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Transport study of pure and mixed gases through PDMS membrane

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Abstract

The permeation behavior of pure gases, binary and ternary gas mixtures of O_2, N_2 and CO_2 through poly(dimethylsiloxane) (PDMS) membrane was investigated with different pressures and compositions of feed gas. An analytical model expressed in terms of pressure and feed composition was derived from permeation behavior of pure gases and binary gas mixtures to predict quantitatively the flux and composition of permeated streams. Furthermore, the model was extended to the application of the ternary case and the results showed a good agreement with the experimental data. It was indicated that the model could be used to evaluate the separation properties and to choose the optimal feed conditions for the membrane separation system of O_2, N_2 and CO_2.

Keywords: PDMS membrane; Transport phenomena; Mixed-gas permeation; Analytical model

1. Introduction

Understanding the transport behavior of the target gases through membranes is the foundation of realizing effective separation of mixed gas and selecting the appropriate feed conditions. Generally, the permeation behavior of pure gas through membrane depends mainly on the properties of the gas and membrane as well as the feed conditions. As for gas mixture, the transport behavior of one component through membrane is affected by the presence of other penetrants so that it deviates from that of the pure gas. Therefore, using the permeation data of pure gas to estimate the separation properties of gas mixture may lead to wrong results. There have been extensive studies on the comparison of the difference between pure and mixed gas permeation behaviors [1–12]. The coupling effect (solution coupling and diffusion coupling) is an important factor that makes the transport behavior of mixed gas deviated from pure gas [1,6–9]. And the deviation is more prominent in glassy membranes than in rubbery membranes [6–8]. In addition, the plasticization effect greatly influences the transport, particularly in the case of the mixtures containing some components such as CO_2 and organic vapors. The condensable penetrants interact strongly on the membrane matrix, causing the swelling of matrix and the enhancement of the permeability [9–11]. Moreover, the concentration polarization that usually reduces actual permselectivity at low flow rates is another important factor contributing to the deviation phenomena [12].

In an actual membrane separation application, to optimize the separation design and determine the proper feed conditions, it is necessary to establish a mathematical model based on the available experimental data. The model can be used as a powerful tool to evaluate or predict the performance of the separation system at various feed conditions for a specific gas pair–membrane system. However, as far as we know, there are a few models being applied to predict practical performance of membranes as a function of experimental parameters. Ettouney and Majeed [7] developed permeability functions to describe the permeation behavior for pure and mixtures of N_2, O_2, CH_4 and CO_2 through polysulfone and silicone rubber membranes, in which the permeability of a component is expressed in a linear relationship with the partial pressure of the species. Prabhakar et al. [13] established a self-consistent model to describe the dependence of gas and vapor permeability on the concentration and temperature in rubbery polymers. The variation of the propane permeability with the permeate pressure was accurately predicted in their models. Conesa et al. [14] investigated H_2–N_2 binary gas mixtures transport across ceramic membranes, and derived a mathematical model based on mass balance to calculate successfully the composition of the penetrants as a function of the different experimental parameters.

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Nomenclature

D	diffusivity coefficient (cm^2/s)
l	the thickness of membrane (cm)
M	permeation parameter of a pure gas
M_{id}	the permeation parameter of the mixed system
p	the permeability coefficient (cm^3(STP) cm/(cm^2 s MPa))
ΔP	the pressure difference (MPa)
Q	the steady-state permeation flux ($cm^3/(cm^2\ s)$)
Q'_i	the permeation flux of ith gas ($cm^3/(cm^2\ s)$)
Q_t	the total permeation flux ($cm^3/(cm^2\ s)$)
S	solubility constant (cm^3(STP)/(cm^3 MPa))
t	permeation time interval (s)
V	the volume of permeation gas (cm)
X	the molar fraction of one component in feed stream
Y	the molar fraction of one component in the permeation stream
Greek letter	
ϕ	mol fraction

In this study, based on the permeation behavior of pure CO_2, N_2 and O_2 gas, binary gas mixtures including O_2–N_2, O_2–CO_2 and N_2–CO_2 through poly(dimethylsiloxane) (PDMS) membrane at various feed conditions, a simple and practical mathematical model expressed in terms of pressure and feed composition was derived to predict quantitatively the permeation flux and the composition of permeated stream. Furthermore, the model was extended to the application of the ternary case of O_2–N_2–CO_2, and the calculated results were compared with the experimental data.

2. Experimental

2.1. Materials

PDMS with an average molecular weight of 5000 was provided by Shanghai Synthetic Resin Company, PR China, and used without any further purification. *n*-Heptane solvent, tetraethyl orthosilicate (TAOS) curing agent and dibutyltin dilaurate (DBTDL) catalyst were obtained from Shanghai Chemical Agents Company, PR China. Cellulose acetate (CA) porous membrane was purchased from the Shanghai Xinya Purification Company, PR China. Nitrogen, oxygen and carbon dioxide used in the permeation experiments were purchased from Nanjing Tongguang Special Gas Company, PR China. All gases were guaranteed to have a purity of over 99% by the producer and used as received.

