

Mathematical modeling of temperature and pressure effects on permeability, diffusivity and solubility in polymeric and mixed matrix membranes

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Abstract

Due to the temperature and pressure dependency of gas transport through membranes, probing of their separation performance at different operational conditions seems crucial to determine an optimal operational condition. To minimize the number of costly and time consuming experiments, a modified form of van't Hoff-Arrhenius model was developed to consider the simultaneous effects of temperature and pressure on the separation performance of membranes. Moreover, the proposed model is capable to consider pressure dependency of energetic parameters of Arrhenius model including activation energies of permeability and diffusivity, heat of sorption and the corresponding pre-exponential factors. The validity of the proposed model was investigated by using permeation coefficients of CO₂ and N₂ in a binary mixture through 6FDA-DAM at different temperatures in the range of 35 to 55 °C and in the feed pressure range from 2 to 5 atm. Besides, from data taken from the literature, the proposed model was validated by the prediction of temperature and pressure dependency of transport properties of glassy and rubbery polymers as well as mixed matrix membranes (MMMs) for different gas molecules including He, H₂, CO₂, O₂, N₂, CH₄ and C₄H₁₀. Predictions corresponding to 300 data points revealed that the maximum average absolute relative error was 5.1-%.

Keywords: Membrane, Permeability, Diffusivity, Solubility, Temperature, Pressure, Mathematical modeling.

1. Introduction

During the past decades, membrane technology has been widely accepted for gas separation due to capital and energy intensive of conventional separation processes such as condensation, adsorption, cryogenic and distillation [1, 2]. Transportation of gas molecules through membranes is governed by the size and the shape of the penetrants as well as their interaction with the membrane [3].

In membrane gas separation technology, the main goal is achieving to high selectivity and permeability. Due to the temperature dependency of polymer chain mobility as well as plasticization effects related to the presence of penetrants in the polymer matrix [4, 5], investigation of transport properties of prepared membranes at different operational temperatures and pressures is required. This would allow determining suitable membrane materials for a given gas separation application and optimum operational conditions.

On one hand, higher pressure difference between feed and permeate sides provides greater flux through membranes. This is beneficial to keep them at high pressure difference as high as possible [6]. On the other hand, because of the sensitivity of polymeric materials to high temperatures as well as the possibility of swelling of polymer chains in the case of high concentration of penetrants [7], investigation of their separation performance at different operational conditions seems crucial.

Moreover, analysis of activation energies for permeability and diffusivity as well as the heat of sorption can provide a proper insight into the effect of interactions between the membrane and penetrants on the temperature and pressure dependence of the transport of gases through membranes [8-10].

As measurement of transport properties of membranes over a wide range of conditions is time consuming and costly, in order to optimize membrane process design, an estimation of their separation performance based on existing experimental data is valuable. In this regard, so far different modeling attempts have been done to take into account the effects of temperature and pressure on the transport properties of membranes. For instance, Arrhenius and dual mode sorption models were developed to indicate the respective effects of temperature and pressure on permeability [11-13].

Furthermore, Safari model, based on combining the above models, describes both temperature and pressure dependencies of gas permeability through glassy polymers [14]. In spite of its merits, Safari model is unable to investigate activation energy of permeability for the polymers.

To overcome this limitation, in this study van't Hoff-Arrhenius model was modified in which, both effects of temperature and pressure are simultaneously considered on transport properties of membranes. In order to test the capability of the model, transport properties of 6FDA-DAM for CO₂ and N₂ in a binary mixture with 10 vol.% CO₂ over a wide range of operational conditions were assessed. Furthermore, a set of published experimental data, including permeability, diffusivity and solubility for different gas molecules including He, H₂, CO₂, O₂, N₂, CH₄ and C₄H₁₀, was considered to explore applicability of the proposed model in predicting temperature and pressure dependency on transport properties through glassy and rubbery polymeric membranes as well as MMMs.

2. Background

As well known, transportation of gas molecules through a dense polymer film is governed by solution diffusion mechanism [15, 16]. Based on this mechanism, gas molecules initially dissolve into the polymeric media and then diffuse through polymer chains. Consequently, permeability coefficient, P , of polymeric membranes can be expressed as a product of diffusivity, D , and solubility, S , coefficients [17]:

$$P = D * S \quad (1)$$

In a temperature range away from the thermal transition of the polymer, the temperature dependency of P , D and S can be often described satisfactory by van't Hoff- Arrhenius model as follow [8, 11]:

$$P = P_0 * \exp\left(\frac{-E_p}{RT}\right) \quad (2)$$

$$D = D_0 * \exp\left(\frac{-E_d}{RT}\right) \quad (3)$$

$$S = S_0 * \exp\left(\frac{-\Delta H_s}{RT}\right) \quad (4)$$

where E_p , E_d and ΔH_s are the activation energies of permeability and diffusivity and heat of sorption, respectively. Moreover, P_0 , D_0 and S_0 are the corresponding pre-exponential factors, R is universal gas constant and T is absolute temperature.

Combining Eqs. (1) to (4) the activation energy of permeability can be described as follows:

$$E_p = E_d + \Delta H_s \quad (5)$$

It is notable that the effect of temperature on transport properties of polymer/particle composites, can be analyzed by the van't Hoff- Arrhenius model [18, 19].

A self-consistent model was developed to consider concentration, pressure and temperature dependency of gas permeation through rubbery polymers [20]:

$$P = \left(\frac{\exp(-\tau)}{\Delta p} \right) * \left(\frac{\exp(\xi E_{d2}) - \exp(\xi E_{d1})}{-v * E_d^o * \omega} \right) \quad (6)$$

$$v = \frac{1}{R} * \left(\xi - \frac{1}{T} \right) \quad (7)$$

$$E_{dn} = E_d^o * (1 - \omega * C_n), n = 1,2 \quad (8)$$

where Δp is the pressure difference between feed and permeate sides. E_d^o indicates the activation energy of diffusion in an infinite dilution. τ , ξ and ω are adjustable parameters. Moreover, subscripts 1 and 2 refer to the permeate and feed sides of membrane, respectively. C is the concentration of penetrant, which in rubbery polymers is estimated based on Flory-Huggins expression as [21]:

$$\ln \frac{p}{p^{sat}} = \ln \phi_2 + (1 - \phi_2) + x(1 - \phi_2)^2 E_d \quad (9)$$

$$\phi_2 = 1 + \frac{22.414}{C \bar{V}_2} \quad (10)$$

where ϕ_2 and p^{sat} are volume fraction and saturated vapor pressure of the penetrant at feed side. x and \bar{V}_2 are related to the interaction parameter of Flory-Huggins and partial molar volume of penetrant.

