Understanding the solution-diffusion mechanism in gas separation membrane for engineering students

Ahmad Fauzi Ismail[1,2] , Tutuk Djoko Kusworo[1,3], Azeman Mustafa[1,2] and Hasrinah Hasbullah[1,2]

[1]Membrane Research Unit, Faculty of Chemical and Natural Resources Engineering, Universiti Teknologi Malaysia, 81310 UTM, Skudai, Johor Bahru, Malaysia, E-mail: afauzi@utm.my

[2]Department of Gas Engineering, Faculty of Chemical and Natural Resources Engineering, Universiti Teknologi Malaysia, 81310 UTM, Skudai, Johor Bahru, Malaysia

[3]Permanent Address: Department of Chemical Engineering, Diponegoro University Semarang, Indonesia

Abstract

An ongoing struggle for many lecturers is to motivate their students to learn and understand what they learn. Students seem to be particularly unmotivated to learn materials that appear uninteresting to them or unrelated to their own life experiences and career goals. However, educational developments are an important process for the students to adapt to the new and interesting phenomenon. So that, they can fully appreciate the technical breakthrough in certain field that leads to the commercialization of certain research products. Membrane technology is one of the successful products or processes that has been commercialized for gas mixture separation. This process employs the established solution-diffusion model in order to explain the transport of gases in polymeric membrane. In this paper, we derive simple phenomenological equations for transport of gases in membrane based on the solution-diffusion model.

Keywords: Gas separation, Solution-diffusion model, polymer membrane

1. Introduction

Gas separation with polymer membranes is rapidly becoming a mainstream separation technology for industrial gas separation [1-2]. It is one of the most recent advanced technologies and recognized as a viable and economical unit operation, offering lower overall costs of gas processing as compared to the conventional separation technique such as chemical and physical processes. Membrane gas separation process also offers relatively simple operational procedures, process flexibility and low energy consumption. Membrane is also known for its capability to separate gases of different sizes, shapes, polarity and simplicity in its design. Furthermore, they have no moving parts, making them mechanically robust and more suitable to be used in remote locations where reliability is critical [3]. The most widely practiced separations are enriched nitrogen production from air, hydrogen separation in ammonia plants and refineries, removal of carbon dioxide from natural gas. The separation of oxygen from environmental air is one of the most another application of membrane technology [4].

Gas separation membranes are often packaged in hollow-fiber modules. Hollow fiber membrane consists of fibers installed as a bundle in a stainless steel tube. The shell side hollow fiber module is shown in Figure 1. Two types of hollow fiber modules are used for gas separation applications. Shell-side feed modules are generally used for high-pressure applications up to 1,000 psig. Bore side feed modules are generally used for medium-pressure feed streams up to 150 psig, for which good flow control to minimize fouling and concentration polarization on the feed side of the membrane is desired [5]. The inside and outside diameters of each fiber are 150 and 300 micrometers, respectively [4-5]. Typically, the

fiber wall is approximately 75 micrometers thick with a very thin, dense separation membrane layer of 500 to 1000 Å (0.05 to 0.1 micrometers) thick, on the outside of the fiber. Ideally, this thin layer provides all of the mass transfer resistance and separation ability of the hollow fiber. The remaining 74.9 to 74.95 micrometers of the fiber wall are comprised of a porous polymer layer that provides mechanical support to the thin membrane, but offers little or no mass transfer resistance. (To put fiber dimensions in perspective, the diameter of a typical human hair is about 100 micrometers). Gas (air in this example) flows under pressure into the module, where it is distributed to the bores of the fibers. The air gases permeate through the wall of the fibers into the shell of the hollow-fiber module, which is essentially maintained at atmospheric pressure. The gas permeating through the fibers and into the shell is collected and leaves the module as the permeate stream. Hollow fiber permeators have approximately three times as much area per unit volume as the spiral wound units [5]. Taveira et al (2001) reported that hollow fiber membrane could pack larger quantities of membrane area into small volumes. Hollow fiber membranes have five major advantages over flat sheet membranes: (1) hollow fibers have a much larger ratio of membrane area to unit volume (ratio as high as 10,000 m^2m^{-3}) and hence higher productivity per unit volume of membrane module, (2) they are self-supporting with ease of manufacture and replacement, (3) they have good flexibility in operation, (4) hollow fiber modules do not require costly membrane supports and (5) they are more damage resistant than other types modules [7].
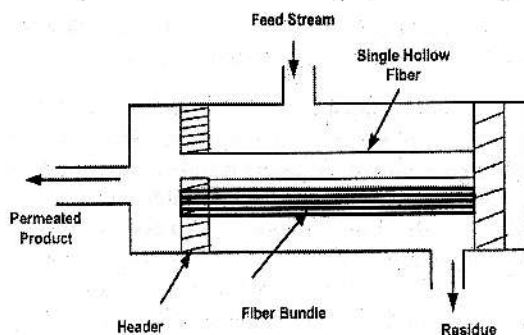