2.2. Membrane preparation

A casting solution consisted of 5 wt.% PDMS with proper ratio of TAOS and DBTDL in *n*-heptane. One kind of CA porous membrane was put on the surface of water in a basin to act as the support. Then the casting solution was cast on the CA porous membrane and the solvent was evaporated at ambient temperature for 6 h. The membrane was afterward put into a vacuum oven at 60 °C for 6 h to complete the cross-linking. The cross-sectional picture of PDMS composite membrane by SEM was shown in Fig. 1. It could be seen that the thickness of the PDMS skin layer was approximately 14 μm and the support layer was microporous structure, so the effect of the support layer on the gas transport across membranes could be negligible in comparison with that of dense PDMS layer.

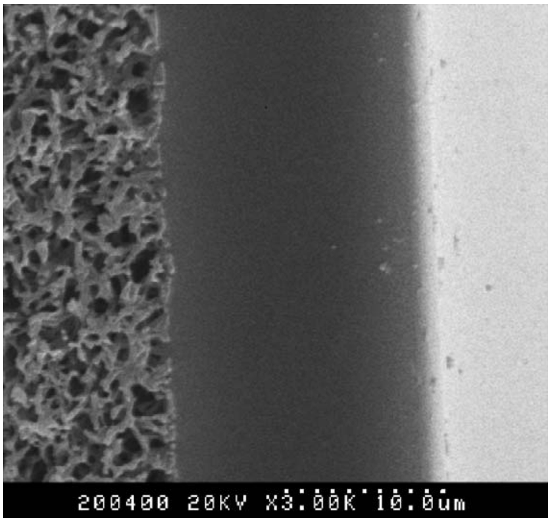

Fig. 1. Cross-sectional picture of PDMS composite membrane by SEM.

2.3. Permeation measurements

A schematic diagram of the gas permeation experiment was shown in Fig. 2. The permeation properties of gases across the prepared PDMS membranes were determined by utilizing a constant pressure/variable volume apparatus. The PDMS membranes were fixed into a membrane cell to offer an effective membrane area of 64 cm^2. The feed gas was provided from the compressed gas cylinders. The pressure regulators and the exhaust valve controlled the upstream pressure, and the downstream pressure was atmospheric. The temperature was main-

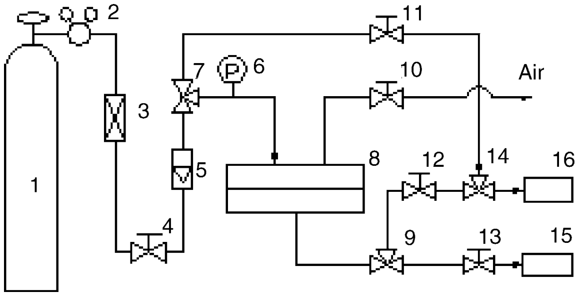

Fig. 2. Schematic diagram of experimental setup. (1) Gas cylinder; (2) pressure regulator; (3) air cleaner; (4) flow regulator; (5) rotameter; (6) pressure gauge; (7, 9, 14) three-way tie-in; (8) membrane cell; (10–13) pin valve; (15) soap bubble flowmeter or rotameter; (16) gas chromatograph.

tained at 25 °C using a temperature control system. One PDMS composite membrane was used for all permeation measurements. Flow rate measurements for feed and permeate stream were made by soap-film bubble flowmeters or rotameters. The ratio of the permeate flow rate to the feed flow rate (i.e. stage cut) was always kept less than 0.5% to minimize concentration polarization effects.

When a steady-state condition was achieved, the following equations were used to evaluate the permeation flux:

$$p = \frac{Ql}{\Delta P} = D \cdot S \qquad (1)$$

$$Q = \frac{V}{At} = \frac{p}{l}\Delta P \qquad (2)$$

where p is the permeability coefficient of the gas in the polymer and is described as the product of diffusivity D and solubility S of the gas in the polymer, l the thickness of the membrane, ΔP the pressure difference, Q the steady-state permeation flux, A the effective area of membrane and V is the volume of the permeation gas at the time interval t.

Feed and permeate compositions were determined by Agilent 6890N gas chromatograph (GC) equipped with a thermal conductivity detector (TCD). The GC column was 2 m long with 1/8 in inside diameter and packed with TDX-01, which was provided by Lanzhou Institute of Chemistry and Physics, PR China. The GC temperature profile was 70 °C (oven), 70 °C (injector) and 180 °C (detector). The samples could be injected into the column and thereby the compositions were measured quickly and accurately with the help of the GC chemstation attached.

The permeation data were the average values of triple the measurements under the same condition and the experimental error of the permeabilities of PDMS films was estimated to be about ±5%.

3. Result and discussion

3.1. The effect of pressure on the permeation properties of pure gases through PDMS

The permeation properties of the pure gases O_2, N_2 and CO_2 through the PDMS membrane were measured over a pressure difference range of 0.1–0.6 MPa. The results shown in Fig. 3 indicated that the fluxes of three gases increase with the increase of pressure difference to some extent in the following order: $CO_2 > O_2 > N_2$. In general, the gas permeation behavior through dense polymer membrane is typically described by the solution–diffusion model, that is, the permeability of gas is determined by the solubility and diffusivity of gas in the membrane [15]. Rubbery membrane PDMS has weak molecular sieves ability due to its weak intermolecular forces, resulting in broad distribution of intersegmental gap sizes responsible for gas diffusion. The diffusion coefficients of penetrants often change less than solubility coefficients so that more soluble penetrants are more permeable. Consequently the relative permeability of the penetrants through PDMS is mainly determined by its relative solubility [2,6,8]. Merkel et al. [2] and Stern [5] summarized the solubility and diffusivity of three gases, N_2, O_2 and CO_2 in PDMS, as listed in Table 1. For the least soluble penetrants O_2 and N_2, the solubilities are independent of pressure, and the diffusivity decreases slightly with the increase of pressure due to the hydrostatic compression of rubbery membrane. In contrast, the solubility of the more soluble penetrant CO_2 increases with pressure, and the diffusivity decreases less than O_2 and N_2 with pressure [2,4]. So CO_2 is more permeable than O_2 and N_2 in PDMS with the increase of pressure, that is, CO_2 is faster gas against O_2 and N_2, as the same as O_2 against N_2.