The pressure dependency of permeability through glassy polymers can be estimated by the dual mode sorption model for a binary gas mixture as follows [12]:

$$P_A = K_{DA} * D_{DA} * \left(1 + \frac{F_A * K_A}{1 + B_A * f_A + B_B * f_B} \right) \quad (11)$$

$$P_B = K_{DB} * D_{DB} * \left(1 + \frac{F_B * K_B}{1 + B_A * f_A + B_B * f_B} \right) \quad (12)$$

$$F_A = D_{HA}/D_{DA} \quad (13)$$

$$F_B = D_{HB}/D_{DB} \quad (14)$$

$$K_A = C'_{HA} * b_A / K_{DA} \quad (15)$$

$$K_B = C'_{HB} * b_B / K_{DB} \quad (16)$$

where f_i is fugacity of penetrant i at the feed side, D_{Di} and D_{Hi} represent the diffusion coefficient of component i at Henry and Langmuir sites, respectively. K_{Di} is the constant of Henry's law for penetrant i , C'_{Hi} and B_i are the respective Langmuir capacity and affinity constants for penetrant i . It should be noticed that, in the dual mode sorption model, downstream pressure is considered to be zero.

Safari model was developed based on combining Arrhenius and dual mode sorption models to consider both effects of temperature and pressure on permeability of glassy polymer membranes in a single equation as [14]:

$$P = \beta * \exp\left(\frac{-\gamma}{RT}\right) + \frac{\delta * \exp\left(\frac{-\varphi}{RT}\right)}{1 + \frac{\mu * p_f}{T}} \quad (17)$$

where β , γ , δ , φ and μ are adjustable parameters and p_f is upstream pressure. Due to the gradually saturation of Langmuir sites in glassy polymers for CO₂ as pressure increases, the following relation was proposed for the CO₂/CH₄ selectivity, α_{CO_2/CH_4} , [14]:

$$\alpha_{CO_2/CH_4} = \beta' * \exp\left(\frac{\gamma'}{RT}\right) * \frac{1 + \delta' * p_f}{1 + \varphi' * p_f} \quad (18)$$

where β' , γ' , δ' and φ' are adjustable parameters.

3. Model development

In spite of its merits, the Safari model is unable to investigate the pressure dependency of the activation energy of permeability for glassy polymers. Besides, usage of too many parameters makes it difficult to assess the validity of the model.

To overcome these limitations, the van't Hoff-Arrhenius model was modified to show both temperature and pressure dependency on the transport properties of glassy and rubbery polymeric membranes as well as on MMMs. It is notable that, not only their properties should follow the van't Hoff-Arrhenius model at a constant pressure, but also should have a considerable pressure dependency. In this regard, several of possible and logical models were investigated by using Advanced Grapher software, version 2.1. For this purpose, initially it was necessary to evaluate adjustable parameters of van't Hoff-Arrhenius model, P_0 , D_0 , S_0 , E_p , E_d and ΔH_s at different pressures, based on least square method. Then, by assuming only pressure

dependency of these parameters, among various mathematical forms, the following equations have a fairly good agreement with experimental data:

$$P_0 = a_p * p^{b_p} \quad (19)$$

$$E_p = c_p * \ln p + d_p \quad (20)$$

$$P = P_0 \exp\left(\frac{-E_p}{RT}\right) = a_p * p^{b_p} * \exp\left(\frac{-(c_p * \ln p + d_p)}{RT}\right) \quad (21)$$

$$D_0 = a_d * p^{b_d} \quad (22)$$

$$E_d = c_d * \ln p + d_d \quad (23)$$

$$D = D_0 \exp\left(\frac{-E_d}{RT}\right) = a_d * p^{b_d} * \exp\left(\frac{-(c_d * \ln p + d_d)}{RT}\right) \quad (24)$$

$$S_0 = a_s * p^{b_s} \quad (25)$$

$$\Delta H_s = c_s * \ln p + d_s \quad (26)$$

$$S = S_0 \exp\left(\frac{-\Delta H_s}{RT}\right) = a_s * p^{b_s} * \exp\left(\frac{-(c_s * \ln p + d_s)}{RT}\right) \quad (27)$$

where a , b , c and d are adjustable parameters and p depending on operational conditions can be feed pressure or applied pressure difference. Subscripts p , d and s correspond to permeability, diffusivity and sorption, respectively.

4. Experimental

4.1. Membrane fabrication

For the preparation of 6FDA-DAM membranes, the polymer (Akron Polymer Systems, Inc, Mw = 418 kDa) was first dissolved at room temperature in chloroform (anhydrous, Sigma Aldrich) at 10 wt.% concentration. The solution was then cast on a glass Petri dish, which was left covered overnight to allow the slow evaporation of the solvent. After that, the membranes were peeled off from the Petri dishes and treated in an oven at 100 °C for 24 h to complete the removal of the remaining solvent. The membrane thickness was measured, by [digital micrometer Mitutoyo a-Digimatic Micro-meter](#) with an accuracy of $\pm 1 \mu m$, about $75 \pm 5 \mu m$.