Figure 1: Schematic diagram of hollow fiber module used for air separation

The principle characteristic of membranes that is still useful in separation applications is the ability to control the permeation of different species. This paper presents a brief background on the fundamental of gas transport in polymer membranes. Later, we will discuss the models of mass transfer in gas separation modules. The solution-diffusion model is used to describe this permeation process.

2. Background

The solution-diffusion model is the most widely used transport model for permeation in polymer membrane. The model allows the membrane separation process of dialysis, reverse osmosis, gas separation and pervaporation. The fundamental mechanism of gas transport across a polymer membrane had been proposed by Sir Thomas Graham more than a century ago [8-9]. This mechanism model is known as the solution-diffusion model in which permeants dissolve in the membrane material and then diffuse through the membrane down a concentration gradient. A separation is achieved between different permeants because of differences in the amount of material that dissolves in the membrane and the rate at which the material diffuses through the membrane. Therefore, the solution-diffusion model has postulated a three-step process for gas transport through a polymer: 1) dissolution of the gas into the high-pressure (or high chemical potential) upstream face of the polymer, 2) diffusion of the gas through the polymer, and 3) desorption from the low-pressure (i.e., low chemical potential) downstream face of the polymer. Steps 1 and 3 are very fast relative to step 2, so diffusion through the polymer is the rate-limiting step in mass transport across a membrane.

3. Concentration and pressure gradients in membranes

The permeability coefficient for a particular component can therefore be described as the product of the solubility and diffusion coefficient. The basic concept of a membrane separation process is schematically depicted in Figure 2. For a binary or multicomponent gas mixture, the separation can be achieved using a polymeric membrane which exhibits different resistance to the transport of various molecules. The ratio of permeability of the more permeable component to that of the less permeable through the membrane is known as the selectivity of the

membrane. The resistance to molecular flow across a membrane is a function of chemical and physical properties of the penetrant molecules such as polarity, chemical affinity with the membrane, molecular size and shape of penetrant.
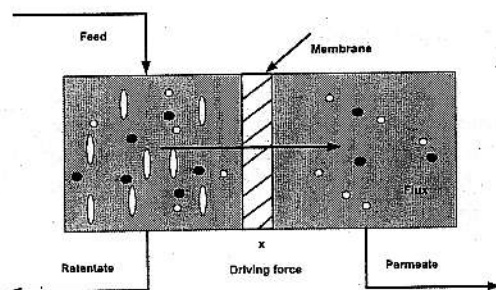

Figure 2: The basic concept of membrane separation process.

The starting point for the mathematical description of permeation in all membranes is the proposition, solidly based in thermodynamics that the driving forces of pressure, temperature, concentration and electromotive force are interrelated and the overall driving force producing movement of a permeant is the gradient in its chemical potential. The diffusion is the process by which a small molecule (organic liquids, vapours, gases, etc.) is transferred in the system due to random molecular motions. It is a kinetic term that reflects the penetrant mobility in the polymer phase. Consider a polymer membrane of thickness l, of surface A subjected to a fluid and Q, is the total amount of penetrant that has passed through this membrane at time t. The diffusive flux of a penetrant molecule (J) is the quantity of penetrant crosses the polymer membrane during one unit of time and area of penetrant molecule (J), is given by,

$$J = Q/At \qquad (1)$$

The Fick's first law establishes a linear relation between the flux of substance diffusing through a membrane and the concentration gradient between both sides of the membrane:

$$J = -D \left(\partial c / \partial x \right) \qquad (2)$$

where D is the diffusion coefficient (cm^2/s). This first law is applicable in the steady state when the concentration does not vary with time and the flux is constant. On the other hand, Fick's second law describes the nonsteady state for transport process, which is given by the rate of change of the penetrant concentration $\left(\partial c / \partial x \right)$ at a plane within the membrane, i.e.