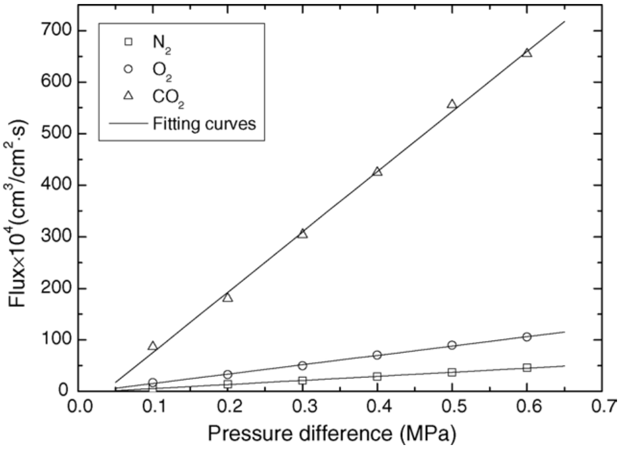

Fig. 3. Effect of the pressure difference on the flux.

Table 1
The solubility and diffusivity of three pure gases N_2, O_2 and CO_2

Pure gas	$D \times 10^5$ (cm^2/s)	$S \times 10^2$ (cm^3(STP)/ (cm^3 mHg))	Kinetic diameter (mm)
N_2	4.00	0.118	0.344
O_2	3.97	0.242	0.366
CO_2	2.63	1.74	0.363

Note: The data obtained from literature [2,5]; D and S are independent of pressure for N_2 and O_2, and weakly dependent on pressure for CO_2.

As shown in Fig. 3, the permeation flux is investigated as a function of the pressure difference. Based on Eq. (2), the relationship between flux and pressure difference can be expressed as linear dependence. And by simple linear fit of experimental data, the expression is given as follows:

$$Q = a\,\Delta P + m \qquad (3)$$

where Q is the flux, ΔP the pressure difference and a and m are the constants whose values are given in Table 2. Comparing Eq.

Table 2
Fitting constants for the dependence of the permeability of pure N_2, O_2 and CO_2 on pressure

Pure gas	$a \times 10^4$ (cm^3/ (cm^2 s MPa))	$m \times 10^4$ (cm^3/(cm^2 s))	Maximum error in model prediction[a] (%)
N_2	79.45	−2.55	4.54
O_2	181.99	−2.83	3.7
CO_2	1168	−41.06	5.3

[a] *Note*: Percentage error in model prediction = $|(Q_{model} - Q_{test})/Q_{test}| \times 100$.

(3) with Eq. (2), it can be seen that the parameter a is the constant related to the permeability coefficient and membrane thickness, m represents the deviation amplitude of the tested flux from the calculated values by Eq. (2).

3.2. The effect of pressure on the permeation of binary mixed gas through PDMS

Fig. 4 shows the variation of the permeation fluxes of O_2–N_2, CO_2–N_2 and O_2–CO_2 binary mixed gases with respect to the pressure difference. With the increase of pressure difference, the total flux of binary mixture increases and are located between those of each pure gas. Moreover, the total flux of O_2–N_2 mixed gas is lower than that of O_2–CO_2 mixed gas, and the total flux of N_2–O_2 mixed gas is lower than that of N_2–CO_2 mixed gas.

Fig. 5 exhibits the dependence of the molar fraction of gas species in the permeated stream on the pressure difference for the mixed gases with various molar compositions. With the increase of pressure difference, the molar fraction of O_2 in the permeated stream ascends for O_2–N_2 mixed gas and it descends for O_2–CO_2 mixed gas. However, the molar fraction of N_2 in the permeated stream descends for both O_2–N_2 and N_2–CO_2 mixed gases. The observed trend indicates that the higher permeable component is dominating the permeation process. And the increase of the pressure difference is favorable to the enrichment of the faster component in the permeated stream.

3.3. The establishment of modified permeation functions

Generally, for ideal permeation in which there is no interactions between the gases, as well as no special gas–polymer interactions in the presence of the second gas, the permeation parameters of the ideal gas mixture could be calculated from those of pure gases as follow rule:

$$M_{\mathrm{id}} = \phi_1 M_1 + \phi_2 M_2 \tag{4}$$

where M_{id} is the permeation parameter of the mixed system, ϕ and M are mol fraction and permeation parameter of a pure gas, respectively, and the subscripts 1 and 2 are component gases, respectively [6].

