

A New Resistance Model for Interpretation of Gas Permeation Data of Composite and Asymmetric Membranes

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Abstract

In this work a new resistance model has been presented based on that of Henis-Tripodi which can be used for interpretation of gas permeation data in composite and asymmetric membranes. In contrast to the previous works, in this model the fraction of the support layer surface that includes the pores filled with coating material has been taken into account. The influences of the filled pores on separation factor and the gas permeation through composite and asymmetric membranes as well as the influence of the effective thickness of substrate on the filled pores have also been analyzed. Then the corresponding unknown parameters for gas separation of the composite and asymmetric membranes have been characterized by nonlinear regression and the results were compared with those of the experimental data from the literature. The pressure dependence of the gas permeability coefficient in glassy polymer has also been considered. The model shows improvement with respect to its capability in the interpretation of the permeation data of gas mixtures by composite and asymmetric membranes.

Keywords: Gas permeation, Asymmetric membrane, Composite membrane, Resistance model, Coating material

Introduction

The industrial application of gas separation membrane processes became possible as a result of the development of composite and asymmetric membranes. The first commercial membrane system for oxygen-enriched air was developed [1]. Subsequent successful applications include hydrogen recovery from ammonia synthesis purge; syngas composition adjustment, nitrogen generation from air [2] and natural gas processing [3,4].

Transport of gases through such membranes is mostly described by "resistance model, RM". These membranes consist of a porous asymmetric substrate, whose dense layer plays a predominant role in separation efficiency, and a coating layer, whose function is to plug the pores in the dense layer of the substrate [5]. The concept of RM type composite membrane was brought forward by Henis and Tripodi [6] In their research, a porous asymmetric polymer substrate was coated with silicone rubber

with high permeability and very low selectivity and the mass transfer through membrane was described by analogy with electric circuits [5]. According to the Henis and Tripodi's model, a gas first permeates through the coating layer and then the flow splits in two parts: one through the polymer matrix and the other through the pores that are filled with coating material. This model was shown to be very useful in elucidating the relationship between the resistance components and the membrane permselectivity and has been used as the basis for further membrane development [2].

According to Henis and Tripodi's model, the resistance of porous support layer in the substrate is generally negligible [6]. However, they believed that when the coating material does not penetrate to the full depth of the pores, but penetrates to only 0.1% or 0.01% of that depth, the results are much the same. This means that

the composite membrane will have a very high separation factor with a very low degree of penetration. The issue is still open to discussion [7].

Further researches were carried out by Kimmerle, et. al [8] and Ashworth [9] who have assumed that the coating materials penetrate and completely fill the pores of the dense layer. He et al [7] established an improved RM, taking into account the depth of penetration of coating material into the defects or pores of the dense layer. In addition, Fouda et al [10] proposed a Wheatstone-bridge model for the transport of gases through composite membranes, which allow calculating the effective pore area and the effective thickness of the skin layer of the porous substrate. The Wheatstone-bridge model can calculate Henis's model as a special case. Feng et al [2] proposed an alternative RM, in which not only the depth of penetration of the coating material in the pores of substrate but also the incomplete plugging of the pores were taken into account. In addition, Peng et al [5] proposed resistances-in-series-model which was based on that of Henis-Tripodi [6] as well as the theory of the boundary layer for gas separation in composite membranes [5].

In this paper we have made some modifications to Henis and Tripodi's resistance model and proposed an improved resistance model. Thus in this study three groups of pores are characterized, first are pores which are completely filled with coating material up to the full depth (L_{eff}), second are those which are partially filled and the third those which are not filled at all. An important and surprising characteristic of the RM for composite membranes described here is the fact that the porous substrate contributes to the separation significantly, therefore the porous substrate was first considered as a separate membrane and the characteristic of the asymmetric substrate was determined. Then the resistance of the coating layer was added.

2. Theory

In this paper we consider the behavior of composite and asymmetric membranes consisting of porous asymmetric substrate with a coating material, applied onto the substrates' surfaces.

2.1. Description of the asymmetric membrane

Asymmetric membranes made from glassy polymers are widely used in separation processes in gas industries. These membranes have a very thin and dense skin integrated with a porous supporting layer. The thickness, porosity and pore sizes of the skin layer determine the permeability and selectivity of the asymmetric membrane for a given operating pressure and temperature. For gas separation, the membrane must have small enough porosity and pore size so as to increase the selectivity, and a thinner skin layer so as to improve gas permeation flux. In addition, the substructure of the asymmetric membrane should have good mechanical strength with negligible gas transport resistance. Asymmetric membranes, having different structures, can be prepared by the selection of suitable membrane making procedures [11].

These asymmetric membranes may be classified according to surface defects into three groups, as described below;

- (1) The skin layer has a large fraction of defects. The transport behavior of gases through this group of asymmetric membranes is similar to those in porous membranes, which is controlled predominantly by pore flow. Many models and equations have been developed to describe gas transport through porous media [11]. Without a coating layer to seal the defects on the surface of the asymmetric membrane, this group of membranes is not commercially attractive due to their low selectivity.
- (2) The skin layer is "defect-free". Gas transport in this group, is similar to that in the dense polymer film, which can be described by the solution-diffusion mechanism.