$$\left(\frac{\partial c}{\partial t} \right) = D \left(\frac{\partial c^2}{\partial x^2} \right) \qquad (3)$$

This is an ideal case in which the membrane is isotropic and the diffusion coefficient is independent of distance, time and concentration. Depending on the boundary conditions, many solutions are available from Eq. (3). Strong polymer penetrant interaction occurs with many organic penetrant molecules. Hence D is depending on concentration. Therefore, Eq. (3) becomes,

$$\left(\frac{\partial c}{\partial t} \right) = D \frac{\partial D(c)(\partial c / \partial x)}{\partial x} \qquad (4)$$

Analytically, this cannot be solved easily and hence another form of Eq. (4) is commonly used as in Eq (5),

$$\left(\frac{\partial c}{\partial t} \right) = D(c) \frac{\partial c^2}{\partial x^2} + \frac{\partial D(c)}{\partial c} \left(\frac{\partial c}{\partial x} \right)^2 \qquad (5)$$

Generally experiments are conducted over a relatively small interval of c and the term $(\partial D(c)/\partial c)$ is negligible compared to $D(c)$. Then we get a mean or integral diffusion coefficient D over a concentration range c_1 to c_2, as given by

$$D = \int_{c_1}^{c_2} D(c) \, dc/(c_1 - c_2) \qquad (6)$$

where c_1 and c_2 is are the concentrations of penetrant at the low and high concentration faces of the membrane, respectively. In the steady state condition, diffusion flow is constant and the diffusion coefficient is independent of concentration. In this case Equation (2) may be integrated to give

$$J = \frac{D(c_1 - c_2)}{l} \qquad (7)$$

where l is the membrane thickness. The penetrant distribution between the penetrant and the polymer phase is described by the Nernst distribution law as,

$$c = KC \qquad (8)$$

where c is the sorbed concentration, C is the ambient penetrant concentration in contact with the polymer surface and K depends on temperature and c. In the case of transport of gases and vapours, pressure p is used instead of surface concentration. According to Henry's law,

$$c = S*p \qquad (9)$$

where S is the solubility coefficient. The combination of Eqs (6) and (8) gives the well known permeation equation,

$$J = \frac{DS(p_1 - p_2)}{l} \qquad (10)$$

where p_1 and p_2 are the ambient pressures on two sides of a membrane of thickness l. The product DS is called the permeability coefficient P, so that

$$P = D*S \qquad (11)$$

The diffusion coefficient D and solubility coefficient S are then calculated as

$$D = \frac{l^2}{6\theta} \qquad (12)$$

$$S = \frac{P}{D} \qquad (13)$$

where θ is the time lag (sec) and l is the membrane thickness (cm). In terms of permeability, the flux Eq. (10) can be written as

$$J = \frac{P(p_1 - p_2)}{l} \qquad (14)$$

In case of separation a binary mixture of gases A and B is shown in Figure 3. The mol fraction of A on the upstream side of membrane is x_A and the mole fraction of A on the downstream or low pressure is y_A. The upstream pressure, p_1 is greater than the downstream pressure, p_2. The flux of A across the membrane can be written as

$$J_A = \frac{P_A}{l}\left(x_A p_1 - y_A p_2\right) \qquad (15)$$

A similar expression can be written for component B as

$$J_A = \frac{P_B}{l}\left[(1 - x_A)p_1 - (1 - y_A)p_2\right] \qquad (16)$$

4. Analytical model

The mole fraction of gas A on the permeate or downstream side of the membrane is given by the flux of component A through the membrane divides by the total gas flux the membrane

$$y_A = \frac{J_A}{J_A + J_B} \qquad (17)$$

$$y_A = \frac{\frac{P_A}{l}(x_A p_1 - y_A p_2)}{\frac{P_A}{l}(x_A p_1 - y_A p_2) + \frac{P_B}{l}\left[(1 - x_A)p_1 - (1 - y_A)p_2\right]} \qquad (18)$$

Equation 18 can be reorganized as follows to permit a direct calculation of permeate purity:

$$y_A = \frac{\left[1 + (\alpha - 1)(\frac{1}{h} + x_A)\right]}{\frac{2}{h}(1 - \alpha)}\left[\left(1 + \frac{\frac{4}{h}(1 - \alpha)\alpha x_A}{\left[1 + (\alpha - 1)(\frac{1}{h} + x_A)\right]^2}\right)^{1/2} - 1\right]$$

$$(19)$$

where the selectivity, α is defined as the ratio of permeability coefficients $(\alpha = P_A/P_B)$ and the pressure ratio, h is defined as the ratio of feed to permeate pressure $(h = p_1/p_2)$. The permeability coefficient for several polymer and gas can be found from the literature. The data is shown in Table 1.

