PERMEATION OF SUPERCRITICAL CARBON DIOXIDE ACROSS POLYMERIC HOLLOW FIBER MEMBRANES

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The use of supercritical carbon dioxide (Sc-CO_2) has been extensively increased in recent applications to replace organic solvents. However, one problem that arises for separations is the regeneration of Sc-CO_2. Generally, the regeneration is performed by decreasing the solubility of the solute in Sc-CO_2 by expansion or cooling the mixture. This is accompanied with large energy consumption, as the carbon dioxide needs to be pressurized again and reheated to supercritical conditions. Selective membrane separation of carbon dioxide could open some new and economically attractive possibilities for the regeneration step [1]. These membranes have to be resistant to the effect of plasticization of the polymer and have to maintain long-time separation performance.

In this work, two different composite polymeric membranes have been tested for this purpose. It has been tested for fluxes of pure carbon dioxide. The effect of pressure difference and the effect of feed pressure have been established. A polyethersulfone (PES) ultrafiltration membrane is used as a base membrane and two different selective polymeric top layers have been applied. This top layer consists of polyvinyl alcohol or polyamide type of polymers. The carbon dioxide fluxes are measured for both types of membranes at 313.4 K, pressures ranging from 10 to 200 bar and at 0 to 4 bar pressure difference across the membrane. Also the membranes have been tested for their physical stability. The effect of cross-linking of the top layer polymer has also been studied to improve the stability of the membranes. During the measurements, both membranes seem to have a typical relation between flux and the feed pressure. At certain feed pressures, a maximum in the flux has been observed. After this maximum, the carbon dioxide flux stabilizes to a certain value for higher pressures. Few other researchers observed this phenomenon also during their work with polymeric membranes. This transport phenomenon can be well explained by Hagen-Poiseuille's law [8].

The cross-linking of the polyamide top layer makes the membrane more stable. However, because of cross-linking the fluxes decrease to some extent. These results demonstrate the possibility of regeneration of supercritical carbon dioxide with reasonably low-pressure loss using the polymeric membranes.

INTRODUCTION

Gas separation by selective separation through polymeric membranes is one of the fastest growing interests of separation technology. Membrane separation techniques present a large application potential to processes involving dense CO_2 in the phase of extract fractionation or solute recovery. During these steps, high depressurizing of the solvent is usually required, and the coupling of both processes can be quite useful in reducing pressure losses and recompression costs. Some of the studies have shown that few of the polymeric membranes used for carbon dioxide separation can be successfully used [3-6]. Sarrade et al [6] have tested the use of organo-mineral nanofiltration membranes for the fractionation of triglycerides and purification of β-carotene in supercritical CO_2.

MATERIALS

The polymeric membranes with polyethersulfone (PES) as base membrane and different polymeric top layer were obtained from TNO, The Netherlands. PES possesses very good chemical and thermal stability as indicated by its T_g value 513 K. There are two different types of top layers have been developed, polyvinyl alcohol (PVA) and copolymer polyamide (IPC). Two different techniques were used to apply a thin top layer on a support, solution coating and interfacial polymerisation. Selective top layer of PVA (0.8 µm thick) was developed by solution coating method and the polyamide top layer is prepared by interfacial polymerization process. By interfacial polymerisation two very reactive bifunctional monomers (e.g. a di-acid chloride and a diamine) or trifunctional monomers (e.g. trimesoylchloride) are allowed to react with each other at water/organic solvent interface and a typical network structure is obtained.

For all experiments carbon dioxide (grade 5.0) is obtained from HoekLoos Amsterdam, The Netherlands).

EXPERIMENTAL

A high-pressure membrane setup has been used to study the permeation through the polymeric membranes. The membranes are placed in an oven (Heraeus) and the temperature was measured with a Pt100 thermocouple inserted at the feed side carbon dioxide stream. Carbon dioxide was first pressurized by a HPLC pump (Jasco) and initially it is introduced on both sides of membrane. The membrane module could be pressurized at the feed and permeate side up to 400 bar.

To start a flux measurement the on-off valve separating permeate and feed side is closed so that the membrane separates the feed and permeation section. Then the needle valve at the permeate side of the membrane was opened carefully to create a desired pressure difference across the membrane. Permeation experiments were performed with a 0.5 to 5 bar as pressure difference across the membrane. The flow rate of carbon dioxide is measured with the aid of flow meters.

RESULTS AND DISCUSSION

Carbon dioxide permeation through two polymeric membranes is studied for a wide range of feed pressures and pressure differences across the membrane. These

measurements have been done for both, subcritical and supercritical conditions for carbon dioxide. Carbon dioxide becomes supercritical at 304.2 K and 7.38 MPa. The fluxes are measured with the aid of flow meters. The amount of flow at certain ΔP is measured for different feed pressures, which in turn gives the flow through the membrane in terms of number of moles of carbon dioxide permeating through fixed surface area of membrane. These measurements are performed with increasing feed pressure and decreasing feed pressure.