4.2. Gas separation analysis

The membrane samples were placed in a module consisting of two stainless steel pieces and a 316LSS macroporous disk support of 13.85 cm² (from Mott Co.) with a 20 μm nominal pore size, and gripped inside with Viton O-rings. The permeation module was placed in a UNE 200 Memmert oven to control the temperature of the experiments. Gas separation measurements were carried out at different temperatures in the range of 35 to 55 °C and in the feed pressure

range from 2 to 5 atm. Feed gas was a CO₂:N₂ mixture (10:90 cm³(STP)·min⁻¹) that its flow rate was controlled by two mass-flow controllers (Alicat Scientific, MC-100CCM-D), while the permeate side of the membrane was swept with a 2 cm³(STP)·min⁻¹ mass-flow controlled stream of He at 1.2 atm (Alicat Scientific, MC-5CCM-D). Concentrations of CO₂ and N₂ in discharged streams were analyzed by an Agilent 3000A online gas microchromatograph equipped with a thermal conductivity detector. Permeabilities were calculated in Barrer (10⁻¹⁰ cm³(STP) cm cm⁻² s⁻¹ cmHg⁻¹) after meeting steady-state condition (for at least 3 h), and the separation selectivity was calculated as the ratio of permeabilities.

5. Results and discussion

5.1. Permeation properties of 6FDA-DAM membranes

The influence of the operating temperature and pressure on the gas separation performance of 6FDA-DAM membranes is presented in [Table 1](#). As shown, the permeability of CO₂ is higher than that of N₂ under all operational conditions. This can be related to the lower kinetic diameter, higher condensability features and preferential affinity of CO₂ with polar groups in the polymer [22]. As shown in [Table 1](#), the permeability of CO₂ through 6FDA-DAM was decreased upon increasing of the feed pressure from 2 to 5 atm, as expected from dual mode sorption model, Eqs. (11) and (12). Moreover, the evaluation of temperature dependency of gas permeability in the polymer represents a negative effect of increasing temperature on CO₂ permeability. Based on Eq. (1), decreasing the solubility of CO₂ in 6FDA-DAM is more than increasing the diffusivity as the temperature increases.

On the other hand, the permeability coefficient of N₂ increases with both temperature and pressure. As the [gas solubility in the membrane material](#) is differently affected for CO₂ and N₂, in contrast of CO₂, [the permeability of N₂ was increased with pressure, while that of CO₂ decreased](#). Consequently, as presented in [Table 1](#), increasing feed pressure from 2 to 5 atm and temperature from 35 to 55 °C, decreases the selectivity of CO₂/N₂.

Table 1. Gas permeability (P , in Barrer) and selectivity (α) values of 6FDA-DAM membrane for CO₂ and N₂ binary mixture (10 vol.% CO₂) at different temperatures and pressures.

Temperature (°C)	Pressure (atm)											
	2			3			4			5		
	P_{CO_2}	P_{N_2}	α_{CO_2/N_2}	P_{CO_2}	P_{N_2}	α_{CO_2/N_2}	P_{CO_2}	P_{N_2}	α_{CO_2/N_2}	P_{CO_2}	P_{N_2}	α_{CO_2/N_2}
35	925	37	25	887	38	23.3	860	39	22.1	825	40	20.6
45	907	42	21.6	874	44	19.9	850	46	18.5	815	47	17.2
55	890	46	19.3	860	49	17.6	838	52	16.2	807	54	14.9

5.2. Model validation

Con formato: Subíndice

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In this work the validity of the proposed models was investigated using our experimental results as well as the literature experimental data. In this regard, initially it is crucial to analyze the energetic parameters of the membranes by using van't Hoff-Arrhenius model. In order to evaluate the accuracy of the proposed model, the percentage of average absolute relative error (%AARE) between experimental data (or calculated parameters) and estimated values was calculated by:

$$\%AARE = \frac{100}{N} \sum_{i=1}^N \left| \frac{est_i - exp_i}{exp_i} \right| \quad (28)$$

where N is the number of data points, exp_i and est_i are experimental (or calculated parameters) and estimated values, respectively.

5.2.1. Validation of the proposed models based on our experimental data

Activation energies and pre-exponential factors of permeability in 6FDA-DAM at different feed pressures in the range of 2 to 5 atm are presented in [Table 2](#). In spite of increasing P_0 and E_p with pressure for CO₂ and N₂, the activation energy of permeability for CO₂ becomes less negative. As shown in [Fig. 1](#), P_0 and E_p can be exceptionally expressed by Eqs. (19) and (20), respectively, in which the maximum AARE is 2%. Presented adjustable parameters of the proposed model in [Table 2](#) indicate a strong pressure dependency for E_p and P_0 . Predictions of the proposed model in [Fig. 3](#), with AARE less than 1%, revealed the capability of the model in representing temperature and pressure dependency of CO₂ and N₂ permeability in 6FDA-DAM.

Table 2. Modified van't Hoff-Arrhenius model parameters for binary mixture of CO₂ and N₂ in 6FDA-DAM from 35 to 55 °C.

Penetrant	Pressure (atm)	E_p (kJ/mol)	P_0 (Barrer)	a_p	b_p	c_p	d_p
CO ₂	2.04	-1.62	492	437	0.17	0.76	-2.15
	3.06	-1.30	535				
	4.08	-1.09	563				
	5.10	-0.93	574				
N ₂	2.04	9.16	1327	429	1.58	3.84	6.43
	3.06	10.7	2482				
	4.08	11.9	4147				
	5.10	12.6	5541				

5.2.2. Validation of the proposed models based on the literature experimental data

Gas separation properties of poly(dimethyl siloxane) (PDMS) in the both cases of pure and mixture were studied under low temperature and pressure conditions [23]. Investigation of the reported gas transport properties of PDMS shows an increase in permeability coefficient of CO₂ in pure and mixed gas (CO₂:N₂:Ar) experiments as pressure increases due to plasticization effects [6, 24]. Increasing upstream pressure leads to the increase of plasticizer agent concentration (CO₂ in this case) in the polymer and consequently the enhancement of solubility of more soluble penetrants in the polymer matrix. As shown in Fig. S1, by contrast of pure gas experiments, the permeation of CO₂ through PDMS in the case of gas mixture decreases with temperature increasing in the range of -30 to 20 °C. This can be attributed to sorption competition as well as decreasing solubility as temperature increased [23]. Furthermore, it is notable that above 0.5 atm upstream pressure, similar to mixed gas experiments, the permeability of pure CO₂ decreased as the temperature increased.

