g., alumina, to make the membrane. The main application of Nanofiltration membranes is the removal of micropollutants, water softening, desalination of brackish water, waste water treatment and in the textile industry.

Reverse osmosis membranes are either asymmetric or composite with a top layer thickness of ~ 1 μ m and a supporting sublayer ~ 150 μ m, pore size is <2 nm. The driving force is pressure in the range of 15-80 bar depending upon application and the separation principle is the solution-diffusion mechanism. Typical polymers used to produce reverse osmosis membranes are aromatic polyamide, cellulose triacetate, polyamide and poly (ether urea). The main applications are the production of ultrapure water, desalination of brackish and seawater, concentration of sugars and fruit juices and the concentration of milk.

CONCENTRATION AS THE DRIVING FORCE

In many processes transport proceeds via diffusion rather convection. Substances diffuse from a high to a low chemical potential. The processes which make use of concentration difference as the driving force are gas separation, vapour permeation, pervaporation, dialysis, diffusion dialysis, carrier mediated transport and membrane contactors. These processes all use a nonporous membrane.

Gas separation: No gas separation in porous membranes can be achieved if the flow is viscous flow, decreasing the pore diameter until Knudsen flow occurs can result in separation, but the separation factor is very low and usually uneconomic. Gas separation through nonporous membranes depends on differences in the permeabilities of various gases through a given membrane where the transport is by the solution/diffusion mechanism.

$$\text{Permeability (P)} = \text{Solubility (S)} / \text{Diffusivity (D)}$$

Fick's law is the simplest description of gas diffusion through a nonporous structure

$$J = -Ddc/dx \quad (6)$$

Under steady state conditions

$$J_i = \{D_i(c_{o,i} - c_{i,i})\}/l \quad (7)$$

Where, $c_{o,i}$ and $c_{i,i}$ are the concentrations in the membrane on upstream and downstream side.

Concentration are related to partial pressures by Henry's law

$$c_i = S_i p_i \quad (8)$$

Combining these equations gives

$$J_i = \{D_i S_i (p_{o,i} - p_{i,i})\}/l \quad (9)$$

And

$$P = D.S \quad (10)$$

Hence,

$$J_i = P_i(p_{o,i} - p_{i,i})/l = P_i \Delta p_i / l \quad (11)$$

The ideal selectivity is given by:

$$\alpha_{i/j \text{ ideal}} = P_i/P_j \quad (12)$$

Membranes for gas separation: The permeabilites of a given gas molecule in various polymers can change by more the 6 orders of magnitude, also for a given polymer the permeability of various gases and vapours can also change over 6 orders of magnitude. Hence in principle many materials can be used as a membrane depending upon the application. Gas separation is also bases on selectivity as well as the permeability.

For separation processes involving large differences in interactions e.g. gases from vapours, the permeability ratio is usually large and a high permeability material may be chosen. Elastomers show rather low selectivities for some separations and glassy polymers with much lower permeability are often used. The permeation rate = P/l and permeation properties may be optimized by minimizing membrane thickness.

Hence two types of membrane are suitable for gas separation:

- Asymmetric membranes and
- Composite membranes
- Ideal gas separation membranes posses a high flux and high selectivity, however, in practice a trade-off is observed between the two properties.

Pervaporation: Pervaporation is a membrane process in which feed side is liquid and the permeate side is a vapour as a result of applying a very low pressure on the permeate side.

Hence on downstream side $P_2 \rightarrow 0$

If partial pressure is put equal to the activity γ , then

$$\gamma_i s_i \cdot c_i s = p_i \quad (13)$$

and

$$J_i = \frac{P_i}{l} c_{i,1} s (1 - p_{i,2} s / p_{i,1} s) \quad (14)$$

From this equation it can be seen that when permeate pressure ($p_{i,2} s$) increases the flux of component i decreases.