(3) The skin layer has a small fraction of defects. When gases transport through this kind of membrane, the overall permeation flux would be the combination of the pore flow and solution-diffusion flow. The relative contribution of each term is determined by the membrane structure parameters and operating pressure and temperature. The ideal separation factor of this kind of asymmetric membrane for a given gas pair, is higher than that of predicted by the Knudsen diffusion mechanism but lower than that predicted by solution-diffusion mechanism.

In general, surface defects of asymmetric membranes could be repaired using the well-known technique developed by Henis and Tripodi based on surface coating with highly permeable materials such as silicon rubbers. In the fabrication and application of the surface coated asymmetric membranes, the situation that the surface defects are not completely plugged may sometimes occur. As a result, the separation factor is lower than "defect-free" membrane [11].

A few experimental studies have been reported in the literature on gas transport through asymmetric membranes with a small fraction of surface defects. A combined transport model which takes into account the pore flow model and dual-mode transport model was used to explain the gas permeation in these membranes [19,20]. A mathematical model which accounts for gas transport through the porous medium and dense medium of the skin layer has been derived to determine skin layer structure parameters based on gas permeation characteristics. The unknown parameters of model have been evaluated by nonlinear regression. The method is described in Appendix 1

2.1.1. Porous polymeric asymmetric membrane

Schematic representations of the cross section of porous polymeric asymmetric membrane as well as the electrical circuit analog of it are shown in Figure 1. We

define three regions in this substrate membrane. The surface region, that is skin with a thickness of L_{eff} , denoted as 1 in the figure, the defects or pores in the skin, denoted as 2, and the porous matrix region, denoted as 3.

The total resistance to permeate flow, R_t , in the porous substrate membrane is a function of the resistance to flow in each of the regions. Referring to Figure 1, R_3 is the resistance to gas flow through the porous region of the substrate membrane and is very small relative to R_1 , R_2 ($R_3 \cong 0$). According to the electrical circuit analog, the total gas flow rate (Q_{total}) can be determined using equation (1):

$$Q_{total} = Q_1 + Q_2 \quad (1)$$

Where Q_1 and Q_2 are gas flow rates through zone 1 and zone 2, respectively.

In zone 1 which is the dense part of surface region, transport mechanism is defined by the solution-diffusion model (dual mode model). Transport mechanism in region 2 which is the defects or pores in the skin layer, is based on pore flow model. These models are discussed briefly below.

Glassy membranes are made from polymers that operate below their glass transition temperature. Their polymer chains are rigid and glass-like. For this type of membranes permeation mechanism is different and follows the dual-mode sorption model.

This model initially assumed a complete immobilization of the gas molecules sorbed in the Langmuir mode. Researchers made plausible that these molecules were only partially immobilized. Therefore, the extended dual-mode sorption model assumes two distinct diffusion coefficients, D_H and D_L characterizing the mobility of component i in the Henry and Langmuir domains, respectively. Combination of this assumption with the general solution-diffusion equation results in an equation for the permeability coefficient as a function of pressure.

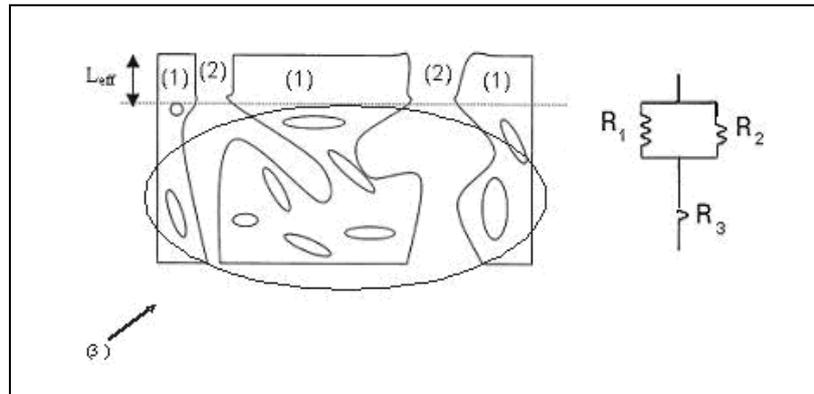


Figure 1: Schematic representation of a porous asymmetric membrane cross sectional view and electrical circuit analog

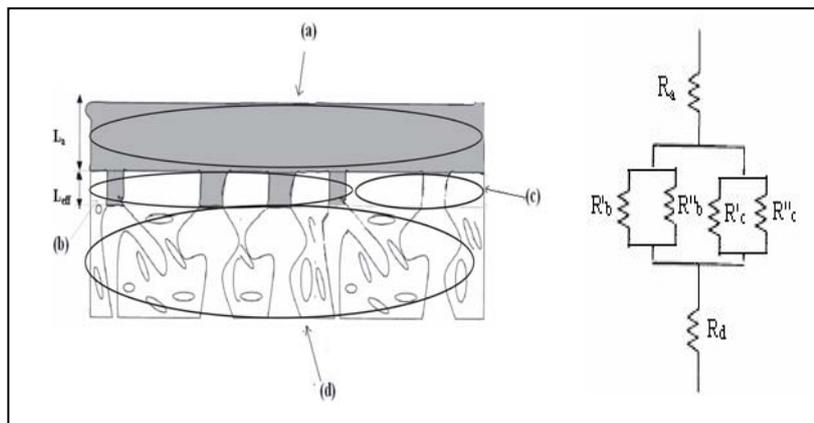


Figure 2: A cross section of a composite membrane along with the electrical circuit analog