As shown in [Table. 3](#), the activation energies of CO₂ permeability and the corresponding pre-exponential factors through PDMS have a significant pressure dependency in both cases of pure and mixture CO₂ permeability. In order to simulate the temperature and pressure dependency of permeability through PDMS, the proposed model was applied. [Fig. 3](#) compares the predictions of the proposed model for P_0 and E_p and the obtained values by Arrhenius model at different pressures. As presented in [Fig. 4](#) (a and b), the predictions of the modified Arrhenius model are in good agreement with the experimental permeabilities of CO₂.

Table 3. Modified van't Hoff-Arrhenius model parameters for CO₂ permeability through PDMS, [23], at different pressures in the cases of pure from -30 to 40 °C and mixture from -30 to 20 °C.

Penetrant	Pressure (atm)	E_p (kJ/mol)	P_0 (Barrer)	a_p	b_p	c_p	d_p
CO ₂ (pure)	0.10	11.6	140178				
	0.25	5.51	13650	396	-2.53	-6.81	-4.13
	0.50	0.61	2237				
	0.80	-2.50	753				
0.05	-5.30	16.9					
CO ₂ (mixture)	0.10	-4.40	34.8	422	1.07	0.96	-2.30
	0.50	-3.03	199				

Although the permeability of pure CH₄ through PDMS is almost independent of the upstream pressure, that of pure n-C₄H₁₀ depends significantly on it [4, 25]. Besides, the permeation of CH₄ increased with pressure in the presence of just 2% n-C₄H₁₀. Discrepancy between the CH₄

permeability in the cases of pure and binary mixture, can be attributed to plasticization of PDMS due to solubility features of n-C₄H₁₀ in the polymer [26].

Table 4, indicates considerable pressure dependency of the activation energies and the corresponding pre-exponential factors for pure and mixed gas CH₄ and n-C₄H₁₀ permeability through PDMS. As indicated in Fig. 4 (c and d), the proposed model predict satisfactorily the temperature and pressure dependency of the permeability through PDMS for CH₄ in binary mixture (containing 2 vol.% n-C₄H₁₀) and pure n-C₄H₁₀.

Table 4. Modified van't Hoff-Arrhenius model parameters for permeability through PDMS, [4], at different pressures for CH₄, in binary mixture (containing 2% n-C₄H₁₀) from -10 to 50 °C, and for pure n-C₄H₁₀ in the range of 25 to 50 °C.

Penetrant	Pressure (atm)	E_p (kJ/mol)	P_0 (Barrer)	a_p	b_p	c_p	d_p
C ₄ H ₁₀ (pure)	1.14	-21.4	6.25				
	1.50	-26.8	0.91	15.35	-6.84	-19.3	-18.8
	1.61	-27.9	0.61				
CH ₄ (mixture)	4.4	6.02	14093				
	7.8	5.23	10483	31463	-0.54	-1.46	8.20
	11.2	4.65	8480				

The temperature and pressure dependency of gas separation through polymers of intrinsic microporosity (PIM-1) has been investigated [27]. Permeability, diffusivity and solubility measurements were made within the temperature range of 25 to 55 °C over a wide pressure range of 1 to 10 atm. Based on the results; by contrast of permeability, diffusivity and solubility of He, H₂, O₂, N₂ and CH₄ are quite significant pressure dependent. Moreover, although the permeability of CO₂ in PIM-1 does not follow the van't Hoff-Arrhenius model, the temperature dependency of both diffusivity and solubility can be analyzed by the model.

The proposed model has been applied to study the influence of the operating temperature and pressure on the estimation of the separation properties of PIM-1 membranes [27]. Table. 5 presents energetic parameters of van't Hoff-Arrhenius model as well as adjustable parameters of the proposed model. As adjusted b_p and c_p for different gas molecules, except for N₂, are close to zero, pressure dependency of permeability through the polymer is negligible.

Table 5. Modified van't Hoff-Arrhenius model parameters for permeability, diffusivity and solubility in PIM-1[27], for He, H₂, CO₂, O₂, N₂ and CH₄ in the range of 25 to 55 °C.

Gas	Pressure (atm)	E_p (kJ/mol)	P_0 (Barrer)	E_d (kJ/mol)	D_0 (cm ² /s)	ΔH_s (kJ/mol)	S_0 (cm ³ /cm ³ atm)	a_p	b_p	c_p	d_p
								a_d	b_d	c_d	d_d
								a_s	b_s	c_s	d_s
He	1	2.705	3993	22.0	0.20	-19.3	14.7 E-5	3997	-0.005	-0.003	2.71
	2.5	2.705	3982	20.9	0.14	-18.4	20.3 E-5	0.21	-0.484	-1.49	22.1