As mentioned previously, the complex factors such as coupling effect, plasticization effect and concentration polarization interact with each other and thus influence the transport of mixed gases through membranes, resulting in the deviation of the permeation behavior of the actual binary gas mixture from that of the ideal gas mixture. Among those factors, the coupling effect is the most prominent. It is necessary to reformulate of Eq. (4) by adding the effect of the feed composition on the permeation parameter of a pure gas. By a least-square fit to experimental data of binary gas mixtures, the actual permeation flux of binary gas mixture through the membrane and the molar fractions of components in permeated stream were deduced and expressed as follows (see Appendix A for details):

$$Q_{\mathrm{t}} = X_1 Q_1' + X_2 Q_2' \tag{5}$$

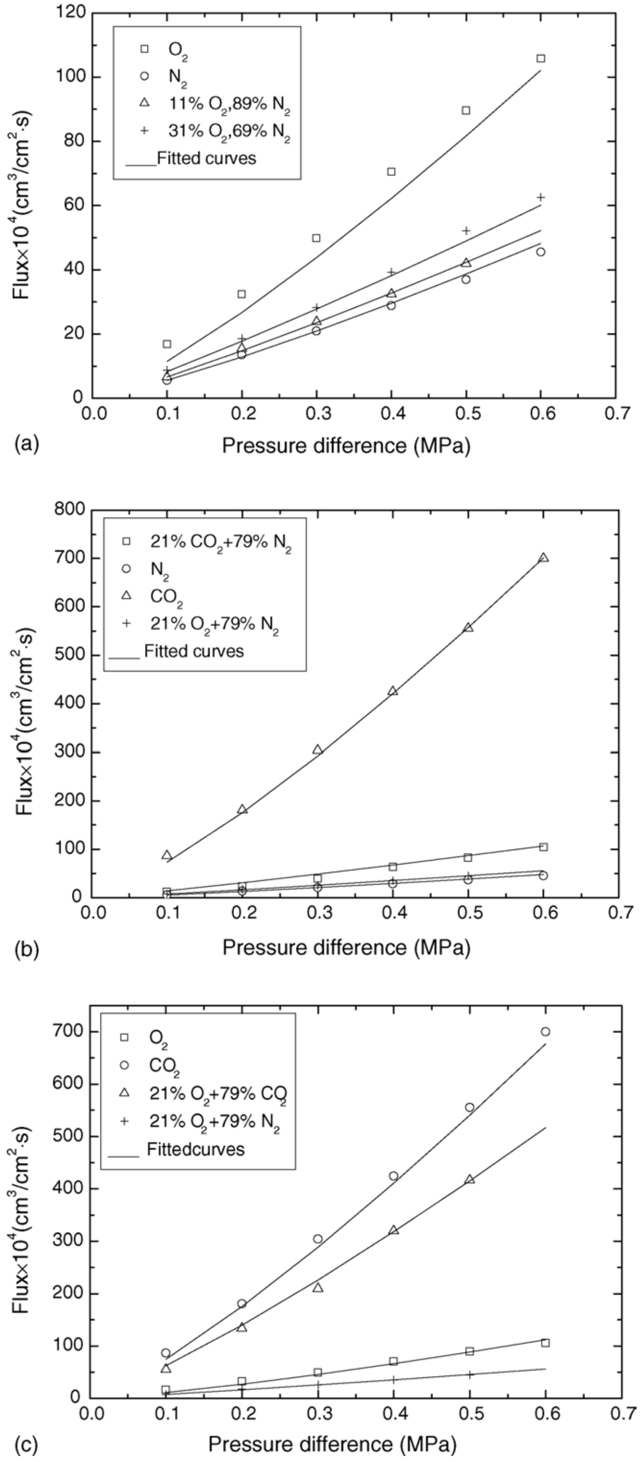

Fig. 4. Effect of the pressure difference on the flux of the mixed gases with various molar compositions. (a–c).

$$Y_i = \frac{X_i Q_i'}{Q_{\mathrm{t}}} \tag{6}$$

$$Q_i' = f(X_i)\Delta P^{g(X_i)} \tag{7}$$

where

$$f(X_i) = a_i X_i + b_i \tag{8}$$

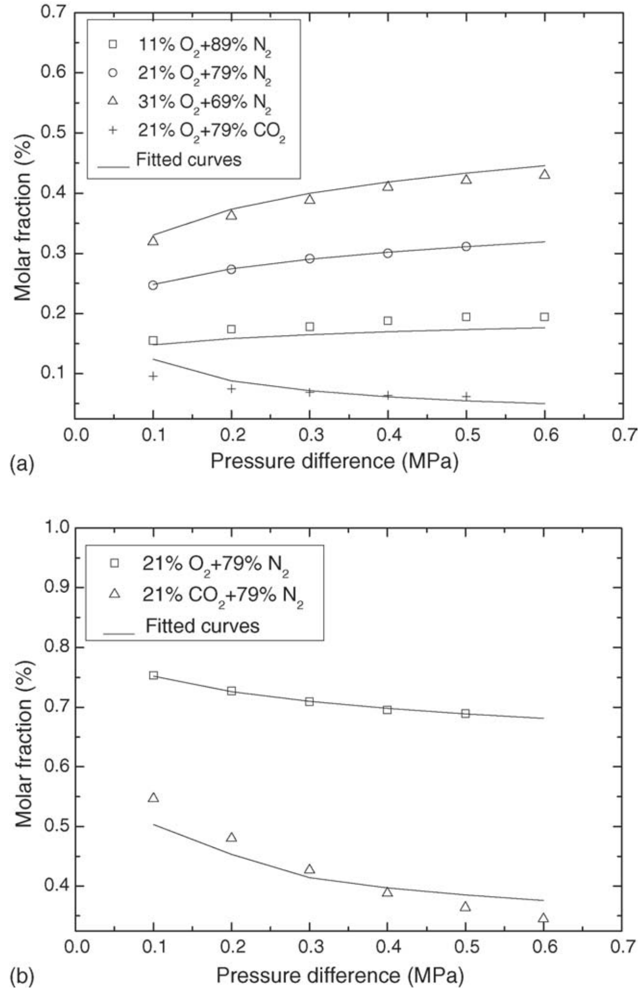

Fig. 5. Effect of the pressure difference on the molar fraction of (a) O_2 and (b) N_2 in permeated streams.

