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Short Communication

Separation of gas mixtures by new type of membranes – Dynamic liquid membranes

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ABSTRACT

The selectivity and permeability of membrane material determines the efficiency of the gas separation process. To prepare a stable high selective and high permeable membrane and, in addition, also cheap, is the dream of most scientists dealing with the membrane technology. We proposed to investigate the gas separation by a completely new type of membranes possessing both; high selectivity and high gas permeability. Our preliminary results are very promising. We are able to prepare a very cheap and very thin liquid film with high separation performance of test CO_2/CH_4 mixture. A next curiosity of the new type of membranes is the continuous regeneration of the liquid film during the separation process. Based on this fact, we named the liquid film "dynamic liquid membrane" (DLM).

1. Introduction

Recently the membrane processes have been considered as a promising technology for the separation of gases and are now used in industry in impressively large scale [1–7]. Since the membrane is the most decisive part of the gas separation technology, it has attracted maximum attention in terms of research and development. The aim of the development of new membranes is to increase the permeability and selectivity or increase the permeability without reducing the selectivity or enhancing the selectivity at constant permeability. In principle, all materials that form sufficiently thin and stable films can be used as membranes. This includes metal, glass, ceramics and polymers as well as ordered molecular monolayers of liquids [2].

Any membrane material has its positive and negative properties. The selectivity and permeability of the membrane material determine the efficiency of the gas separation process. For example, the porous membranes can exhibit in the case of the gas separation very high flux but yield a low separation. On the other hand, non-porous or dense membranes have high selectivity but the rates of transport are usually low. An important property of non-porous dense membrane is that even permeants of similar sizes may be separated if their solubility in the membrane differs significantly, the principle of solution diffusion mechanism [8–10].

Polymeric membranes are in separation processes used largely due to their competitiveness in performance and economics. Many polymers are available; however, the choice of a membrane polymer is not a trivial task. The most common polymers in membrane synthesis are cellulose acetate, nitrocellulose, and cellulose esters (CA, CN, and CE), polysulfone (PS), polyether sulfone (PES), polyacrilonitrile (PAN), polyamide, polyimide, polyethylene and polypropylene (PE and PP), polytetrafluoroethylene (PTFE), polyvinylidene fluoride (PVDF), polyvinylchloride (PVC) [2,7,11–14].

Ceramic membranes based on inorganic materials such as alumina, titanium, silica, zirconia oxides, recrystallized silicon carbide or some glassy materials can be used by contrast with polymeric membranes in separations where aggressive media (acids, strong solvents) are present. In addition, their excellent thermal stability make them usable in high temperature membrane operations [2,3,7].

Liquid membranes (LM) have been extensively studied in last years [15]. One of the most widely researched and fast growing separation techniques in last years is the use of ionic liquids (ILs) due to their unique properties and ecological aspect [15–17]. There are several types of liquid membranes, the supported form – Immobilized Liquid Membrane (ILM), also called a Supported Liquid Membrane (SLM), the unsupported form – Emulsion Liquid Membrane (ELM) and contained liquid membrane (CLM) usually implemented with two well mixed set of porous hollow fibers (called hollow fiber CLM). LMs have relatively high efficiency due to their high selectivity and with the use of transport carriers, specific molecular recognition can be achieved [4–6], but so far they have limited commercial applications. The major problem of ILM and ELM is the adequate long-term stability due to the tendency of liquids to be pushed out of the pores or evaporate or dissolve in the phases in contact with them [7].

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In this paper a new type of membranes for gas separation is presented. A liquid film that is continuously regenerated is designated as "Dynamic Liquid Membrane" (DLM).

In literature is possible to find works reported on moving or flowing LM [18–24]. Teramoto et al. had proposed a new type of the membrane so called "flowing liquid membranes". The liquid solution flows between two hydrophobic microporous membranes (polypropylene, polytetrafluoroethylene) [18–21]. They used different solution for separation: aqueous silver nitrate for separation ethylene and ethane mixture [18] or separation of benzene from cyclohexane [19], di(2-ethylhexyl)phosphoric acid was used in case of chromium and zinc recovery [20]. Bessarabov et al. [21] studied hydrogen transport through flowing liquid membranes where distilled water was the liquid adsorbent. Beckman et al. [22] tried to separate different gas binary mixtures, e.g. carbon dioxide and methane and also ternary mixture carbon dioxide, methane and hydrogen. He used an arrangement – a liquid solution between two hydrophobic membranes from poly(vinyl trimethylsilane), the liquid served as an adsorption medium and its thickness was large. As solution an aqueous solution of monoethanolamine served. Shalygin et al. [23,24] tested similar membrane arrangement; they called it selective membrane valve (SMV). An asymmetric polyvinyltrimethylsilane membrane with nonporous selective layer and distillated water and aqueous potassium carbonate were used as liquid carriers. On this SMV they measured the permeability of hydrogen, oxygen and carbon dioxide. The thickness of the liquid layer was 260 μm.