	5	2.704	3970	19.5	0.10	-17.4	27.9 E-5	14 E-5	0.462	1.42	-19.5
	7.5	2.703	3962	19.1	0.08	-16.6	36.2 E-5				
	10	2.697	3943	18.6	0.07	-16.1	42.4 E-5				
	1	1.67	5706	13.3	7.1 E-3	-11.7	6.08 E-3				
	2.5	1.72	5819	12.9	6.1 E-3	-11.1	7.26 E-3	5757	-0.004	-0.007	1.69
H ₂	5	1.70	5766	12.3	5.2 E-3	-10.6	8.48 E-3	7.2 E-3	-0.195	-0.63	13.4
	7.5	1.63	5601	12.0	4.7 E-3	-10.4	9.04 E-3	6.1 E-3	0.191	0.62	-11.7
	10	1.69	5732	11.9	4.6 E-3	-10.2	9.31 E-3				
	1	-	-	18.0	1.9 E-3	-16.5	0.042				
	2.5	-	-	15.4	0.8 E-3	-14.5	0.068	-	-	-	-
CO ₂ ^a	5	-	-	12.3	0.3 E-3	-12.5	0.109	2 E-3	-1.06	-3.54	18.2
	7.5	-	-	11.1	0.2 E-3	-11.3	0.134	0.042	0.561	2.55	-16.6
	10	-	-	10.1	0.1 E-3	-10.8	0.144				
	1	3.095	3380	18.4	3.5 E-3	-15.9	5.86 E-3				
	2.5	3.214	3532	16.9	2.0 E-3	-14.4	10.2 E-3	3360	0.057	0.19	3.06
O ₂	5	3.335	3662	15.5	1.3 E-3	-12.9	16.4 E-3	3.7 E-3	-0.697	-2.00	18.6
	7.5	3.403	3694	14.5	0.9 E-3	-11.8	24.0 E-3	5.6 E-3	0.718	2.10	-16.1
	10	3.585	3924	13.8	0.7 E-3	-11.0	30.7 E-3				
	1	11.250	24227	25.5	21 E-3	-14.28	8.76 E-3				
	2.5	11.772	29204	24.1	13 E-3	-12.29	17.6 E-3	24529	0.170	0.50	11.3
N ₂	5	12.106	32572	22.7	8.1 E-3	-10.63	30.3 E-3	22 E-3	-0.643	-1.96	25.7
	7.5	12.236	34064	21.7	5.9 E-3	-9.49	43.6 E-3	8.5 E-3	0.810	2.45	-14.4
	10	12.437	36217	21.0	4.8 E-3	-8.57	57.4 E-3				
	1	20.04	1.03 E6	36.1	0.57	-16.1	13.8 E-3				
	2.5	19.95	0.99 E6	34.3	0.32	-14.4	23.4 E-3	1.04 E6	-0.080	-0.14	20.0
CH ₄	5	19.71	0.88 E6	32.1	0.16	-12.4	42.9 E-3	0.64	-0.920	-2.98	36.6
	7.5	19.82	0.91 E6	30.7	0.11	-10.8	65.7 E-3	12.3 E-3	0.840	2.84	-16.5
	10	19.72	0.86 E6	29.2	0.07	-9.46	97.7 E-3				

^aPermeability of CO₂ does not follow Arrhenius model in the range of 25 to 55 °C

Figs. S2 and S3 properly indicate the pressure dependency of activation energy of diffusivity and heat of sorption as well as their corresponding pre-exponential factor (D_0 and S_0) for He, H₂, CO₂, O₂, N₂ and CH₄ in PIM-1 in the range of 25 to 55 °C. Moreover, [Fig. 5](#) and [Fig. 6](#) compare the predictions of the modified van't Hoff-Arrhenius model and experimental data for solubility and diffusivity versus pressure at different temperatures. As shown, the accuracy of the predictions is more than 95%. It is notable that, as diffusivity and solubility of He and CH₄ do not follow Arrhenius model in the range of 25 to 55 °C, their properties were analyzed within the [temperature](#) ranges of 35 to 55 °C and 25 to 45 °C, respectively.

5.3. Sensitivity analysis of the proposed models

Based on the results, the proposed model properly exhibits pressure dependency of energetic parameters as well as pre-exponential factors of van't Hoff-Arrhenius model. As mentioned, the estimation of transport properties of membranes at different operational temperatures and pressures is attractive to reduce the number of costly experiments. In order to investigate the

sensitivity of the proposed models to the number of applied experimental data points for validation, the following procedures were used:

i. Model validation based on related experimental data to two pressures within a temperature range

To minimize the number of experiments, the proposed model is capable to predict the separation properties as well as the energetic parameters of penetrants through membranes over a wide range of operational conditions only by using related experimental data to two pressures within a suitable temperature range, at least 3 points. In this case, the model is called “Two-point modified van't Hoff-Arrhenius model”.

Table. 6 compares modified van't Hoff-Arrhenius model parameters for 6FDA-DAM membranes by using the entire experimental data and corresponding results to 2 and 5 atm in the range of 35 to 55 °C (Table. 1). As shown in Fig. 7, Two-point modified van't Hoff-Arrhenius model satisfactory, with AARE less than 2%, predicts the pressure dependency of the activation energy of permeability through the membrane and its pre-exponential factor. Moreover, Fig. 8 displays an appropriate trend of the experimental CO₂ and N₂ permeation data through 6FDA-DAM.

Table. 6. Modified van't Hoff-Arrhenius model parameters for binary mixture of CO₂ and N₂ in 6FDA-DAM from 35 to 55 °C in the range of 2 to 5 atm based on using the entire experimental data and the corresponding results to Two points pressure of 2 and 5 atm.

Penetrant	a_p	b_p	c_p	d_p
CO ₂	437 ^a	0.17 ^a	0.76 ^a	-2.15 ^a
	435 ^b	0.17 ^b	0.76 ^b	-2.16 ^b
N ₂	429 ^a	1.58 ^a	3.84 ^a	6.43 ^a
	436 ^b	1.56 ^b	3.78 ^b	6.46 ^b

^abased on the entire experimental data

^bbased on the data related to two points pressure of 2 and 5 atm in the range of 35 to 55 °C

Tables. S1 to S3 present the corresponding adjustable parameters of the Two-point modified van't Hoff-Arrhenius model for the other reported experimental data in this study. Besides, Figs. S4 to S6. compare the predictions of the model and published experimental data at different operational conditions with AARE less than 6%.

ii. Model Validation based on related experimental data to different temperatures/single pressure and different pressures/single temperature

Furthermore, the proposed model has the capability to predict temperature and pressure dependency of P , D and S only by using related experimental data to one temperature within a suitable pressure range, at least 3 points, and also one pressure in a suitable temperature range, at least 3 points. In this case, after evaluating E_p , E_d and ΔH_s as well as P_0 , D_0 and S_0 based on Arrhenius model, initially the entire pressure dependency of P , D and S is attributed to E_p , E_d and ΔH_s . In other words, by considering the pre-exponential factor as a constant at different pressures, the values of the energetic parameters are calculated. Afterwards, based on fitting the calculated parameters (E_p , E_d and ΔH_s) by using Eqs. (20)(20), (23)(23) and (26)(26), the corresponding pre-exponential factors are back calculated by Arrhenius model. Finally, the calculated P_0 , D_0 and S_0 are fitted by Eqs. (19)(19), (22)(22) and (25)(25). A schematic diagram of the proposed approach is presented in Fig. 9Fig-9.

