Available online at www.sciencedirect.com

J. of Supercritical Fluids 37 (2006) 367–374

www.elsevier.com/locate/supflu

Permeation of supercritical fluids across polymeric and inorganic membranes

Vishal E. Patil, Jurjen Meeuwissen, Leo J.P. van den Broeke *, Jos T.F. Keurentjes

Process Development Group, Department of Chemical Engineering and Chemistry, Eindhoven University of Technology, P.O. Box 513, 5600 MB Eindhoven, The Netherlands

Received 14 June 2005; received in revised form 26 September 2005; accepted 17 October 2005

Abstract

The permeation of supercritical CO_2 and SF_6 across two different types of microporous membranes has been studied as a function of temperature and feed pressure. A general picture appears where for both species the permeance as a function of the feed pressure has a maximum. For both the polymeric and the silica membranes close to the temperature where the different species become supercritical the maximum in the permeance is observed at the critical pressure. In the supercritical regime the main mechanism for the mass transport is viscous flow, and there is almost no contribution from surface diffusion through the micropores. The permeance of the fluids obtained for different condition can be described by a single mobility constant, which is independent of temperature and pressure.

Keywords: Supercritical fluids; Permeation; Microporous material; Polymeric membrane; Silica membrane; Viscous flow

1. Introduction

Membrane technology offers a suitable option for continuous regeneration of supercritical fluids. One of the main issues in high pressure applications is the regeneration of the supercritical fluid (SCF), which makes up the major part of the operational costs [1]. In particular, the use of a membrane can lead to a reduction in pressure losses and recompression costs.

Thermal and chemical stability of inorganic microporous membranes, i.e. membranes with a pore size smaller than 2 nm, makes this type of membranes suited for high temperature and high pressure applications, ranging from membrane reactors, gas separation, to the regeneration of supercritical fluids [2,3]. A number of inorganic microporous membranes are available, including zeolite membranes [4], carbon molecular sieve membranes [5,6], silica membranes [7,8], and activated alumina membranes [9,10]. At the moment, inorganic membranes have to compete with polymeric microporous nanofiltration membranes, because of the availability of polymeric membranes with different properties. However, polymeric membranes suffer from some drawbacks, in particular lack of stability, when used for regeneration of SCFs. This is mainly a result of plasticization of the polymer [11,12].

The permeation of supercritical fluids across membranes is interesting from both a fundamental and practical point of view [13–16]. In practice, both polymeric and inorganic membranes are being used to regenerate SCFs, like the separation of small species [17–19], oil-like components [20–22], and homogeneous catalysts [23], from the fluid while maintaining supercritical conditions. Transport phenomena in microporous materials have extensively been studied for the diffusion of gaseous species. For a text book on the diffusion in inorganic materials, including zeolites and carbon molecular sieves, see Kärger and Ruthven [24]. However, only a limited number of studies are available dealing with the mass transport in microporous membranes, both inorganic and polymeric, at supercritical conditions [5,25,26].

Katsaros et al. [5] studied the permeation of pure helium and pure carbon dioxide through carbon membranes with a pore size of 0.7 nm, up to pressures of 6 MPa. As a function of the pressure a clear maximum in the carbon dioxide permeance was observed between 3 and 4 MPa. Recently, it was demonstrated that microporous silica membranes have a reasonable flux of supercritical CO_2 [26].

The objective of this work is to describe the permeation of supercritical CO_2 and supercritical SF_6 across two differ-

---

* Corresponding author. Tel.: +31 40 247 3675; fax: +31 40 244 6104.
E-mail address: L.J.P.van.den.Broeke@tue.nl (L.J.P. van den Broeke).