Therefore, the permeability coefficient of pure gases through dense membrane with dual-mode sorption model is given by:

$$P = k_D D_H \left[1 + \frac{FK}{(1 + b p_o)(1 + b p_L)} \right] \quad (2)$$

Where $F = D_L/D_H$ and $K = C_s b/k_D$. [16, 17, 21]

For porous membrane, with normal (Gaussian) pore size distribution between $r = 0$ and $r = r_{max}$, based on kinetic theory of gases, four mechanisms may be postulated for transport of gases in capillaries (pores), namely [15]:

1. If the ratio of pore radius to the mean free path of the gas is less than 0.05, ($r/\lambda < 0.05$), then Knudsen flow exists.
2. If $0.05 < r/\lambda < 50$, slip flow prevails
3. If $r/\lambda > 50$, viscous flow exists
4. In addition to transport of the gases through the pores by the above three

mechanisms, a portion of the gas flows by surface flow which results from the gas-membrane interaction at the pore wall of the membrane.

λ is the mean free path which for each gas molecules.

For a single pore of radius r , the contributions of Knudsen, viscous and slip flow to flux are:

For Knudsen flow:

$$q_k = \left(\frac{32\pi}{9MRT} \right)^{1/2} \frac{r^3 \Delta P}{L} \quad (3)$$

For viscous flow:

$$q_v = \frac{\pi^4 \bar{P} \Delta \bar{P}}{8\eta r TL} \quad (4)$$

For slip flow:

$$q_{st} = \frac{\pi^3 \Delta P}{MCL} \quad (5)$$

\bar{C} is the molecular mean velocity.

The total contribution of the first three mechanisms is calculated from:

$$Q_g = Q_k + Q_{sl} + Q_v \quad (6)$$

$$Q_g = \sum_{r=0}^{0.05\lambda} N(r)q_k + \sum_{r=0.05\lambda}^{50\lambda} N(r)q_{sl} + \sum_{r=50\lambda}^{r_{\max}} N(r)q_v \quad (7)$$

From substitution Eq. (3), Eq. (4), Eq. (5) into Eq. (6) and replacement of the summations with integrals:

$$Q_g = \frac{N_t}{L} [G_1 I_1 + G_2 I_2 + G_3 I_3] \Delta P \quad (8)$$

In which:

$$G_1 = \left(\frac{32\pi}{9MRT} \right)^{1/2} ; \quad G_2 = \frac{\pi}{MC} ; \quad G_3 = \frac{\pi \bar{P}}{8\eta RT} \quad (9)$$

$$I_1 = \frac{1}{\sqrt{2\pi}\sigma} \int_{r=0}^{0.05\lambda} r^3 \exp \left[-\frac{1}{2} \left(\frac{r-\bar{r}}{\sigma} \right)^2 \right] dr \quad (10)$$

$$I_2 = \frac{1}{\sqrt{2\pi}\sigma} \int_{r=0.05\lambda}^{50\lambda} r^3 \exp \left[-\frac{1}{2} \left(\frac{r-\bar{r}}{\sigma} \right)^2 \right] dr \quad (11)$$

$$I_3 = \frac{1}{\sqrt{2\pi}\sigma} \int_{r=50\lambda}^{r_{\max}} r^4 \exp \left[-\frac{1}{2} \left(\frac{r-\bar{r}}{\sigma} \right)^2 \right] dr \quad (12)$$

In porous membranes, a small portion of the gas molecules that pass through the dense layer adsorbs onto the pore walls and then is transferred across the membrane by surface flow.

For calculating surface flow, the following formula is presented based on two dimensional force balances on an adsorbed film of diffusers [15]

$$Q_s = \frac{RT\rho_{app}}{2000\tau C_R L^2} \frac{I_4}{I_5} \int_{p_L}^{p_2} \frac{X^2}{p} dp \quad (13)$$

In which:

$$I_4 = \int_{r=0}^{r_{\max}} N(r)r^2 dr \quad (14)$$

$$I_5 = \int_{r=0}^{r_{\max}} N(r)r dr \quad (15)$$

In Eq.13, X is the absorption isotherm. If this isotherm is described by Henry's law:

$$X = k_D p \quad (16)$$

Gas flux of surface flow mechanism is given by [15]:

$$Q_s = \frac{RT\rho_{app}}{2000\tau C_R L^2} \frac{I_4}{I_5} \int_{p_L}^{p_2} k_D^2 p dp = A_2' \frac{I_4}{I_5} \bar{p} \Delta p \quad (17)$$

Where A_2' is given by:

$$A_2' = \frac{RT\rho_{app}}{2000\tau C_R L^2} k_D^2$$

Finally the total gas flux from all four mechanisms in porous membrane is:

$$Q_{total} = Q_g + Q_s = \frac{N_t}{L} [G_1 I_1 + G_2 I_2 + G_3 I_3] \Delta p + A_2' \frac{I_4}{I_5} \bar{p} \Delta p \quad (18)$$

