Journal of Membrane Science 339 (2009) 120–125

Contents lists available at ScienceDirect

Journal of Membrane Science

journal homepage: www.elsevier.com/locate/memsci

Pervaporative separation of *n*-butanol from dilute aqueous solutions using silicalite-filled poly(dimethyl siloxane) membranes

Elsayed A. Fouad[1], Xianshe Feng*

Department of Chemical Engineering, University of Waterloo, 200 University Avenue West, Waterloo, Ontario, Canada N2L 3G1

ARTICLE INFO

Article history:
Received 23 February 2009
Received in revised form 16 April 2009
Accepted 19 April 2009
Available online 3 May 2009

Keywords:
Pervaporation
Composite membrane
n-Butanol
Silicalite
Poly(dimethyl siloxane)

ABSTRACT

Pervaporative separation of *n*-butanol from dilute aqueous solutions (<0.5 wt%) using a silicalite-filled poly(dimethyl siloxane) composite membrane was investigated. The effects of operating conditions (e.g., feed composition, temperature) on the permeation flux, separation factor and pervaporation separation index were evaluated. It was shown that at a given temperature, water flux increased almost linearly with an increase in feed butanol concentration, whereas the butanol flux increased in a concave fashion due to silicalite fillers that have a strong affinity to butanol molecules. Consequently, the permeate butanol concentration initially increased and then gradually leveled off when the feed butanol concentration was high enough, and the leveling off started to occur at a lower butanol concentration at a higher temperature. The temperature dependence of permeation flux followed a typical Arrhenius relation, and a variation in temperature would increase or decrease the membrane selectivity, depending on feed butanol concentration. These results are especially important for potential use of the membrane for in situ butanol extraction from fermentation where butanol becomes inhibitory at a low concentration of 4–6 g/L.

1. Introduction

In recent years, pervaporation has been widely studied for the separation of close boiling, azeotropic, isomeric and other mixtures that are difficult to separate by conventional techniques. In pervaporation, the separation is based on selective permeability of the membrane to the components in a mixture to be separated. The membrane permeability is primarily determined by the solubility and diffusivity of the permeating component in the membrane, and not the relative volatility as in distillation. Unlike other membrane processes, pervaporation involves a liquid to vapor phase change and the permeate obtained is a low pressure vapor. In addition to the energy consumption used to operate the vacuum pump to create driving force for permeation, the phase change requires additional energy which should be at least equal to the heat of evaporation of the permeate. Thus, from an energy consumption point of view, it is preferable if the membrane can be targeted at selective permeation of the minor component in the mixture.

For the separation of organic compounds from aqueous solutions where the organic compounds are the minor components, poly(dimethyl siloxane) (PDMS) and other rubbery organophilic membranes are often preferred. The rapid chain segment motion in the silicone and other rubbery polymers leads to a large free volume that favors the diffusion of the permeating molecules. While homogeneous membranes may be adequate in basic permeability studies, composite membranes comprising of a thin active skin layer and a microporous substrate are desired for practical applications in order to enhance the mass transfer rate without compromising their mechanical stabilities. The substrate should be highly porous to minimize its resistance to mass transfer of the permeating components. Otherwise, the overall permselectivity of the composite membrane will be lowered. On the other hand, the pores on the substrate membrane should be small enough so as to prevent intrusion and filling of the pores with the top layer material during surface coating, which is commonly used in membrane formation.

Based on the solution-diffusion mechanism, the membrane performance can be enhanced by improving either selective sorption or selective diffusion or, if possible, both. Therefore, efforts have been made to incorporate microporous "filler" materials with high sorption selectivity into a membrane matrix, and zeolites are the most popular filler materials due to their well-defined microstructure and hydrophilicity/hydrophobicity. Over the past few years, zeolite-filled membranes have received significant attention for various applications (see, for example, [1–8]). Silicalite, an organophilic silica molecular sieve [9], has shown to be especially effective for improving membrane permselectivity because of its unique crystalline microporous structure and surface chemistry. As a result, water permeability is generally reduced as water

---

* Corresponding author. Tel.: +1 519 888 4567; fax: +1 519 746 4979.
E-mail address: xfeng@uwaterloo.ca (X. Feng).

[1] Present address: High Institute of Technology, Benha University, Benha 13512, Benha, Egypt.

0376-7388/$ – see front matter © 2009 Elsevier B.V. All rights reserved.
doi:10.1016/j.memsci.2009.04.038

molecules are excluded from entering the pores of the filler particles. This causes not only a decreased sorption of water but also an increased path length for water molecules to travel through the membrane because they have to take a more tortuous path [1]. It has been found that the mass transport of small organic molecules is generally enhanced, but depending on the relative size and shape of the molecules, bulky molecules may be partly or totally excluded from entering the zeolite pores due to the molecular sieving effect [2].

This study deals with pervaporative separation of butanol from dilute aqueous solutions. Butanol is widely used in the manufacture of resins, plasticizers, cleaning agents and ester compounds as well as in the food and cosmetic industries as an extractant. In addition, the depleting supply of crude oil has recently created extensive interest in converting biomass and agricultural wastes for energy production, and biobutanol has become an attractive transportation fuel. If used as a fuel for internal combustion engines, butanol has many advantages over ethanol, including a higher (30% more) energy density, a higher octane rating, more miscible with gasoline and diesel fuel but less miscible with water, and a lower Reid vapor pressure (which is 7.5 times lower than ethanol). Many studies have been carried out on the use of pervaporation to separate butanol/water mixtures using either hydrophobic membranes for butanol concentration [10–13] or hydrophilic membranes for butanol dehydration [14–17].