0896-8446/$ – see front matter © 2006 Elsevier B.V. All rights reserved.
doi:10.1016/j.supflu.2005.10.005

Nomenclature

b	Langmuir parameter (Pa^{-1})
D_s	surface diffusion coefficient ($m^2\,s^{-1}$)
D_k	Knudsen diffusion coefficient ($m^2\,s^{-1}$)
J	flux ($mol\,m^{-1}\,s^{-1}$)
L	selective layer thickness (m)
M	molecular weight of fluid ($g\,mol^{-1}$)
ΔP	pressure difference (Pa)
q	amount adsorbed ($mmol\,g^{-1}$)
q_{sat}	saturation amount adsorbed ($mmol\,g^{-1}$)
Q	permeance ($mol\,m^{-2}\,s^{-1}\,Pa^{-1}$)
r	pore radius (m)
R	universal gas constant ($J\,K^{-1}\,mol^{-1}$)
T	temperature (K)
x	space coordinate (m)

Greek letters

β	mobility parameter ($m\,mol\,g^{-1}$)
ε_{inter}	inter-particle porosity
ε_{intra}	intra-particle porosity
η_f	fluid viscosity (Pa s)
θ	surface occupancy
ρ_f	fluid density ($kg\,m^{-3}$)
ρ_{mem}	membrane density ($kg\,m^{-3}$)
τ	tortuosity

ent types of membranes at different operating conditions. The permeation of the two SCFs has been obtained for composite polymeric membranes and for a microporous alumina supported silica membrane.

2. Experimental

2.1. Membrane setup and methods

The high pressure permeation setup used to measure the steady-state flux through the membranes is schematically depicted in Fig. 1. The experimental setup is designed to test the membranes up to feed pressures and temperatures of 40 MPa and 473 K, respectively. The membranes were placed in a temperature controlled oven (Heraeus) and the temperature was measured with a Pt100 thermocouple. A thermocouple was placed at the feed side of the gas stream in order to measure the temperature of the fluid stream entering the membrane module. The inlet stream was filtered by an inline filter to feed pure liquid CO_2 and SF_6 for smooth operation of the HPLC pump (Jasco). To make sure that the feed to the pump is in the liquid phase, the pump piston heads were cooled to a temperature of 278 K. The gas stream was heated to supercritical conditions by a coil, which was placed inside the oven. The amount of fluid flowing in the system was measured by a Corriolis type mass flow meter.

To start the permeation experiments, a fluid stream was fed to the feed and permeate side of the membrane by keeping the valve VP open. Both sides of the membrane were pressurized to ensure that no excess pressure difference across the membrane could exist, which could damage or break the membrane. When the desired pressure at the feed side was obtained valve VP was closed. The pressure in both compartments of the membrane was controlled by a back pressure regulator (BPR, Tescom). The BPR on the permeate side was fine-tuned to create the desired pressure difference across the membrane. The pressure on both sides of the membrane was measured by two pressure sensors (AE Sensors) with an accuracy of 0.01 MPa.

The BPRs were placed in a temperature controlled water bath to ensure steady operation. This was necessary because in case of carbon dioxide it was expanded during regulation of the pressure and the BPRs were cooled severely due to the Joule–Thompson expansion effect [27]. The flow of the expanded gas stream was measured using a wet gas meter (Schlumberger). Small flows were measured with a soap bubble flow meter.

Permeation experiments were performed using a pressure difference across the polymeric membrane between 0.05 and 0.3 MPa and across the silica membrane between 0.1 and 1.5 MPa, using a dead end configuration. The amount of CO_2 or SF_6 going through the membrane at a certain ΔP was measured for different feed pressures, which in turn gives the flux through the membrane in terms of number of moles of CO_2 or SF_6 permeating through a fixed surface area of the membrane per unit time. The complete series of experiments was repeated with different feed pressures ranging from 1 to 18 MPa for CO_2 and ranging from 1 to 6 MPa for SF_6, using about the same pressure difference across the membrane.

2.2. Equilibrium adsorption isotherms

Equilibrium isotherms of CO_2 on silica powders were obtained for four different temperatures and for pressures up to 0.8 MPa. The isotherms were measured gravimetrically using an Igasorp (Hiden Analytical).

2.3. Density and viscosity

The values for the CO_2 density and viscosity as a function of the pressure have been calculated with the Modified-Benedict-Webb-Rubin (MWBR) model [27]. The values for the SF_6 density and viscosity as a function of the pressure have been obtained from literature [28].

2.4. Gases

Carbon dioxide (grade 5.0) and sulfur hexafluoride (grade 2.8) were obtained from HoekLoos (Amsterdam, The Netherlands).

2.5. Silica membrane

Microporous alumina supported silica membranes were obtained from ECN (Petten, The Netherlands). The supported silica membranes consist of the alumina support plus the selective top layer, at the outer wall of the tube, which is made of