So gas permeance in porous membrane is [15]:

$$J_{total} = \frac{Q_{total}}{S_{total} \Delta p} = A_1 [G_1 I_1 + G_2 I_2 + G_3 I_3] + A_2 \frac{I_4}{I_5} \bar{p} \quad (19)$$

In which:

$$A_1 = \frac{N_t}{S_{total} L} , \quad A_2 = \frac{RT\rho_{app}}{2000\tau C_R L^2 S_{total}} k_D^2$$

Therefore the total gas permeance through asymmetric membrane is expressed as:

$$J_{total} = \frac{N_t}{L S_{total}} (G_1 I_1 + G_2 I_2 + G_3 I_3) + \frac{A_2'}{S_{total} I_5} \frac{I_4}{p} + \frac{S_1}{S_{total} L_{eff}} p \quad (20)$$

For asymmetric membranes suitable for gas separation, the surface porosity has to be very small (usually less than 10^{-5}) [11]. In this case, Equation (20) can be simplified as:

$$J_{total} = A_1 (G_1 I_1 + G_2 I_2 + G_3 I_3) + A_2 \frac{I_4}{I_5} \frac{p}{L_{eff}} + \frac{p}{L_{eff}} \quad (21)$$

2.2. Simplified description of the composite membrane

In general surface defects of asymmetric membranes could be repaired by surface coating using highly permeable elastomers such as silicon rubbers. The pore sizes on the substrate skin are not normally uniform, therefore there is no guarantee that all the pores, are filled completely by the coating

material down to the same depth since different pore sizes will cause different capillary forces for penetration of the coating solution into the pores. Thus in this study three groups of pores are characterized, first are pores which are completely filled with coating material up to the full depth (L_{eff}), second are those which are partially filled and the third are those which are not filled at all. A schematic representation of the cross section of such composite membrane is shown in Figure 2.

We define four regions in composite membranes as shown in Figure 2:

1. The coating layer of thickness L_a , with R_a as the resistance of the coating layer.
2. The dense layer where coating material penetrates through the full depth (L_{eff}), denoted by "b", with R'_b as the resistance of the dense portion of the skin layer; R''_b is the resistance of the pores or defects that are filled by coating material.
3. The dense layer in which the pores or defects are not filled, that is denoted by "c", with R'_c as the resistance of the dense portion of the skin layer and R''_c as the resistance of the pores or defects.
4. The highly porous substrate region, denoted by "d", with R_d as the resistance of the porous matrix.

The relationship between permeability coefficient (P) and permeance (J) are defined as:

$$Q = \frac{P S \Delta p}{L}, Q = J S \Delta p \Rightarrow J = \frac{P}{L} \quad (22)$$

Then the gas flow rate through each region is described according to the mechanism of mass transport in that region at steady state. Accordingly, from the mass balance:

$$Q_{\text{total}} = \Delta p_{\text{total}} \left(\frac{P}{L} \right)_{\text{total}} S_{\text{total}} = Q_a = Q_b + Q_c \quad (23)$$

Where

$$Q_a = \frac{P_a}{L_a} S_{\text{total}} \Delta p_1 = \left(\frac{P}{L} \right)_a S_{\text{total}} \Delta p_1 \quad (24)$$

It has been assumed that the length of the pores or defects of section b is equal to the effective thickness of substrate ($L_{\text{eff}} = L'_b = L''_b$) and as mentioned before, the surface porosity is very small. Then:

$$\varepsilon = \frac{S''_b}{S_b} \Rightarrow \frac{S'_b}{S_b} = 1 - \varepsilon \cong 1 \quad (25)$$

$$\begin{aligned} Q_b &= \left(\frac{P}{L} \right)_b S_b \Delta p_2 = \frac{P'_b}{L_{\text{eff}}} S'_b \Delta p_2 + \frac{P''_b}{L_{\text{eff}}} S''_b \Delta p_2 \\ &\Rightarrow \left(\frac{P}{L} \right)_b S_b = \frac{P'_b}{L_{\text{eff}}} S'_b + \frac{P''_b}{L_{\text{eff}}} S''_b \\ &\Rightarrow \left(\frac{P}{L} \right)_b = \frac{P'_b}{L_{\text{eff}}} \frac{S'_b}{S_b} + \frac{P''_b}{L_{\text{eff}}} \frac{S''_b}{S_b} \\ &\Rightarrow \left(\frac{P}{L} \right)_b = \frac{P'_b}{L_{\text{eff}}} + \frac{P''_b}{L_{\text{eff}}} \varepsilon \end{aligned} \quad (26)$$

Region (c) acts according to the asymmetric membrane (see: Eq. (21)), then:

$$Q_c = J_c S_c \Delta p_2, \quad J_c = \left(\frac{P}{L} \right)_c \quad (27)$$

Considering the above equations the following equation is obtained:

$$\left(\frac{P}{L} \right)_a \Delta p_1 = \left[\left(\frac{P}{L} \right)_b \frac{S_b}{S_{\text{total}}} + J_c \frac{S_c}{S_{\text{total}}} \right] \Delta p_2 \quad (28)$$

The percent of support surface that includes the pores filled with coating material θ is defined as:

$$S_b + S_c = S_{\text{total}} \Rightarrow \frac{S_b}{S_{\text{total}}} \times 100 = \theta \quad (29)$$

