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Mathematical Modeling and Investigation on the Temperature and Pressure Dependency of Permeation and Membrane Separation Performance for Natural gas Treatment

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Abstract: Due to special features, modules comprising asymmetric hollow fiber membranes are widely used in various industrial gas separation processes. Accordingly, numerous mathematical models have been proposed for predicting and analyzing the performance. However, majority of the proposed models for this purpose assume that membrane permeance remains constant upon changes in temperature and pressure. In this study, a mathematical model is proposed by taking into account non-ideal effects including changes in pressure and temperature in both sides of hollow fibers, concentration polarization and Joule-Thomson effects. Finite element method is employed to solve the governing equations and model is validated using experimental data. The effect of temperature and pressure dependency of permeance and separation performance of hollow fiber membrane modules is investigated in the case of CO_2/CH_4. The effect of temperature and pressure dependence of membrane permeance is studied by using type Arrhenius type and partial immobilization equations to understand which form of the equations fits experimental data best. Findings reveal that the prediction of membrane performance for CO_2/CH_4 separation is highly related to pressure and temperature; the models considering temperature and pressure dependence of membrane permeance match experimental data with higher accuracy. Also, results suggest that partial immobilization model represents a better prediction to the experimental data than Arrhenius type equation.

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1 Introduction

In gas separation membrane systems, glassy polymers have demonstrated excellent and robust mechanical properties to withstand high-pressure natural gas feeds [1–5]. In glassy polymers, the permeation of gases through membrane surface and the solution and diffusion of gases can appropriately be described by dual-mode sorption model [6,7]. The dual-mode sorption model provide a quantitative representation of gas sorption isotherms and describe the dependence of gas permeability and diffusion coefficients [8]. As a whole view, permeability coefficients define the transport of gas components across the membrane and diffusion coefficients define the transport of gas components in a polymer matrix [9]. The basic dual-mode sorption neglects the effects of plasticization. Thus, to consider the effects of plasticization on the polymer membrane the dual-mode sorption model was extended [10]. According to this model, the total dissolved gas in the polymeric membrane matrix is defined by Henry's law and Langmuir type of sorption [11]:

$$C = C_D + \left(C'_H b/K_D\right) \frac{C_D}{1 + bC_D/K_D} \tag{1}$$

where C_D and C'_H are the Henry and the Langmuir total concentration in the sites of polymer, b is the affinity of the gas molecules to be absorbed in the polymer and K_D is the Henry's law dissolution constant.

So far the effect of temperature and pressure on permeability of gas components have been justified by the partial-immobilization and Arrhenius-type equations, respectively. The first partial-immobilization equation was proposed by introducing a new diffusion coefficient for the mobility of the Langmuir mode species [12]. To include the effect of temperature and pressure simultaneously Safari et al. [1] presented a model based on partial-immobilization model.

In this study, a mathematical model representing the performance of asymmetric hollow fiber membrane modules is applied to study the effect of temperature and pressure dependence of membrane permeance by using Arrhenius-type and partial immobilization-type equations. Also it is desired to specify which of these equations could represent experimental data better.

2 Model developments

To develop the mathematical model, hollow fiber membrane type was selected among different modules due to its high packing density and large surface area. To develop the main governing equations, a membrane permeator containing dead-end asymmetric hollow fibers was considered in which the feed flows in the shell-side in the counter-current mode (Figure 1) [13].

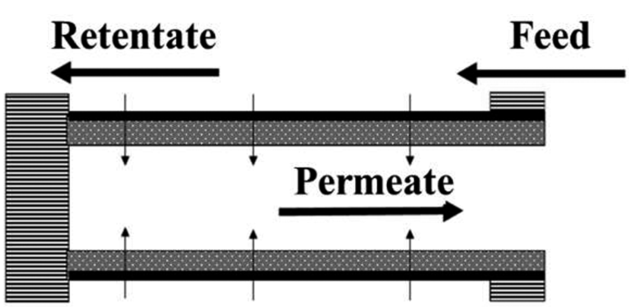

Figure 1: Schematic representation of a hollow fiber membrane with countercurrent flow configuration.