$$g(X_i) = m_i X_i + n_i \quad (i = 1, 2) \tag{9}$$

where Q_t is the permeation flux, Q'_i the calibrated permeation flux of the ith gas in gas mixture, $f(X_i)$ and $g(X_i)$ the functions of molar fraction of the ith gas and X and Y are the molar fractions of one component in the feed and permeated streams, respectively. The coefficients, a, b, m and n, are the constants for a certain binary gas mixture. The resulting permeation functions for PDMS membrane are given in Table 3, and the corresponding fitted curves shown in Figs. 4 and 5 reveal a high accuracy. Comparing Eq. (7) with Eqs. (2) and (3), it can be seen that $f(X_i)$ reflects directly the magnitude of the permeability coefficient of one component in gas mixture and $g(X_i)$ represents the deviation amplitude of the transport behavior of this component from that of pure gas state due to the existence of the other components. Therefore, the coefficients a and b are the constants related to the permeability coefficient and the membranes thickness, and the coefficients m and n can be regarded as the deviation amplitude from the value by Eq. (2).

There are only two feed variables (pressure difference and molar fractions of components in feed gas) presented in the permeation function in this study. The intrinsical transport parameters such as diffusion coefficient and solution coefficient are not introduced into the permeation function, due to the difficulty in obtaining the accurate values of them in practical application. So it is more convenient for the researchers to use these permeation functions developed in this study to calculate the flux and composition of an actual binary gas mixture through PDMS membrane regardless of the above intrinsical parameters. The variations of the intrinsical parameters could be considered to be embodied in the change of the external variables (pressure and composition) of these permeation functions.

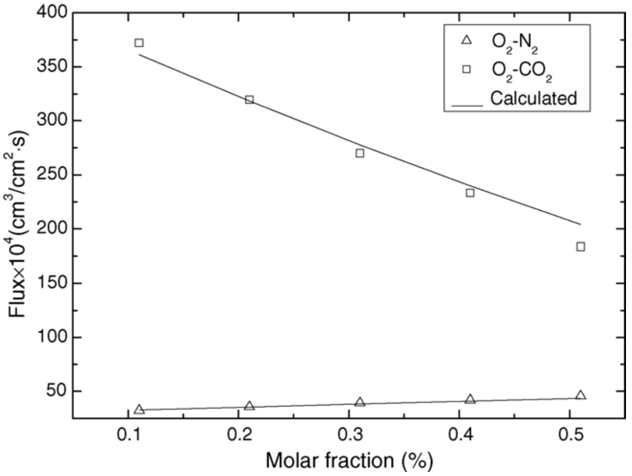

Fig. 6. Effect of molar fractions of O_2 in binary mixed gases on permeation flux.

In order to verify the applicability of the developed permeation function, a series of mixed gases with different molar composition were carried out at the pressure difference of 0.4 MPa. The calculated results, as shown in Figs. 6–8, were compared with the experimental data. The calculated results are found to be in good agreement with the experimental data. The maximum errors of the model prediction, as listed in Table 3, are no more than 12%. Meanwhile, Figs. 6–8 also reveal the dependence of the permeation behavior of binary mixed gases on the feed composition. With the increase of the molar fraction of O_2 in the feed gases, the total flux increase for O_2–N_2 mixed gas and decrease for O_2–CO_2 mixed gas. The total flux of mixed gas containing N_2 descends with the increase of the molar fraction of N_2 in

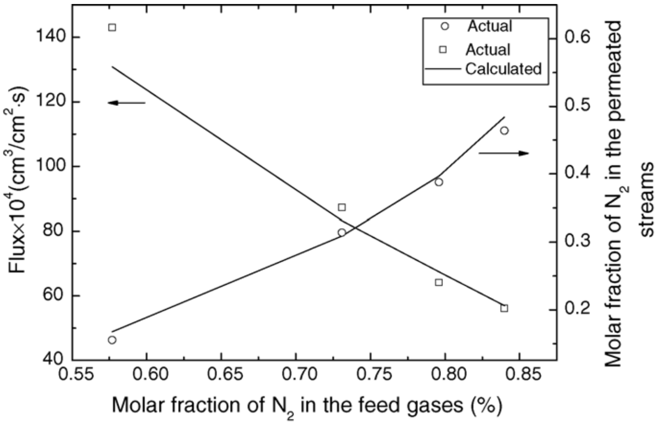

Fig. 7. Effect of the molar composition of the feed gases on the flux and the molar fraction of N_2 in the permeated streams for N_2–CO_2 mixed gases.