To estimate the separation properties of 6FDA-DAM in the range of 2 to 5 atm and 35 to 55 °C, experimental permeability data of CO₂ and N₂ at 3 atm from 35 to 55 °C and related measurements at 45 °C from 2 to 5 atm, have been applied. Fig. 10Fig-10, revealed that the predictions of the proposed model, in this case, with accuracy of higher than 98% are in good agreement with the experimental data. Moreover, Figs. S7 and S8 compare the appropriate predictions of the proposed model with this methodology and the reported experimental data.

In addition to pure polymeric membranes, the proposed model can be used to show simultaneously the temperature and pressure dependency of MMMs transport properties. The effects of operational temperature and pressure on the CO₂/CH₄ separation properties of Matrimid®-5218 based MMMs at different loadings of sodium zeolite Y (NaY) were investigated [19]. In spite of the negligible pressure dependency of CH₄ permeability coefficient, Fig. S9, the influence of pressure on CO₂ permeation is considerable as particle loading increases. As shown in Fig. 11Fig-11, the proposed model provides a reasonable permeability prediction through Matrimid®-5218-NaY MMMs over a wide range of conditions by using the corresponding experimental data at 35 °C in the feed pressure range from 2 to 12 atm and at 2 atm from 35 to 75 °C.

Based on the capability of the proposed model, in order to minimize the number of experiments, instead of evaluating transport properties of membranes in a suitable temperature range at a constant pressure and one temperature at different pressures, it is suggested to investigate their separation performance at two pressures and different temperatures. Because, in this way not

only the operational dependency of transport parameters, but also the energetic parameters of the van't Hoff-Arrhenius model can be analyzed over a wide range of pressures.

6. Conclusions

In membrane gas separation technology due to the temperature and pressure dependency of transport properties of membranes, the measurement of their separation performance at different operational temperatures and pressures is crucial to optimize the membrane process design. To reduce the number of costly and time-consuming experiments, in this study the van't Hoff-Arrhenius model was modified. The modification of this model allowed to determine the effects of temperature and pressure simultaneously on the transport properties of membranes including permeability, diffusivity and solubility. It is notable that the applicability of the proposed model is limited to the membranes where not only their separation properties follow the van't Hoff-Arrhenius model at a constant pressure, but also show a sensible pressure dependency. The validity of the proposed model was satisfactorily assessed using the transport properties of a variety of membrane results from our experiments and the literature including those achieved from glassy and rubbery polymers as well as MMMs. The validation included data from single gas and mixture measurements. Moreover, the pressure dependency of both energetic parameters (activation energies of permeability, diffusivity and heat of sorption) and the corresponding pre-exponential factors of van't Hoff-Arrhenius model can be fairly estimated by the proposed model. Furthermore, to minimize the number of experiments, the proposed model is capable to predict properly the transport properties as well as the energetic parameters of penetrants through membranes over a wide range of operational conditions, only by measuring their properties at two pressures within a suitable temperature range including at least 3 points. Predictions corresponding to 300 experimental data points indicate that the accuracy of the proposed model is about 95%.

Nomenclature

AARE	Average Absolute Relative Error
a	Adjustable parameter of pre-exponential factors in modified van't Hoff-Arrhenius model
B_i	Affinity constant for penetrant i
b	Adjustable parameter of pre-exponential factors in modified van't Hoff-Arrhenius model
C	Concentration of penetrant
C'_{Hi}	Langmuir capacity constant for penetrant i

Con formato: Fuente: Negrita

c	Adjustable parameter of energetic parameters in modified van't Hoff-Arrhenius model
D	Diffusivity coefficient
D_0	Pre-exponential factor of diffusivity coefficient
D_{Di}	Diffusion coefficient of component i in Henry sites
D_{Hi}	Diffusion coefficient of component i in Langmuir sites
d	Adjustable parameter of energetic parameters in modified van't Hoff-Arrhenius model
E_d	Activation energy of diffusivity
E_d°	Activation energy of diffusion in an infinite dilution
E_p	Activation energy of permeability
f_i	Fugacity of penetrant i at feed side
K_{Di}	Constant of Henry's law for penetrant i
P	Permeability coefficient
P_0	Pre-exponential factor of permeability coefficient
p	Pressure
p^{sat}	Saturated vapor pressure of penetrant
R	Universal gas constant
S	Solubility coefficient
S_0	Pre-exponential factor of solubility coefficient
T	Absolute temperature
\bar{V}	Partial molar volume of penetrant
x	Interaction parameter of Flory-Huggins
α	Selectivity
β	Adjustable parameter of permeability in Safari model
β'	Adjustable parameter of selectivity in Safari model
γ	Adjustable parameter of permeability in Safari model
γ'	Adjustable parameter of selectivity in Safari model
ΔH_s	Heat of sorption
Δp	Pressure difference between feed and permeate sides
δ	Adjustable parameter of permeability in Safari model
δ'	Adjustable parameter of selectivity in Safari model
τ	Adjustable parameter of permeability in Self-Consistent model
ϕ	Volume fraction of penetrant

φ	Adjustable parameter of permeability in Safari model
φ'	Adjustable parameter of selectivity in Safari model
μ	Adjustable parameter of permeability in Safari model
ξ	Adjustable parameter of permeability in Self-Consistent model
ω	Adjustable parameter of permeability in Self-Consistent model

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Comentado [JC2]: Saaid, maybe you have to add something from your side.