For single component transport

$$J_i = -L_i d\mu_i/dx \quad (15)$$

Where, L_i is a proportionality coefficient

The chemical potential μ_i , is given by:

$$\mu_i = \mu_i^0 + RT \ln a_i \text{ with } a_i = p_i/p_i^0 \quad (16)$$

p_i^0 being the saturation pressure of component i and p_i its vapour pressure

Since

$$d\mu_i/dx = (RT/p_i) \cdot dp_i/dx \quad (17)$$

Hence,

$$J_i = (L_i RT/p_i) dp_i/dx \quad (18)$$

Or

$$J_i = P_i/l \cdot \Delta p_i \quad (19)$$

This is the basic equation for liquid transport and is the same as for gas transport.

Membranes for pervaporation: For pervaporation and gas separation, nonporous membranes are required preferably with an anisotropic morphology and asymmetric structure with a dense top layer and an open porous sublayer. The requirements for the sublayer are the same as for gas separations membranes: an open structure to minimize resistance to vapour transport and to avoid capillary condensation and a high surface porosity with narrow pore size distribution. Pressure loss on permeate side results in an increase in partial pressure and hence a

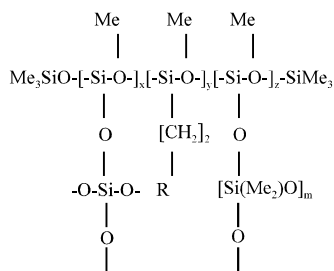


Fig. 2: Cross-linked organofunctional siloxane membrane

decrease in driving force and flux. If pores are too small pressure loss may be sufficiently high for capillary condensation to occur.

The choice of polymeric material for the membrane depends strongly upon the particular application.

It has been shown that substituting groups on the polymer polydimethylsiloxane with receptor groups to improve the selectivity of the membrane as shown in Fig. 2.

This approach has been used in developing new membrane materials for gas, vapour and pervaporation membranes. The groups R can be chosen such that the solubility of the desired component in the membrane material can be increased thus improving the permselectivity of the membrane for gas and vapour separations (Ashworth *et al.*, 1995). For pervaporation membranes the group can be chosen to make the membrane organophilic/hydrophobic or organophobic/hydrophilic depending upon the application i.e water removal or organic recovery.

Some of the groups R that have been studied are given by Bennett *et al.* (1997) for the recovery of organics from aqueous streams and for the recovery/removal of phenolic compounds from aqueous streams (Wu *et al.*, 2001a, b).

Carrier mediated transport: A membrane has been defined as an interphase between two phases and so far have only considered using solids. It is also possible to use a liquid as a membrane with a receptor molecular present in the fluid either in solution or chemically bonded to transport the desired product from one phase to the other. There are two basic types of liquid membrane:-

- A supported liquid membrane where the liquid is immobilized within the pores of a porous solid,
- An emulsion liquid membrane

Liquid membranes have potential for use as highly selective extractants from liquids, but suffer from problems of long term stability and loss of the extractant

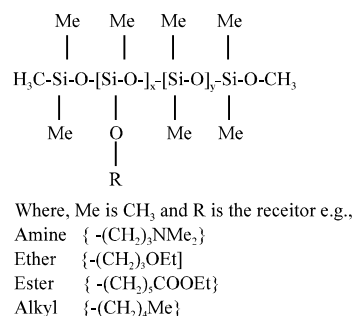


Fig. 3: Linear functionalised PDMS

due to partitioning effects. A review into liquid membrane separations has been published (Sastre *et al.*, 1998). Studies have been undertaken at Bath (England *et al.*, 1990; Yahaya *et al.*, 2000a, b; 2001), using functionalised PDMS (polydimethyl siloxane membranes) of the type shown in Fig. 3 and high selectivities for organic removal from aqueous media have been achieved and have been shown to be stable over 100 h. However these materials are relatively expensive and would probably have application only in the recovery of high value products.

APPLICATIONS IN WATER TREATMENT

There are many water shortage problems in the world and in several of them membrane technology can make a significant contribution as membranes (Nanofiltration and reverse osmosis membranes) can produce water of high purity for both the chemical and bioprocess industries. Effluent and process waters can be treated by membranes to enable recycle and reuse of the water thus reducing the need for fresh supplies. The use of membrane bioreactors to treat effluent streams and to deal with difficult wastes are becoming more widespread and the water produced is of a purity to enable direct discharge of the stream to the environment without causing pollution. An example of the use of membrane bioreactors is the successful integration of them into waste managements systems onboard cruise liners to conform with the MARPOL regulations. Howell (2004) has recently reviewed the future of membranes and membrane reactor in green technologies and for water reuse and has concluded that membrane bioreactors will be increasingly important in waste treatment due to the need for compact plant, uprating of capacity, the quality of the effluent and the value of recycling.