Table 3
Fitting constants for the actual permeation function of binary mixtures in PDMS membrane

Serial	Component	$a \times 10^4$ (cm^3/(cm^2 s MPa))	$b \times 10^4$ (cm^3/(cm^2 s MPa))	m	n	Maximum error in model prediction[a] (%)	
						Total flux	Molar fraction
1	O_2	35.90	154.56	0.12	1.23	4.7	8.9
	N_2	28.04	61.14	0.66	0.55	4.7	2.6
2	O_2	53.72	162.21	0.78	0.51	11.2	5.4
	CO_2	505.77	763.63	0.02	1.21	11.2	3.1
3	N_2	18.87	70.23	0.93	0.27	5.2	9.0
	CO_2	938.68	395.70	0.05	1.21	5.2	5.1

[a] *Note*: Percentage error in model prediction = $|(Q_{model} - Q_{test})/Q_{test}| \times 100$ and $|(Y_{model} - Y_{test})/Y_{test}| \times 100$.

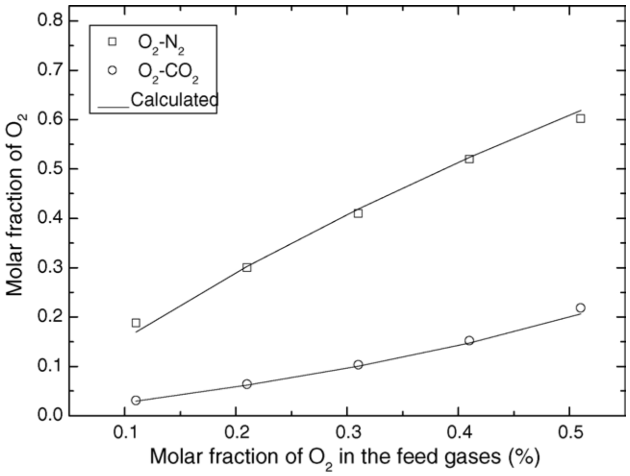

Fig. 8. Effect of the molar composition of the feed gases on the molar fraction of O_2 in the permeated streams.

feed gases. The above phenomena indicated that the contribution of the faster gas to the total flux is dominating. Fig. 8 also shows that the molar fraction of O_2 in permeated stream is lower than that in the feed gases for O_2–CO_2, and the opposite trend is found for O_2–N_2, which indicates that the faster gas gets the upper hand in the permeation competition.

3.4. *The extension of the modified permeation function to ternary mixed gas through PDMS*

Similar to the binary gas mixture, there also exists complex effect among species of ternary mixed gas. Therefore, an attempt to extend the above deduced model into the ternary mixtures was made to validate the applicability of the model in more than two components cases. The corresponding expressions of permeation flux and composition functions of ternary mixed gas can be given as follows:

$$Q_t = \sum X_i Q_i' \tag{10}$$

$$Y_i = X_i \frac{Q_i'}{Q_t} \tag{11}$$

where

$$Q_i' = f(X_i) \Delta P^{g(X_i)} \tag{12}$$

$$f(X_i) = a_i X_i + b_i \tag{13}$$

$$g(X_i) = m_i X_i + n_i \quad (i = 1, 2, 3) \tag{14}$$

Q_t is the total permeation flux, subscripts 1, 2, 3 are the species, $f(X_i)$ and $g(X_i)$ are the linear function of the molar fraction of the ith component in mixed gas and a, b, m and n are the constants for a certain ternary mixed gas. Due to the permeation transport of one component influenced by others in the mixed gas, the effect can be evaluated from the corresponding data obtained from binary mixed gases. Therefore, it is assumed that the values of four constants, a, b, m and n, were determined by the geometry mean of the values in the corresponding two mixed gases listed in Table 3, and the calculated values of the four constants are given in Table 4 (see Appendix A for details).

In order to verify the permeation function, a series of permeation experiments of O_2, N_2 and CO_2 ternary mixed gases with different molar compositions were carried out with the pressure difference varying from 0.1 MPa to 0.6 MPa at 25 °C. The experimental results are shown in Figs. 9–11. It is evident that the calculation is comparable to the experimental data with the maximum deviation less than 14% (see Table 4). The extended permeation model into ternary mixed gases in this study was proven to be reasonable and feasible. As shown in Fig. 9, the

Table 4
Fitting constants for the actual functions of ternary mixtures in PDMS membrane

Component	$a \times 10^4$ (cm^3/(cm^2 s MPa))	$b \times 10^4$ (cm^3/(cm^2 s MPa))	m	n	Maximum error in model prediction[a] (%)	
					Total flux	Molar fraction
Ternary mixture						
O_2	44.81	158.39	0.31	0.79	13.3	14.7
N_2	23.46	65.69	0.78	0.39	13.3	12.4
CO_2	722.23	579.65	0.03	1.21	13.3	11.0

[a] *Note*: Percentage error in model prediction = $|(Q_{model} - Q_{test})/Q_{test}| \times 100$ and $|(Y_{model} - Y_{test})/Y_{test}| \times 100$.