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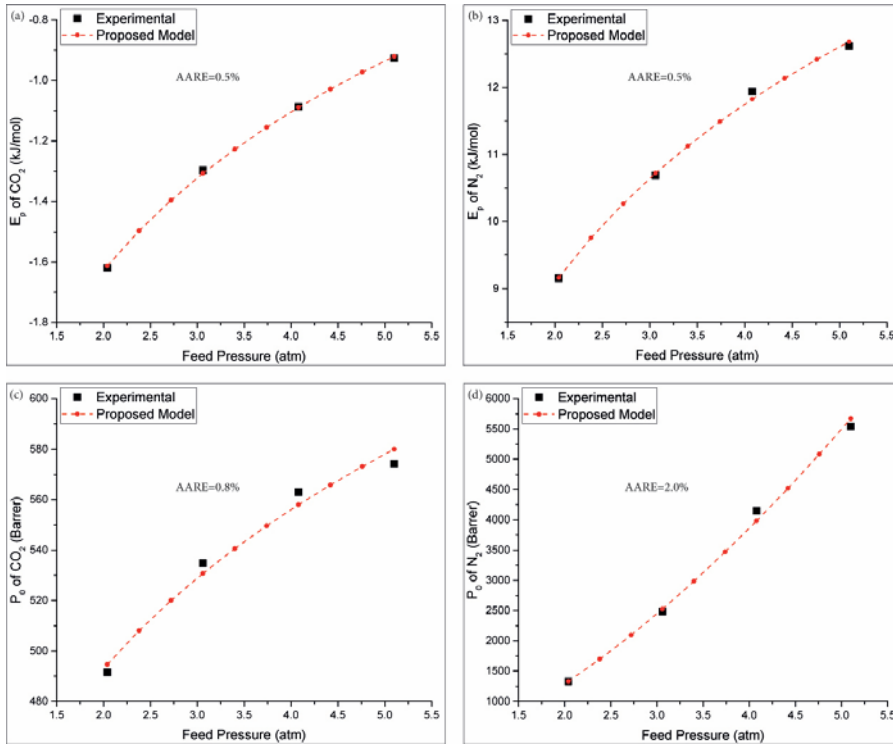


Fig. 1. Comparison of obtained Arrhenius model parameters (P_0 and E_p) by experimental data with predictions of the proposed model through 6FDA-DAM for CO_2 and N_2 .

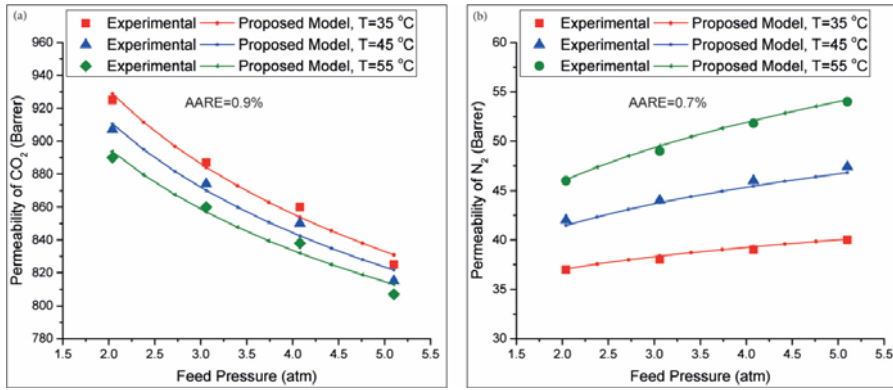


Fig. 2. Comparison of permeability predictions of the proposed model and experimental data for binary mixture of CO₂ and N₂ containing 10 vol.% CO₂ in 6FDA-DAM.

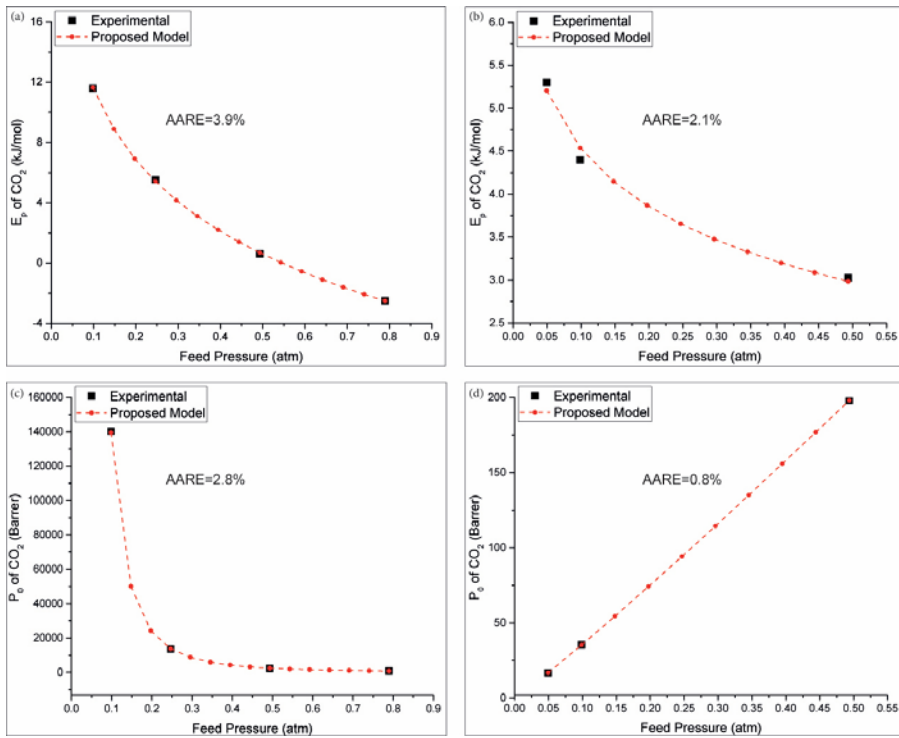


Fig. 3. Comparison of obtained Arrhenius model parameters (P_0 and E_p) by experimental data with predictions of the proposed model through PDMS, [23], for CO₂ (a and c) in pure and (b and d) in ternary mixture of CO₂, N₂ and Ar containing 95 vol.% CO₂, 3 vol.% N₂ and 2 vol.% Ar.