The permeation at 313.4 K with respect to feed pressures is shown in figure 1a for IPC membrane and figure 1b for PVA membrane.
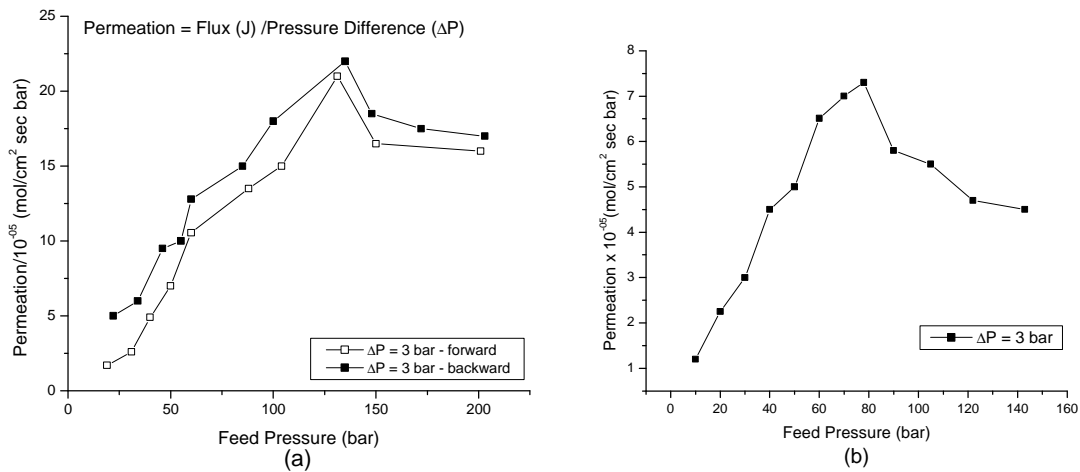
Figure 1: Permeation of carbon dioxide through IPC (a) and PVA (b) membrane at ΔP=3 bar

As it can be seen in figure 1, the permeation values increase with a increase in feed pressure. The permeation rise to a maximum point at about 130 bar for IPC and 85 bar for PVA membrane and then it decreases a bit as feed pressure increases thereafter. It also attends fairly stable value of permeation around 17x 10^{-5} for IPC and 4 x 10^{-5} (mol/cm^2 sec bar) for PVA membrane.

The maxima of permeation in IPC and PVA membranes are approximately 22 x 10^{-5} and 7.5 x 10^{-5} (mol/cm^2 sec bar) respectively. Maximum permeation of CO_2 through IPC is approximately 3 times more than in PVA membrane. These differences can be correlated to the effective pore size in the top layer of the membranes. Also, the methods of preparing the top layers are totally different, which makes the changes in the thickness of the layer, which shows the differences in the fluxes.

This typical trend of permeation at various feed pressure can be well explained by Hagen-Poiseuille's law for viscous flows.

$$Q = \frac{e}{t} \frac{r^2 \boldsymbol{r}_m}{8 \boldsymbol{h}_m l M_{CO_2}} \qquad (1)$$

where Q = permeation, e = porosity , r = average pore radius, l = top layer thickness or effective pore length, τ = tortuosity, M_{CO_2} = Molecular weight of carbon dioxide, ρ_m= mean density, η_m = mean viscosity

If all molecules move through pores at the same average velocity and in a laminar flow regime, the transport for viscous flows can be described by Hagen-Poiseuille's law [6]. For such small pore one can expect that the Knudson type of transport mechanism would dominate the overall flux behavior. However, from our calculations it comes out to be negligible. From figure 2 it can be seen that the experimental results are in good agreement with the Hagen-Poiseuille's model given by equation (1).
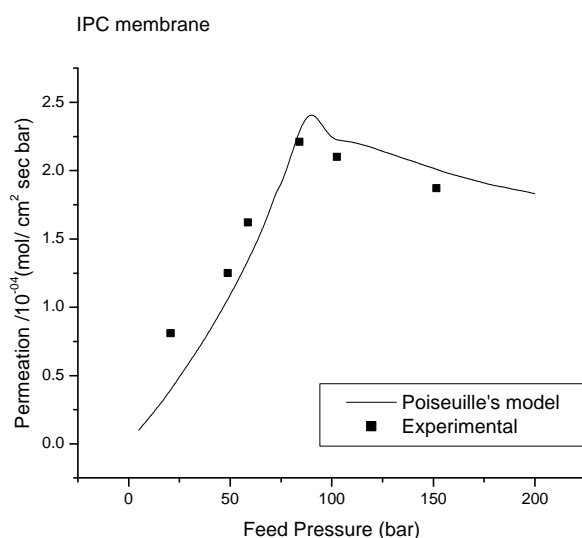

Figure 2: Hagen-Poiseuille's model fitting to the permeation data for IPC membrane

Membrane stability in supercritical carbon dioxide is important in order to get constant rejection performance. The well-known effect of plasticization and swelling of polymer due to carbon dioxide is certainly detrimental to the membrane performance. So to check these effects the stability of the membrane was experimentally determined. The flux through both the membranes was measured at 150 bar feed pressure and constant ΔP for a few hours, say up to four hours. PVA and IPC membrane showed some variations in the flux during the long run measurements. This indicates that these two membranes are not completely stable for use in supercritical carbon dioxide.