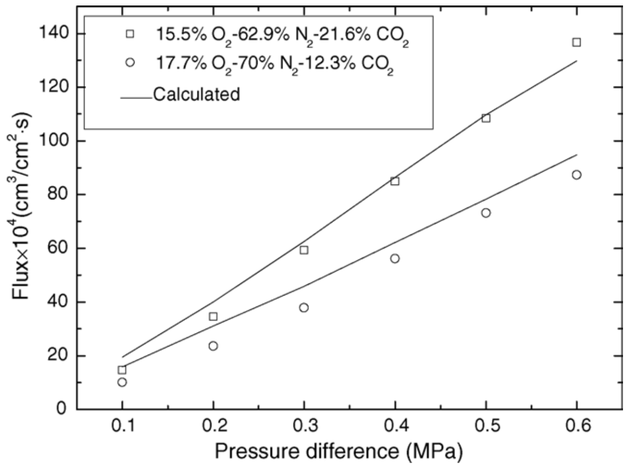

Fig. 9. Effect of the pressure difference on the flux.

fluxes of ternary gas mixtures rise with the increase of the pressure difference. Similar to binary mixture, the parameters *a* and *b* are the constants related to permeability coefficient and the membrane thickness, and the parameters *m* and *n* represent the deviation amplitude from the values by Eq. (2). Fig. 10 demonstrates the molar fraction of one component in the permeated streams as a function of pressure difference. With the increase of the pressure difference, the molar fractions of the slower components O_2 and N_2 in permeated stream descend and that of the faster CO_2 ascends. Fig. 11 illustrates that the dependence of the permeation flux and the molar fraction in the permeated streams on the feed composition of the ternary mixed gases at constant pressure difference of 0.4 MPa. The total fluxes decrease with the decrease of the molar fraction of the faster gas CO_2 in feed gases. When changing the proportion of three species in the feed mixture, the molar fractions of N_2 in the permeated streams is always lower than those in the feed gases and the opposite trend is found for CO_2. But the molar fractions of O_2 in the permeated streams are higher than those in the feed gases in a certain proportion, which is maybe due to the presence of the much slower gas N_2, i.e. the effect of N_2 on the transport of O_2 exceeds the effect of CO_2 on the O_2.

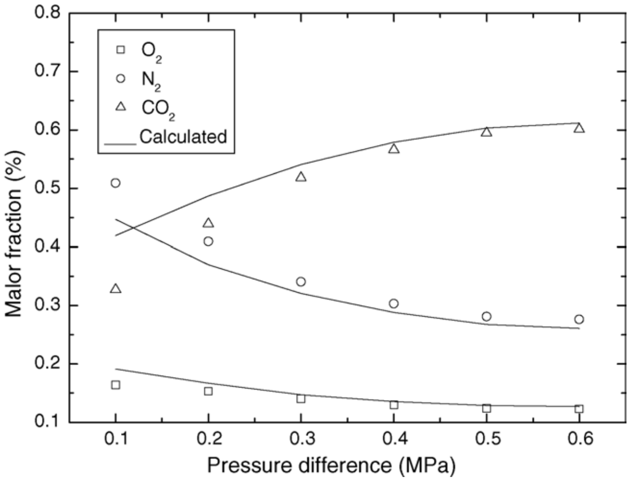

Fig. 10. Effect of the pressure difference on the molar fraction of the permeated stream for feed gas: 15.3%O_2, 62.1%N_2 and 22.7%CO_2.

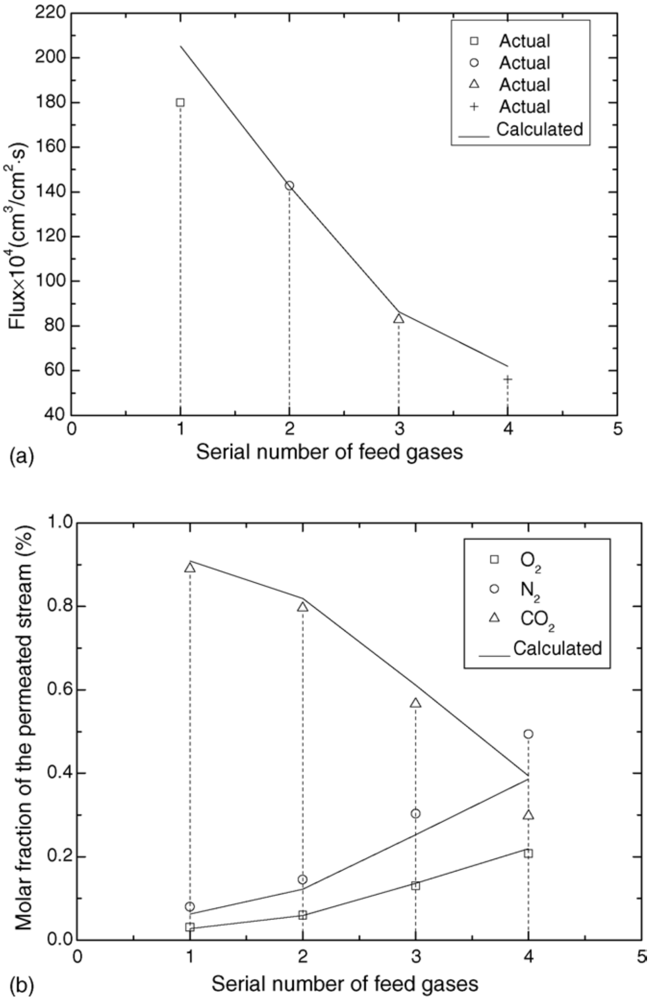

Fig. 11. Effect of the composition of the feed gases at pressure difference of 0.4 MPa on (a) the flux and (b) the molar composition of the permeated streams for various mixed gases: (1) 7.5%O_2, 32.8%N_2 and 59.7CO_2; (2) 10.9%O_2, 46.7%N_2 and 42.4%CO_2; (3) 15.3%O_2, 62.1%N_2 and 22.7%CO_2; (4) 18%O_2, 70%N_2 and 12%CO_2.