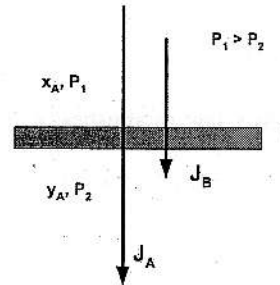Figure 3: Schematic diagram of a gas separation membrane of thickness l being used to separate a gas mixture of component A and B.

Table 1: Oxygen and Nitrogen permeability in selected polymer [2,4,8]

Polymer	α O₂/N₂
Poly(1-trimethylsilyl-propene)	1.6
Poly(dimethyl siloxane)	2
Poly(4-methyl-1pentene)	4.2
Poly(phenylene oxide)	4.4
Ethyl cellulose	3.4
6FDA-durene	3.84
Polysulfone	5.8
Polyaramid	6.8

5. Effect of pressure ratio, feed composition and membrane selectivity on predicted permeate purity

Figure 4 shows the effect of pressure ratio on the composition product. As the pressure ratio increases, the permeate mole fraction y_A will increase. If the downstream pressure decreases toward zero or $r \to \infty$ then Equation (18) becomes,

$$y_A = \frac{\alpha x_A}{1 + (\alpha - 1)x_A} \qquad (20)$$

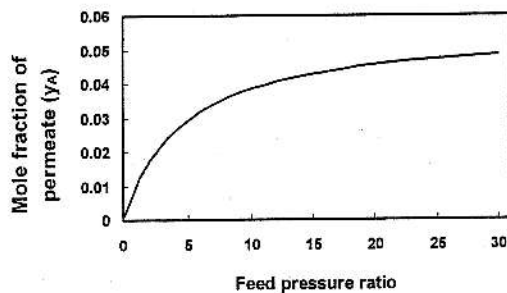and the composition product is limited by membrane selectivity.

Figure 4: Effect of feed pressure ratio on the mol fraction of permeates at 1 mole percent of component A on the feed and a membrane selectivity of 5.8 (Polysulfone)

The effect of membrane selectivity on the product composition could be seen in Figure 5. As the polymer membrane selectivity increases, the product mole fraction y_A increases and y_A achieve the maximum value at the point that the partial pressure of component A on the upstream side (x_A p_1) of the membrane equals that on the downstream side (y_A p_2). Therefore, at high selectivity the mole fraction of component A on the downstream is limited by the pressure ratio. Thus, at the limited condition Equation (18) reduces to,
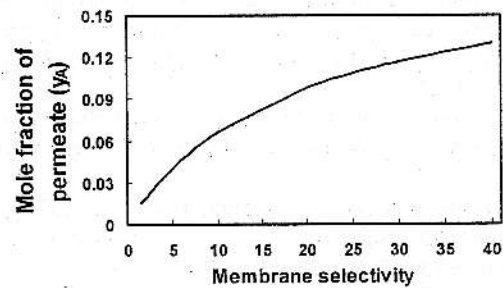
$$y_A = h x_A \qquad (21)$$

Figure 5: Effect of membrane selectivity on the mol fraction of permeate at 1 mole percent of component A on the feed and a pressure ratio of 20

The effect of feed composition is depicted in Figure 6. The mole fraction or the purity of product increases as the mole fraction of component A increases.
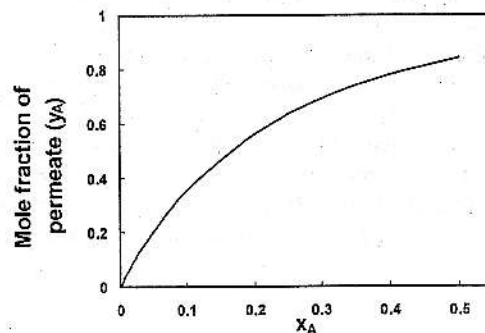

Figure 6: Effect of feed composition on the product purity membrane selectivity (polysulfone) and pressure ratio of 20

6. Conclusion

This paper has discussed on the application of polymer membranes as separation agents. The gas transport phenomenon can be described by solution-diffusion model. The model can be assist student to understand the performance of gas separation membrane better.

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