Where $0 \leq \theta \leq 100$

Substituting Eq. (26) and Eq. (29) into Eq. (28):

$$\left(\frac{P}{L} \right)_a \Delta p_1 = \left\{ \left[\left(\frac{P'_b}{L_{\text{eff}}} \right) + \left(\frac{P''_b}{L_{\text{eff}}} \right) \varepsilon \right] \frac{\theta}{100} + J_c \left(1 - \frac{\theta}{100} \right) \right\} \Delta p_2 \quad (30)$$

2.2.1. Calculation of θ for a given pressure differential and permeance

In order to calculate θ , pressure differentials of the two layers ($\Delta p_1, \Delta p_2$) have to be determined. From Eq. (23) and Eq. (24):

$$Q_a = \Delta p_1 \left(\frac{P}{L}\right)_a S_{total} = Q_{total} = \Delta p_{total} \left(\frac{P}{L}\right)_{total} S_{total} \Rightarrow \Delta p_1 \left(\frac{P}{L}\right)_a = \Delta p_{total} J_{total} \quad (31)$$

$$\left(\frac{P}{L}\right)_a \Delta p_1 = \left[\left(\frac{P}{L}\right)_b \frac{\theta}{100} + \left(\frac{P}{L}\right)_c \left(1 - \frac{\theta}{100}\right) \right] \Delta p_2 \quad (32)$$

In the above equation by specifying the quantities of J_{total} , Δp_{total} and $\left(\frac{P}{L}\right)_a$, the values of Δp_1 , Δp_2 and subsequently θ are obtained.

For calculation of the permeability coefficient, the pressure within the membrane layers (p_m) is required. However, the pressure can only be known at upstream (p_o) and downstream (p_L) sides of the membrane. For calculating interlayer pressure, however, mass conservation law can be used which is described by the following flowchart (Figure 3).

2.2.1. Calculation of permeance for a given pressure differential and θ

According to Eq (30);

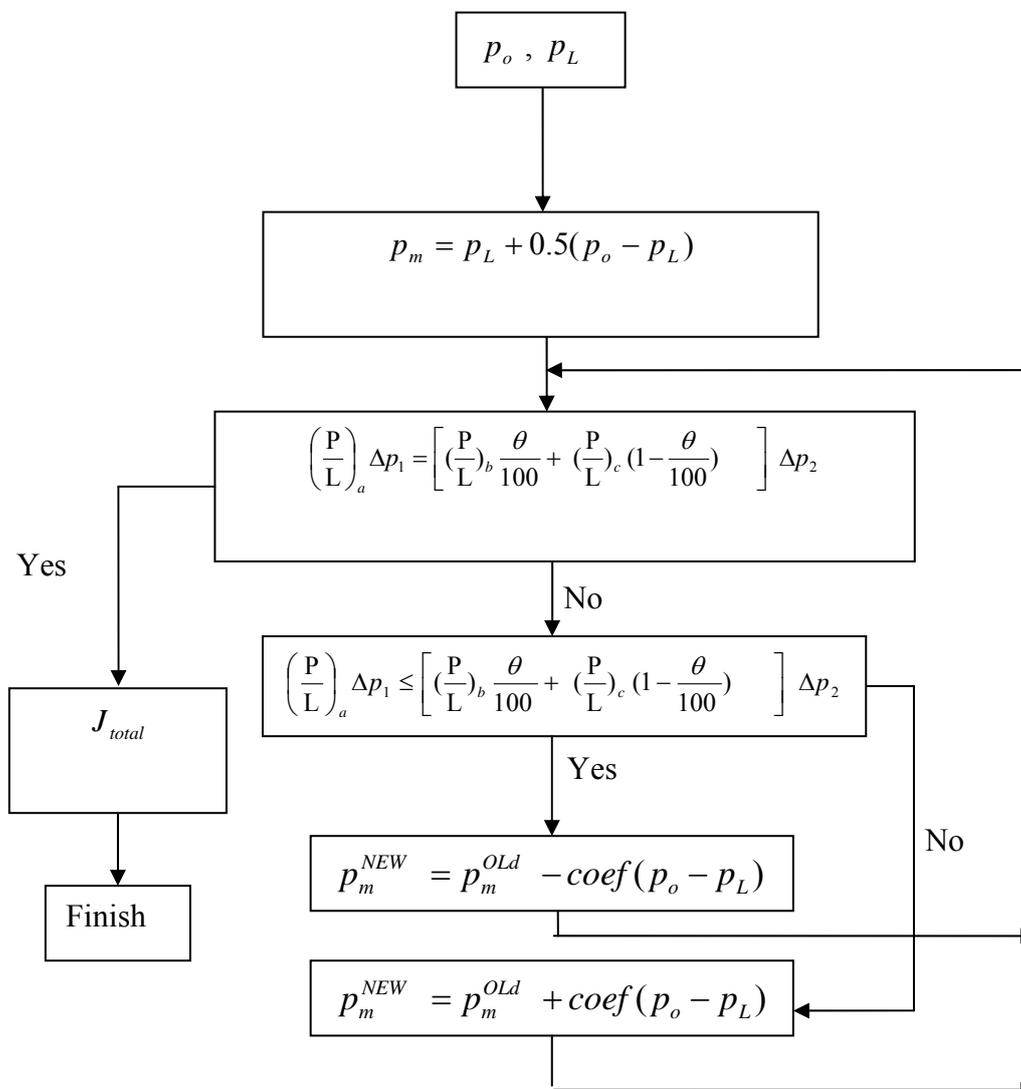


Figure 3: Calculation of the total permeance across composite membranes

Table 1: Model parameters' results for H₂

$(A^\circ)L_{\text{eff}}$	$\left[\frac{1}{m^3}\right] A_1 \times 10^{-16}$	$\left[\frac{\text{kmol}}{m^3 \cdot s \cdot \text{pa}^2}\right] A_2 \times 10^9$	$(A^\circ) \bar{r}$	$(A^\circ) \sigma$
20000	3.03	1.89	62.73	7.84