4. Conclusion

The permeation behaviors of pure gases, binary and ternary mixtures of O_2, N_2 and CO_2 through PDMS membrane were investigated at different pressure differences and feed compositions. For pure gases, the permeation fluxes increase with the pressure difference. As for binary and ternary gas mixtures, the permeation fluxes depend on not only the pressure difference but also the molar compositions of the feed gas. The permeation fluxes rise with the increase of the pressure difference, and the enhancement of the proportion of the faster gas in the feed gas can increase the permeation flux.

A modified permeation model expressed in terms of pressure difference and molar compositions of the feed gas was developed to predict quantitatively the permeation flux and the molar compositions of permeated stream. The model was further extended to the ternary case by taking into account the influence of the coupling effects on the transport. Comparison of the experimental data with the calculated results showed an excellent agreement. The model is established by the introduction of two controllable feed parameters, while common permeation models depend on some intrinsic factors such as the diffusion coefficient, and the solution coefficient. The advantage of the model in this study is obvious for avoiding the difficulty in achieving the accurate values of those above mentioned interior factors. The flux and the composition of the permeated stream are the interest of actual membrane separation system and also the most important indexes to evaluate the actual separation capability. This model is practical and simple in choosing the optimal separation conditions of gas mixtures. Although the model is presented based on the permeation behaviors of O_2, N_2 and CO_2 through the PDMS membrane, the research method can be extended to other gas separation membrane systems.

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Appendix A

For a binary mixture with one certain proportion, the total permeation flux Q_t and the molar fraction Y_i of one component in permeated stream varied with the pressure difference ΔP at constant temperature, so Q_t and Y_i can be considered as the function of the pressure difference ΔP as below:

$$Q_t = F(\Delta P) \tag{A.1}$$

$$Y_i = G(\Delta P) \tag{A.2}$$

By fitting the corresponding experimental data in Figs. 4–6 with the pressure difference ΔP as variable, the expression of $F(\Delta P)$ and $G(\Delta P)$ is drawn as follows:

$$F(\Delta P) = A\Delta P + B \tag{A.3}$$

$$G(\Delta P) = C\Delta P^D \tag{A.4}$$

where the coefficients A, B, C and D varied with the proportion of binary mixture. Moreover, considered that $Q_t \to 0$ when $\Delta P \to 0$, i.e. the coefficient B was very little and approach zero, to simple the calculated process, let

$$B = 0 \tag{A.5}$$

Based on Eq. (4)

$$M_{id} = \phi_1 M_1 + \phi_2 M_2$$

the total flux and the molar fraction of one component in the permeated stream can be expressed as follows:

$$Q_t = X_1 Q'_1 + X_2 Q'_2 \tag{A.6}$$

$$Y_i = \frac{X_i Q'_i}{Q_t} \tag{A.7}$$

Table A.1

Serial	Composition	a	b	m	n
1	O_2–N_2	35.90	154.56	0.12	1.23
2	O_2–CO_2	53.72	162.21	0.78	0.51

where Q'_i is the calibrated permeation flux of ith component in gas mixture.

The combination of Eqs. (A.3), (A.4), (A.6) and (A.7) leads to

$$Q_t Y_i = AC\Delta P^{D+1} = X_i Q'_i \tag{A.8}$$

Then the calibrated permeation flux Q'_i of ith component can be deduced as below:

$$Q'_i = \frac{AC}{X_i}\Delta P^{D+1} = k\Delta P^l \tag{A.9}$$

where

$$k = \frac{AC}{X_i} \tag{A.10}$$

$$l = D + 1 \tag{A.11}$$

and the coefficients k and l can be obtained by the corresponding values of coefficients A, C and D in Eqs. (A.3) and (A.4), when the proportion of feed gas is changed, a serial of corresponding values of k and l can also be obtained in the same way. Thus, the coefficients k and l can be considered as the function of the molar fractions X_i of components in feed stream as follows:

$$k = f(X_i) \tag{A.12}$$

$$l = g(X_i) \tag{A.13}$$

By a least-squares fit, the expression of $f(X_i)$ and $g(X_i)$ can be deduced as below:

$$f(X_i) = a_i X_i + b_i \tag{A.14}$$

$$g(X_i) = m_i X_i + n_i \tag{A.15}$$

So the coefficients a, b, m and n are constants for a certain binary mixture no matter how the proportion of two gases varies.

When the model was extended into ternary mixed gas, it can be assumed that the coefficients a, b, c and d of one component were determined by the geometry mean of the values in corresponding two binary mixtures contained it. For instance, the corresponding coefficients of O_2 in binary mixture of O_2–N_2 and O_2–CO_2 were listed in Table A.1 excerpted from Table 3. So the coefficients of O_2 in ternary mixture could be calculated as follows:

$$a = \sqrt{a_1 a_2} = 44.81$$

$$b = \sqrt{b_1 b_2} = 158.39$$

$$m = \sqrt{m_1 m_2} = 0.31$$

$$n = \sqrt{n_1 n_2} = 0.79$$

In the same way, the corresponding coefficients of N_2 and CO_2 could be calculated.

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