This short contribution is focused on the description of our laboratory device for gas separation and the first results of its using for separation of binary mixture methane/carbon dioxide. Advantages of the proposed dynamic liquid membrane compared to other reported types of membranes are very small thickness of liquid film and no additional resistance for gas transport due to the required supports in form of other polymeric layers.

2. Experimental

2.1. Prototype of a separation device and procedure

A prototype of a new device for separation of gaseous mixtures by a stable thin liquid film as a selective membrane, so called "dynamic liquid membrane" (DLM), was designed in our laboratory. Its simple scheme is depicted in Fig. 1. The separation device consists of a permeation cell with DLM of the area 276 cm^2 that is made of stainless steel (only some segments are from flat PVC), a liquid pump ensuring the cycling of the solution for the film preparation, a liquid storage vessel, vacuum pump to collection of retentate, liquid separator, gases supply, flow meter controllers (FMC), valves and silicon tubes, copper tubes and brass Swagelok fittings.

A continuous very thin layer of the solution (film) flows down wires attached to a steel underlay, see Fig. 1. The film is continuously dripping at the end of wires. The distance between the wires is 6 mm. The liquid pump serves to continuous refreshing of the liquid film in order to form the stable liquid film. The flowmeter controllers (FMC) are able to set the desired composition of the separated gaseous mixture.

The feed gas mixture entering the permeation cell flows along the thin liquid film that has a separation function of the membrane. The gas components more soluble in the liquid of the film permeate through the thin membrane preferably and gas components with low solubility in the liquid continue flowing along the bottom side of the film and leave the cell as the retentate. The collection of product (retentate) is ensured by a small decreasing of pressure using vacuum pump. The sample of retentate was after taken off by a syringe analyzed by gas chromatography.

2.2. Material for DLMs preparation

Suitable composition of the liquid film can lead to high efficiency of the separated system. Water is the main component of the liquid. As a tested mixture for the study of gas separation by DLM the system carbon dioxide – methane was chosen. The much higher solubility of carbon dioxide than methane in water is reason of this selection. The aqueous solution containing the anionic surfactant and next additional agents, its internal identification is S31, was mentioned in Patent Number: CZ201200725-A3. This composition was developed to increase a long time stability of the film (approximately week) and to obtain the best separation performance.

2.3. Estimation of binary mixture CO_2 and CH_4 separation by DLM

The transport of components in non-porous dense membranes can be described by a solution diffusion model [8–10]. According to this model the transport through homogeneous membrane consists of three steps: (1) dissolution of the permeant in the membrane material at the upstream boundary, (2) diffusion of the dissolved species across the membrane, and (3) desorption or evaporation on the other side. The driving force of solution–diffusion mechanism is a difference in chemical potentials at the upstream and downstream faces of the membrane. The permeability coefficient can be obtained from experiments by:

$$P = \frac{JL}{\Delta p} \tag{1}$$

where J is mass flux, L is the thickness of membrane and Δp is the pressure difference of permeating gas across the membrane.

Similarly, the solution-diffusion mechanism can be used for the description of gas permeation in liquids. This means that the performance of liquid membranes depends strongly on the solubility and diffusivity of permeating species in liquid membrane. Based on this information it is possible to predict the transport behavior of liquid membranes to selected permeants.

We estimated the permeability and separation efficiency of the studied system CO_2/CH_4 using the solution diffusion model [8–10] and the data available in the literature [25]. The base component of DLMs for the CO_2/CH_4 separation is water, so the data of pure water was used and calculated data are given in Table 1.

The flux, J, of carbon dioxide through the water film with the thickness L = 1 μm at 20 °C for the pressure difference 1 bar across the film is calculated:

$$J = D\frac{(c_1 - c_2)}{L} = 1.67 \times 10^{-9}\ \frac{39}{10^{-6}} = 6.51 \times 10^{-2}\ \text{mol m}^{-2}\ \text{s}^{-1} = 5.3\ \text{m}^3\ \text{m}^{-2}\ \text{h}^{-1}$$

The concentration c_1 of permeating substance on downstream side of the liquid is given by the gas solubility. The concentration c_2 on the opposite side of the liquid film is supposed to be negligible.

Permeability P of carbon dioxide in water film:

$$P = \frac{JL}{\Delta p} = 6.51 \times 10^{-2}\ \frac{10^{-6}}{10^{5}} = 6.51 \times 10^{-13}\ \text{mol m m}^{-2}\ \text{Pa}^{-1}\ \text{s}^{-1} = 1940\ \text{Barrer}$$

Flux and permeability of carbon dioxide through the water film of 1 μm thickness at 20 °C for pressure difference 1 bar are J = 5.3 $m^3\ m^{-2}\ h^{-1}$ and permeability P = 1940 Barrer. The same values for methane are J = 0.17 $m^3\ m^{-2}\ h^{-1}$ and permeability P = 63 Barrer. The ratio of permeability of carbon dioxide and methane, i.e. the ideal separation factor α, is in this case α = 31.