Butanol production by fermentation is severely limited by product inhibition, resulting in a low reactor productivity and a low final butanol product concentration (0.04–1.5 wt%) [18], which are the primary factors impeding commercial acceptance of butanol production from biomass. This, however, appears to represent a niche application for pervaporation to alleviate product inhibition and to facilitate product recovery by simultaneous removal of butanol as soon as it is produced. For this potential application, organophilic membranes will be appropriate. In consideration that butanol becomes inhibitory at a low concentration of 0.4–0.6 wt%, it is of interest to investigate the pervaporation behavior for butanol removal from dilute solutions that are relevant for in situ removal of butanol. In this paper, a silicalite-filled poly(dimethyl siloxane) thin film composite membrane was evaluated, and the effects of feed concentration of *n*-butanol (0.01–0.4 wt%) and operating temperature (25–65 °C) on the separation performance were studied. This information will be useful to the assessment of technical feasibility of using pervaporation for in situ recovery of butanol. It may be mentioned that butanol recovery by pervaporation from dilute solutions is not well studied, and the prior work reported in the literature is often for feed concentrations too high to be relevant to the in situ recovery. Jonquieres and Fane [19] reported separation of butanol/water mixtures with a silicalite/PDMS membrane at three different concentrations (i.e., 1, 2.5 and 5 wt%) at a temperature of 40 °C. El-Zanati et al. [13] studied butanol separation from water at 33 °C in a feed concentration range of 0.6–5.0 wt% using a reportedly Sulzer 2200 membrane (which might not be true as this poly(vinyl alcohol)-based commercial membrane is a hydrophilic membrane appropriate for dehydration of organic solvents). As will be reported in this work, the membrane behaved quite differently in terms of permselectivity at low feed concentrations because of the silicalite fillers in the membrane, and it would be unreliable to obtain the membrane permselectivity at low concentrations by extrapolating the experimental data obtained at high concentrations.

2. Experiments

n-Butanol was supplied by Fisher Scientific. The membrane used in the experiments was a silicate-filled composite PDMS membrane (Pervap 1070) manufactured by GFT (now Sulzer Chemtech). It is comprised of a thin selective skin layer of PDMS filled with a certain amount of hydrophobic silicalite particles and a microporous asymmetric polyacrylonitrile substrate, which is backed on a non-woven polyester fabric for increased mechanical strength. The precise composition of the active skin layer is proprietary. The pervaporation experiments were carried out using a laboratory scale pervaporation unit; the setup and the procedure have been described elsewhere [20]. The membrane was mounted in a stainless steel permeation cell with an effective permeation area of 13.85 cm^2.

The permeation cell was designed to allow the feed to enter the permeation cell through a center opening and then flow radially along the membrane surface, while the retentate exited through a thin channel located peripherally near the edge of the membrane. The feed solution was admitted to the membrane cell via a centrifugal pump and the retentate was circulated back to the feed tank. A relatively high flow rate (1.6 L/min, corresponding to a linear flow velocity on the membrane of >20 cm/s) was used to minimize the boundary layer effect. Vacuum was provided on the down stream-side of the membrane using a vacuum pump, and the permeate pressure was maintained at ∼5 mmHg for all experiments. The permeate was initially collected in one of the cold traps immersed in liquid nitrogen, and it was then sampled periodically (∼1 h) by switching to the other cold trap. This allows permeate to be sampled without interrupting the pervaporation system.

The permeate flux was determined gravimetrically from the weight of the permeate sample collected over a given period of time. The concentration of butanol in the permeate was determined using a Total Organic Carbon Analyzer (Shimadzu TOC-500); double distilled water was used as a diluent to the permeate sample during composition analysis. For each set of experiments, the operating parameter was varied one at a time and covered the following ranges: feed concentration 0.01–0.4 wt% butanol and operating temperature 25–65 °C. Based on the experimental data of pervaporation, the membrane performance can be characterized in terms of permeation flux (J) and separation factor (α) shown below:

$$J = \frac{Q}{At} \quad (1)$$

$$\alpha = \frac{x_P/(1-x_P)}{x_F/(1-x_F)} \quad (2)$$

where Q is the mass of permeate collected over a time interval t, A is the effective membrane area for permeation, and x_P and x_F are the mass fractions of butanol in the permeate and feed, respectively. The partial permeation fluxes can be easily obtained from the total flux and the permeate concentration. Sometimes the pervaporation separation index (PSI) may also be used as a composite parameter to characterize the overall performance of the membrane:

$$\mathrm{PSI} = J(\alpha - 1) \quad (3)$$

3. Results and discussion

To study the effect of *n*-butanol concentration in the feed solution on the performance of the PDMS composite membrane, pervaporation experiments were performed at different concentrations and temperatures. Figs. 1 and 2 show the effects of feed composition on the total permeation flux and butanol concentration in the permeate at different temperatures, respectively. At a given temperature, the total flux increased with an increase in the feed butanol concentration over the low feed concentration range (0.01–0.5 wt%) studied. An increase in temperature will increase the permeation flux, but the concentration dependency of the flux does not appear to be affected significantly by the temperature. While this pattern can often be observed for pervaporation of dilute solutions, it is interesting to notice that the permeate butanol concentration initially increased and then gradually leveled off when the feed butanol concentration is high enough. A striking point