Table 2: Model parameters' results for N₂

$(A^\circ)L_{\text{eff}}$	$\left[\frac{1}{m^3}\right] A_1 \times 10^{-16}$	$\left[\frac{\text{kmol}}{m^3 \cdot s \cdot \text{pa}^2}\right] A_2 \times 10^{10}$	$(A^\circ) \bar{r}$	$(A^\circ) \sigma$
20000	6.13	8.40	47.34	5.05

3. Results and discussion

For assessing this model, gas flow rates through asymmetric and composite membranes under various operating pressures should be known. For this purpose the data obtained by Wang et al. were used in this work. An asymmetric polysulfone membrane was prepared and gas flow rates under various operating pressures were determined. Then coating was carried out using silicon rubber. H₂ and N₂ were used as test gases. The methods for membrane preparation and permeation tests have been described in detail in literature [12].

For calculating the parameters of the pore flow and dual-mode sorption models, the following numerical values were used in this study [2, 13, 14]. The parameters S , C_s , b , and diffusion coefficients D_H and D_L are available for N₂ using polysulfone (PS) membranes, but such information on H₂ have not yet been published. Therefore, in this study for H₂ the intrinsic permeability coefficient has been used.

$$k_D(N_2, PS) = 0.0753 \left(\frac{\text{cm}^3}{\text{cm}^3 \cdot \text{atm}} \right)$$

$$b(N_2, PS) = 0.0156 \left(\frac{1}{\text{atm}} \right)$$

$$D_H(N_2, PS) = 1.03 \times 10^{-8} \left(\frac{\text{cm}^2}{s} \right)$$

$$D_L(N_2, PS) = 0.468 \times 10^{-8} \left(\frac{\text{cm}^2}{s} \right)$$

$$P(H_2, PS) = 1.216 \times 10^{-7} \frac{\text{cm}^3 \cdot \text{cm}}{\text{cm}^2 \cdot s \cdot \text{atm}} = 1.6 \times 10^{-9} \frac{\text{cm}^3 \cdot \text{cm}}{\text{cm}^2 \cdot s \cdot \text{cmHg}}$$

$$d(N_2) = 3.798 \text{ [}^\circ\text{A]}$$

$$\eta(N_2) = 178 \times 10^{-7} \text{ [pa.s]}$$

$$d(H_2) = 2.827 \text{ [}^\circ\text{A]}$$

$$\eta(H_2) = 90 \times 10^{-7} \text{ [pa.s]}$$

3.1. Asymmetric membrane

The method given in Appendix 1 was applied to the data obtained from the literature for hydrogen and nitrogen gases permeating through polysulfone asymmetric membrane determined experimentally under various operating pressures by Wang et al., [12]. The optimum values of the four parameters \bar{r} , σ , A_1 and A_2 determined by the method described above are given in Tables 1 and 2. It should be noted that the maximum pore size was set to 100°A in the above calculation.

The comparison between experimental and predicted values of J_{total} at different pressures for hydrogen is shown in Figure 4. It can be seen that the agreement between the two are clearly achieved. Figure 4 also shows the results for different individual mechanisms of transport. It is to be noted that at these pressures viscous flow does not appear. Corresponding to the above results and by calculating the parameters, the permeances of different mechanisms have been determined.

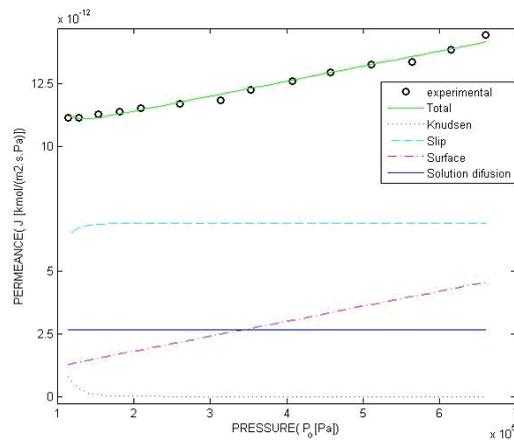


Figure 4: Experimental and calculated values of permeance J_{total} , vs. applied pressure and the contribution of different mechanism to the total permeance

Table 3: Effect of the effective thickness of substrate on the percent of filling