For a binary system, the governing equations which describe the changes of gas molar flow and composition in the feed (x) and permeate stream (y) over a differential length of the membrane dz and thickness of δ are as follows:

$$-\frac{d(U(1-x))}{dz} = \pi d_0 (Q_b/\delta)(P_F(1-x) - P_P(1-y')) = -\frac{d(V(1-y))}{dz} \quad (2)$$

where U, z, d_o, Q_b, P_F, P_P and y' are gas molar flow rate, fiber length, module diameter, permeability of less permeable component, feed pressure, permeate pressure and local permeate-side mole fraction of the more permeable component in the membrane porous layer which is defined as:

$$y' = \frac{d(Ux)}{dU} \quad (3)$$

In this model, SRK equation was used to justify the non-ideal behavior of gas mixtures and Joule-Thomson equation was employed to take into account the changes in the temperature due to permeation. Also the changes in temperature along shell side was calculated via thermodynamic principles. Furthermore, a surface mole fraction parameter is used to consider the effect of accumulation of less permeable component adjacent to the membrane surface in the feed side. Also pressure changes at both shell- and lumen-sides were taken into account by appropriate equations [13]. Finally, the proposed model solved using finite element method.

In this study, to determine the temperature dependence of membrane permeance in the proposed mathematical model, the Arrhenius-type equation (equation (4)) was selected. Also to investigate the temperature and pressure dependence of membrane permeance partial immobilization-type equation (equation (5)) presented by safari et al. [1] was applied:

$$Q = Q_{\mathrm{Ref}} \exp\left[-\frac{E}{R}\left(\frac{1}{T_F} - \frac{1}{T_{\mathrm{Ref}}}\right)\right] \quad (4)$$

$$Q = a\exp\left(-\frac{b}{RT}\right) + \frac{c\exp(-d/RT)}{1+(e/T)P} \quad (5)$$

where in above equations, E, R and T are activation energy, ideal gas constant and temperature, respectively. Also a, b, c, d and e are constants to be determined experimentally. According to experimental data presented by Tranchino et al. [14], empirical constants were obtained by fitting equation (4). Table 1 represent the permeability coefficients of the hollow fiber membrane as a function of temperature and pressure.

3 Results and discussion

The validity of the mathematical models examined through experimental data reported in the literature [14]. The tests were carried on a binary CO_2/CH_4 gas mixture having a composition of 60% CO_2 flowing in a cylindrical module of 1 cm internal diameter and 15 cm length. This module houses 100 fibers with internal diameter of 389 μm and external diameter of 735 μm. Figures 2 and 3 represent the variation of mole fraction of CO_2 in permeate stream in different stage cuts based on

Table 1: Permeability coefficients of membrane as a function of temperature and pressure (K [=] $cm^3(std).min^{-1}.\ cm^{-2}.\ atm^{-1}$).

Temperature (*K*)	Pressure (*atm*)					
	2		4		7	
	K_{CO2}	K_{CH4}	K_{CO2}	K_{CH4}	K_{CO2}	K_{CH4}
298.15	0.043	0.0118	0.043	0.0120	0.044	0.0126
318.15	0.066	0.01722	0.067	0.0178	0.068	0.0188

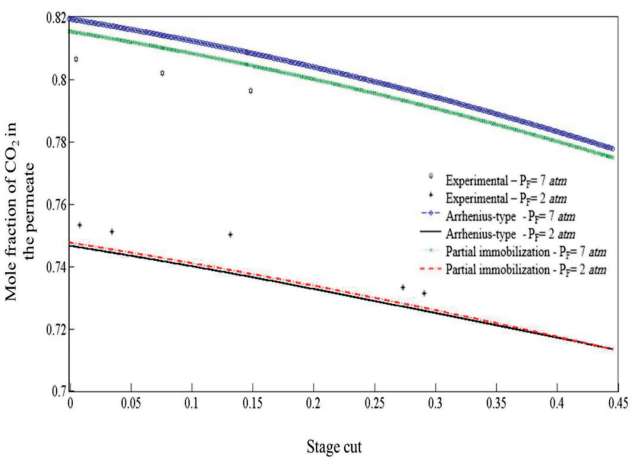

Figure 2: The results of modeling based on Arrhenius-type and partial immobilization-type equations in the case CO_2/CH_4 separation (Feed temperature: 298.15 K).