DEVELOPMENTS IN CERAMIC MEMBRANES

Ceramic membranes are becoming increasingly important with the development of methods for making

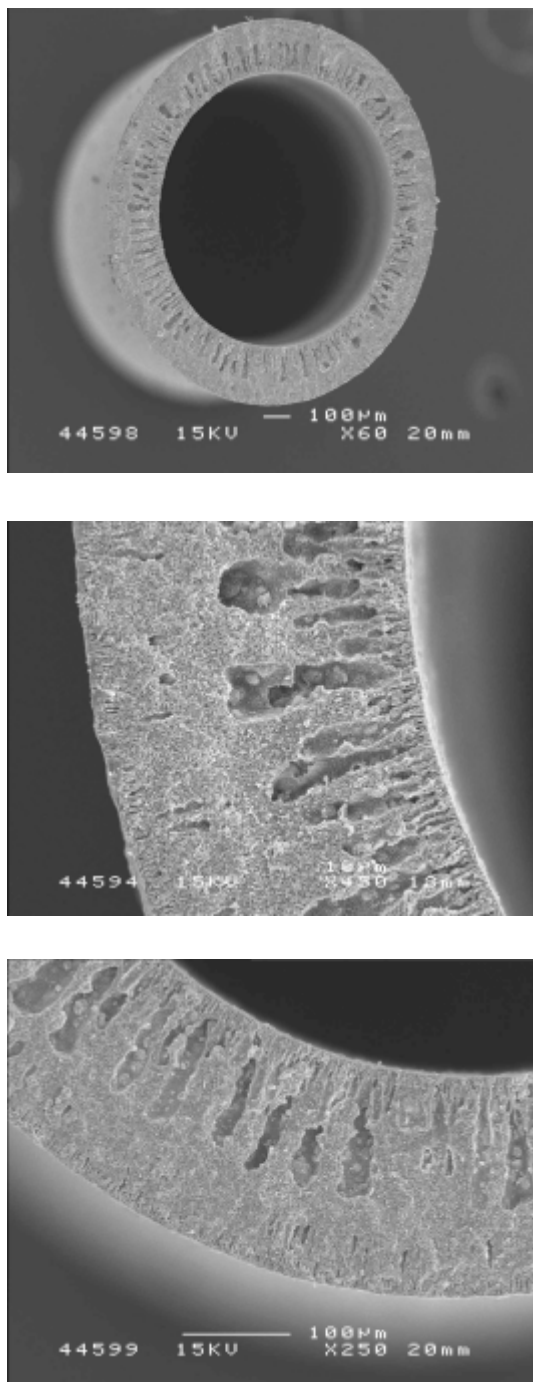


Fig. 4: Ceramic hollow fibre membranes (Based on Alumina) pore diameter ~1 nm

hollow fibres in addition to monoliths and flat sheet membranes. Perera (2005) has succeeded in making nanoporous membranes with a pore size of approximately 1 nm. Micrographs of an alumina hollow fibre are shown

in Fig. 4. The fibre were developed for high temperature separations and it is possible to doped the material with a catalyst so that it can be used simultaneously for catalysis and separation. It is proposed to use the experience in the development of PDMS derived pervaporation membranes and vapour transport membranes to form composite membranes with a very thin separation layer deposited upon the active ceramic membranes. These demonstrated that the use of modified polysiloxanes could give rise to significant improvements in both flux and selectivity.

CONCLUSION

Membranes separation systems will continue to play an increasing role in the chemical and bioprocessing industries. The development of ceramic and ceramic/composite membranes will extend the range of applications permitting high temperature operation. Membrane system will increasingly be used in the area of water and waste water treatment due to the inherent flexibility and now proven reliability of membrane systems.

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