L_{eff} (°A)	θ (%)
12000	98
15000	92
20000	86

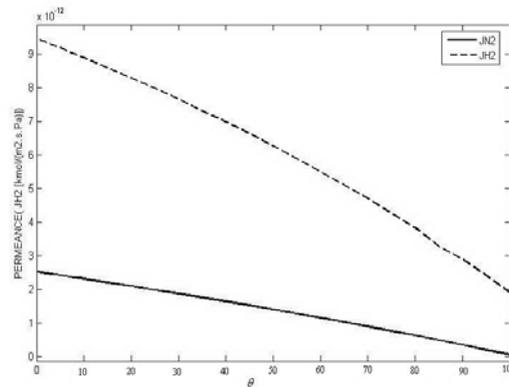


Figure 5: Effect of the degree of filling on the total gas permeance of composite membrane

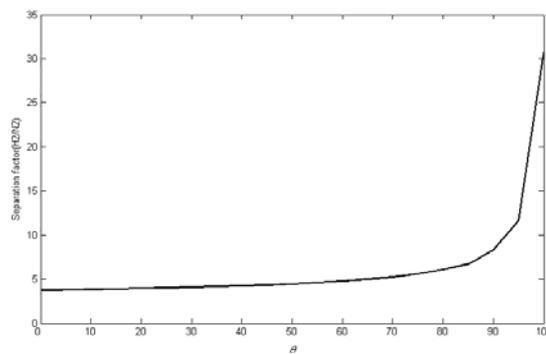


Figure 6: Effect of the degree of filling on the separation factor of composite membrane

3.2. Variation of L_{eff} of substrate with percent of filling

Table 3 shows that the probability of complete filling of pores or defects in the dense layer with coating materials is increased by a decrease in the effective thickness of substrate.

3.3. Effect of the percent of filling on total gas permeance and separation factor

The above method is used for calculation of permeance at a given pressure differential and θ . For this purpose, the data of Wang, et al. (1990) for silicone rubber coated polysulfone composite membrane was used). The following data were used for this calculation:

$$L_1 = 50000 \text{ [}^\circ\text{A]}$$

$$\Delta p = 5 \times 10^5 \text{ [pa]}$$

$$L_{\text{eff}} = 20000 \text{ [}^\circ\text{A]}$$

$$T = 298 \text{ [K]}$$

The ideal separation factor of gas i over gas j is calculated from the pure gas permeances by the following equation:

$$\alpha_j^i = \frac{J_i}{J_j} \Rightarrow \alpha_{N_2}^{H_2} = \frac{J_{H_2}}{J_{N_2}} \quad (33)$$

The influences of θ on the total gas permeance (H_2 , N_2) through the composite membrane as well as on the membrane separation factor α are shown in Figures 5 and 6, respectively. It is shown that the permeance of the fast moving gas (i.e. H_2), decreases more rapidly with θ , comparing to that of the slow moving gas (i.e. N_2). In other words, the effect of θ on permeance for the fast moving gas is stronger than for the slow moving gas. When the coating material penetrates completely through the pores or defects (i.e. when θ is increased), the pore flow is essentially eliminated where the solution-diffusion model is applicable and higher separation factor is obtained.

4. Conclusion

The improved resistance model introduced here describes the gas permeance process in asymmetric and composite membranes. It shows that the

percent of filling is the most important factor which influences the membrane separation properties.

The results show that the effect of θ on permeance for the fast moving gas is stronger than for the slow moving gas and when the coating material penetrates completely through the pores or defects (i.e. when θ is increased), the pore flow is eliminated where the solution-diffusion model is applicable and higher separation factor is obtained. Furthermore, the probability of complete filling of pores or defects in the dense layer with coating materials is increased by a decrease in the effective thickness of substrate.

The described model shows the permeances of different individual mechanisms of transport and it is able of considering the performance of membranes and reforming of membranes preparation methods.

APPENDIX 1:

Evaluation of unknown parameters

It was shown in this work that the transport of a gas through a asymmetric membrane can be fully characterized by Eq. (21). The quantities G_1, G_2 and G_3 can be calculated from the physical properties of the feed gas and the operating conditions, while the quantities I_1, I_2, I_3, I_4 and I_5 can be calculated when the pore size distribution is given by a normal distribution. The quantity \bar{p} is the average of the feed and the permeate gas pressures. The parameter A_1 is the ratio of the total number of pores per unit area of the membrane involving the adsorption and mobility characteristics of the each gas component in the membrane polymer. Note that parameters \bar{r}, σ and A_1 are related to the membrane pore structure, while A_2 is related to the interaction between gas molecules and the polymeric material of the membrane. It was shown that the transport of a gas through a membrane can be fully characterized by the four parameters \bar{r}, σ, A_1 and A_2 . In order to

determine these parameters, the gas permeability coefficient (J_{total}) values are obtained experimentally under various feed gas pressures, to give J_{expi} . Then, J_{total} values corresponding to a given set of \bar{r} , σ , A_1 and A_2 are calculated from Equation (21). The latter J_{total} values are called J_{calci} . Then sum the squared residuals (SS_R) is calculated according to the equation:

$$SS_R = \sum_{i=0}^n (J_{expi} - J_{calci})^2 \quad (34)$$

Accordingly a set of \bar{r} , σ , A_1 and A_2 which minimize SS_R , is obtained. In this study we have used a parallel local search technique. In most of optimization techniques, one should first assign the orders of parameters to guess an initial point. Hence for the first step, we have specified the orders of parameters as follows:

(\bar{r}): The quantity of mean pore radius is more than 0 and less than r_{max} .