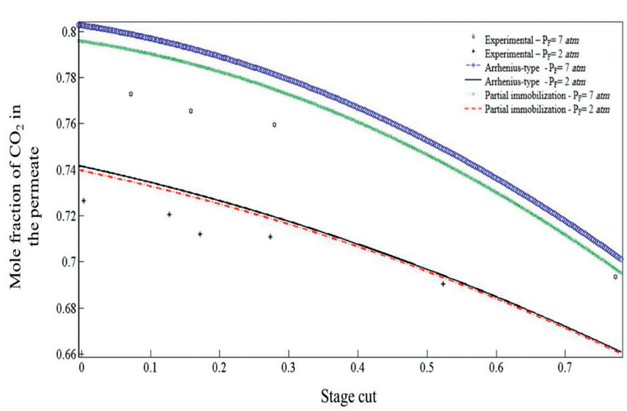

Figure 3: The results of modeling based on Arrhenius-type and partial immobilization-type equations in the case CO_2/CH_4 separation (Feed temperature: 338.15 K).

Arrhenius-type and partial immobilization-type equations for different feed temperatures. Figure 2 represents the results obtained for the developed model by applying Arrhenius-type and partial immobilization-type equations at 298.15 K. Generally, results show that the predictions made by adopting both equations are in a good agreement with the experimental data. From the Figure 2, the model used partial immobilization-type equation has a better predictions than the Arrhenius-type. It is clear that by increasing stage cut, the mole fraction of CO_2 in permeate decreases. Also by increasing the pressure, the non-ideal behavior of gas mixture increases so that the models overestimate experimental data at 7 atm. On the other hand, at this pressure the deviation between predictions of Arrhenius-type and partial immobilization-type is more. Cleary, the partial immobilization-type equation benefits from a term in which considers pressure changes along the fibers. Also another advantage of the partial immobilization-type equation is that the constants are directly specified using experimental data so that it could predict the variation of gas permeation with more accuracy.

Figure 3 represents the mole fraction of CO_2 at different stage cuts by applying the Arrhenius-type and partial immobilization-type equations at 338.15 K. Findings reveal that both models are in an acceptable agreement with the experimental data. According to the results, increasing temperature has an intense effect on non-ideal behavior of gas mixture so it makes models to overestimate experimental data at 338.15 K. From the figure, it is clear that at higher stage cuts, the models have better predictions especially for the model that uses the partial immobilization-type equation. Also it is clear that at higher stage cuts the predictions of both models approach each other. Similar to the previous case, the accuracy of the predictions obtained by the model that uses the partial immobilization-type equation is more. Compared to 298.15 K, the deviation between the model that uses the partial immobilization-type equation and the model that uses Arrhenius-type equation is a bit more. In addition, decreasing the feed pressure makes the gas mixture to behave more ideally so that the predictions are in higher accuracy.

It seems that the partial immobilization-type equation takes in to account the variation of pressure with a reasonable trend. In all of the above cases, the model that used the partial immobilization-type equation demonstrate better predictions. This becomes more important at high pressures in which by increasing pressure permeability of both CO_2 and CH_4 decreases. So related to equation (5), the partial immobilization-type equation could predict this variation. Also related to equations (3) and (4) the permeability of both CO_2 and CH_4 increases by increasing temperature.

4 Conclusions

Mathematical models were developed based on binary gas separation for an asymmetric hollow fiber membrane module with counter-current flow pattern. The validity of models examined through experimental data; indicating a good agreements in between. Results suggest the use of the partial immobilization-type equation than Arrhenius-type equation for considering the effects of changing operating variables on the membrane permeance. Furthermore, partial immobilization-type equation considered the effect of pressure changes. Thus, it could predict experimental data better. Findings revealed that the prediction of membrane performance for CO_2/CH_4 separation is highly related to pressure and temperature.

Nomenclature

b	affinity of the gas molecules to be absorbed in the polymer
C	total dissolved gas in the polymeric membrane matrix
C_D	Henry total concentration
C'_H	Langmuir total concentration in the sites of polymer
d_o	fiber outer diameter
E	activation energy for permeation through the membrane
K_D	Henry's law dissolution constant
L	active fiber length
N	total number of active fibers in the hollow fiber module
P	pressure
Q	permeability
R	ideal gas constant
T	temperature
U	retentate gas flow rate in the hollow fiber module
V	permeate gas flow rate in the hollow fiber module
V^*	normalized permeate gas flow rate in the hollow fiber module
x_F	feed mole fraction of the more permeable component
x_s	surface mole fraction of the more permeable component in the feed-side stream
y	permeate mole fraction of the more permeable component in the bulk permeate stream
y'	local permeate-side mole fraction of the more permeable component in the membrane porous layer
z	hollow fiber length variable measured from the open end

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