There are few techniques that have already been used by several other researchers to stabilize polymeric membranes. One of the techniques is adding the cross-linking in the top layers of the membrane. We obtained IPC membrane with cross-linking carried out with 1,5,8,12-tetraazadodecane (N_4). After inducing cross-linking (with 0.1wt% N_4) in top layer the permeation of carbon dioxide is found to be fairly constant over a time range of at least six hours. In figure 3 the permeation through cross-linked IPC membrane is given which is measured at 150 bar feed pressure and ΔP = 3 bar. But the cross-linking the top layer results in a less permeable membrane.

This is because the cross-linking makes the effective diameter of the pores reduced in size. The stability is acquired because entanglement of polymer chains. Cross-linked top layer reduces the freedom and flexibility of the polymer chains eventually reducing the permeation.
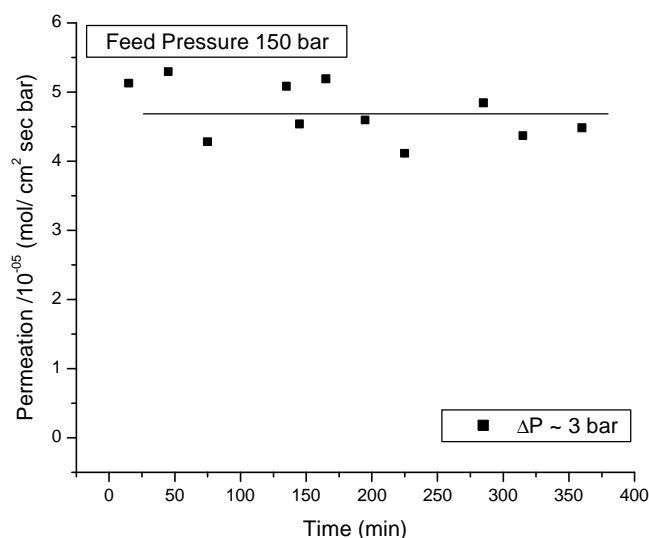
Figure 3: Stability test for IPC membrane

IPC membrane with more degree of cross-linking (0.3 wt% N_4) was also tested for its fluxes but there were no fluxes observed through the membrane. As the degree of cross-linking increases the carbon dioxide is unable to go through the membrane even up to 200 bar feed pressure and 4 bar ΔP. So we can conclude from these results that more cross-linking after a certain limiting value is not advantageous as it makes the effective pore size so small that CO_2 molecules can not enter into the polymer matrix to show any fluxes.

CONCLUSIONS

Different polymeric membranes have been compared in terms of flux and their stability towards carbon dioxide permeation. For PVA and IPC membranes, which are not cross-linked, have similar permeation behavior. Both membranes show a maximum in the permeation as a function of feed pressure of CO_2. In terms of stability, permeation of CO_2 through both membranes is stable for three to four hours. After cross-linking the IPC membrane the permeation of CO_2 decreases and stable permeation behavior for more than six hours has been observed. These results open the possibility for regeneration of supercritical carbon dioxide using polymeric membranes.

REFRENCES

[1] CHIU, Y., Tan, C., *J. Supercrit. Fluids*, 21, **2001**, 81

[2] SPRICIGO, C., J Memb Sci, 205(1-2), **2002,** 1-6

[3] HSU, J., J Memb Sci, 81(3), **1993,** 273

[4] HIGASHIJIMA, T., J Memb Sci, 93(2), **1994,** 165

[5] SEMENOVA, S., J Memb Sci, 74(1-2), **1992,** 131

[6] SARRADE, S., Sep Purif Tech, 14(1-3), **1998**, 19

[7] SANDERS, E., J Memb Sci, 37(1), **1988,** 63

[8] SARRADE, S., Sep Purif Tech, 114(1), **1996**, 81

[9] MULLER, A., Proc. First International Conference on Inorganic Membranes, Montepellier, **1989**, 337

[10] SCHELL, W., CEP, 78, **1983**, 52

[11] SARTORELLI, L., BRUNNER, G., Proceedings of the Fifth International Symposium on Supercritical Fluids, Atlanta, USA, **2000**

[12] HAO, J., Chemical Journal on Internet, Vol 2(8), (**2000**), Pg 9

[13] KULCKE, W., Brunner, G., *PhD Thesis*, Technical University of Hamburg, **2002**.