(σ): The ratio $\frac{N(r)}{N_t}$ is equal to the probability density function ($f_R(r)$). Therefore the following equation can be defined and the quantities of σ and \bar{r} should also satisfy this equation [18].

$$\int_0^{r_{max}} f(r) dr = 1 \quad (35)$$

(A_1, A_2): For a given set of σ and \bar{r} equation (21) can be expressed as:

$$Y_i = a_i X_1 + b_i X_2 + c_i \quad (36)$$

A_1, A_2 were defined as independent variables and J was defined as dependent variable. And a_i, b_i and c_i are constant at a given mean pressure:

$$a_i = G_1 I_{1,i} + G_2 I_{2,i} + G_3 I_{3,i} \quad (37)$$

$$b_i = \frac{I_{4,i}}{I_{5,i}} \bar{p}_i, \quad c_i = \frac{P_i}{L_{eff}} \quad (38)$$

Therefore, for a given set of σ and \bar{r} :

$$SS_R = \sum_{i=1}^n [Y_{expi} - (a_i X_1 + b_i X_2 + c_i)]^2 \quad (39)$$

According to equation (39) a set of A_1, A_2 which minimizes SS_R is obtained by simultaneous solution of the following partial derivatives equations.

$$\frac{\partial SS_R}{\partial X_1} = 0, \quad \frac{\partial SS_R}{\partial X_2} = 0 \quad (40)$$

By this method the exact orders of A_1, A_2 were obtained.

In this study, the objective function (SS_R) is nonlinear, subject to the nonlinear constraints. Therefore Optimization Toolbox of Matlab (Fmincon function) was used for evaluating of unknown parameters. Fmincon attempts to find a minimum of a constrained nonlinear multivariable function. This is generally referred to as constrained nonlinear optimization or nonlinear programming.

Notations

b	Langmuir affinity parameter (pa^{-1})
C_R	Coefficient of resistance for the transport of absorbed molecules (kg/cm^2)
C_s	Pore saturation constant $\left[\frac{cc(gas)}{cc(polymer)} \right]$
\bar{C}	Mean speed of the gas molecules (m/s)
D	Diffusion coefficient (m^2/s)
M	Molecular weight of gas (kg/kmol)
N_t	Total number of pores
$N(r)$	Pore size Guassian distribution function
p	Pressure (pa)
Δp	Pressure differential across the membrane (pa)
\bar{p}	Mean pressure across the membrane (pa)
P	Permeability coefficient of gas in membrane ($\text{cc.cm}/\text{cm}^2.\text{s.cm-Hg}$)
P_a	Permeability coefficient of gas in the coating layer (region a)
P_b	Permeability coefficient of gas in the dense part of region (b)
P_b''	Permeability coefficient of gas in the pores of region (b) that are filled
P_c	Permeability coefficient of gas in the dense part of region (c)
r	Pore radius (m)

\bar{r}	Mean pore radius (m)	Δp_1	Pressure differential across the coating layer (pa)
r_{\max}	Pore radius of the largest pore (m)	Δp_2	Pressure differential across the substrate of composite membrane (pa)
R	Gas constant	S'_b	Nonporous area of region (b) [m ²]
k_D	Henry's law constant (ccs (gas)/cc (polymer).pa)	S''_b	Porous area of region (b) that is filled by coating material [m ²]
T	Temperature (K)	S_C	Area of region (c) [m ²]
X	Amount of gas absorbed in a given amount of membrane material (kmol/kg)	Q_a	Gas flow rate through region a
d	Collision diameter of gas molecules (m)	Q_b	Gas flow rate through region b
N	Avogadro number	Q_c	Gas flow rate through region c
L	Length of the pore (m)	ε	Surface porosity
S_{total}	Membrane area (m ²)	Subscripts	
q_k, q_v, q_{sl}	Quantity of gas transported through a single capillary by knudsen, viscous and slip flow respectively	L	Low pressure side
J	The gas permeance through the membrane [$\frac{\text{kmol}}{\text{m}^2 \cdot \text{pa} \cdot \text{s}}$]	o	High pressure side
A_1	Constant for a given membrane related to the porous structure [m ⁻³]	H	Henry's type
A_2	Constant related to surface transport [$\frac{\text{kmol}}{\text{m}^3 \cdot \text{s} \cdot \text{pa}^2}$]	L	Langmuir's type
A'_2	Constant related to surface transport [$\frac{\text{kmol}}{\text{m}^3 \cdot \text{s} \cdot \text{pa}^2}$]	K	Knudsen flow
L_{eff}	Effective thickness of substrate [m]	sl	Slip flow
L_1, L_a	Coating layer thickness [m]	v	Viscous flow
S_1	Nonporous area on the substrate [m ²]	s	Surface flow
p_o	Pressure on the high pressure side of the membrane (pa)	Greek letters	
p_L	Pressure on the low pressure side of the membrane (pa)	η	Coefficient of viscosity of gases (pa.s)
p_m	Pressure in the boundary (pa)	λ	Mean free path of gases (m)
		ρ_{app}	Apparent density of the membrane (kg/m ³)
		σ	Standard deviation for the pore size distribution (m)
		τ	Tortuosity factor for the pores
		θ	The percent of support surface with its pores filled with coating materia

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