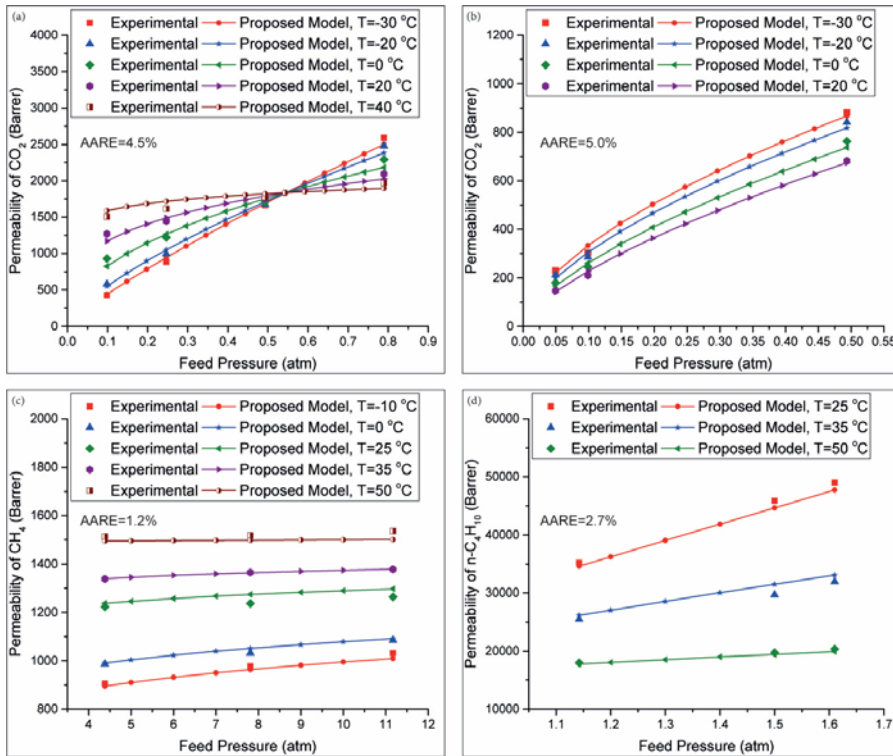


Fig. 4. Comparison of permeability predictions of the proposed model and experimental permeability data through PDMS for (a) pure CO₂, (b) mixture of CO₂ (containing 95 vol.% CO₂, 3 vol.% N₂ and 2 vol.% Ar.), [23], (c) CH₄ in binary mixture (containing 2% n-C₄H₁₀) and (d) pure n-C₄H₁₀ [4].

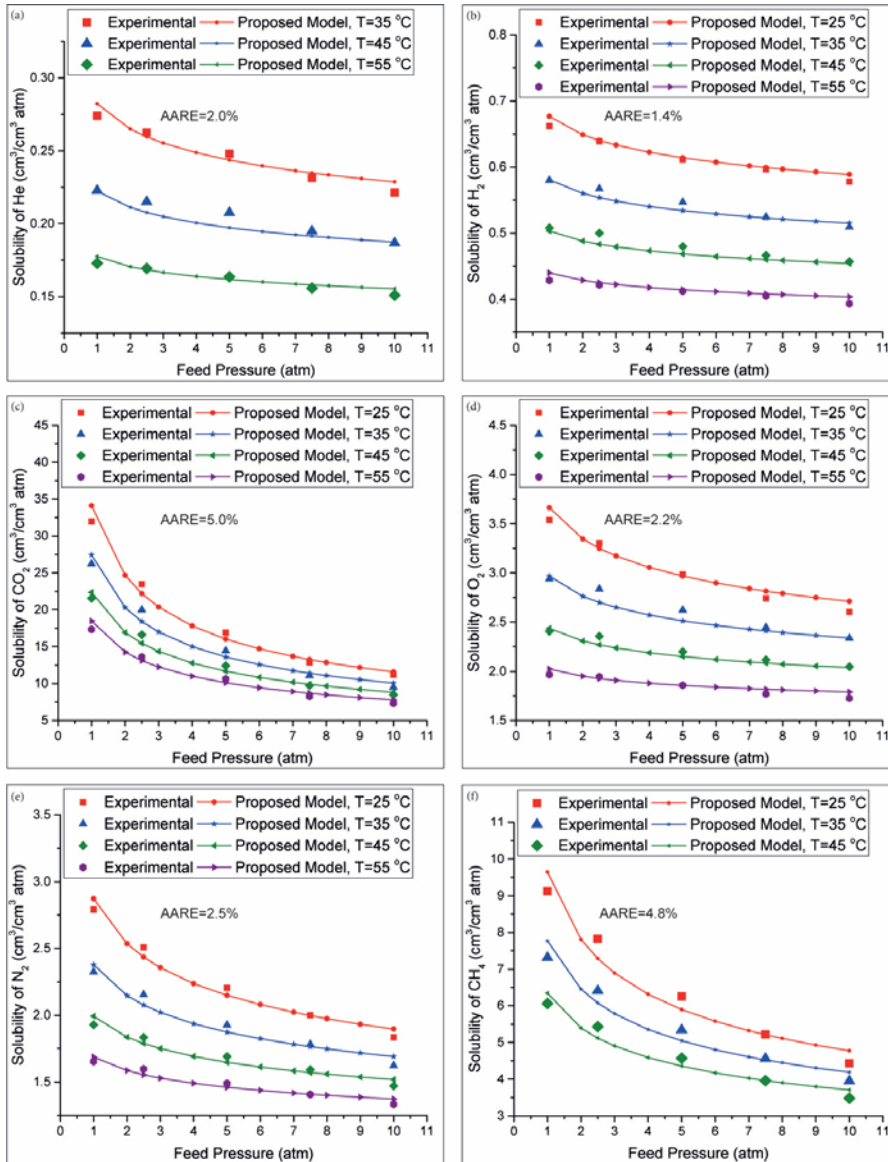


Fig. 5. Comparison of solubility predictions of the proposed model and experimental data [27] for He, H₂, CO₂, O₂, N₂ and CH₄ in PIM-1.

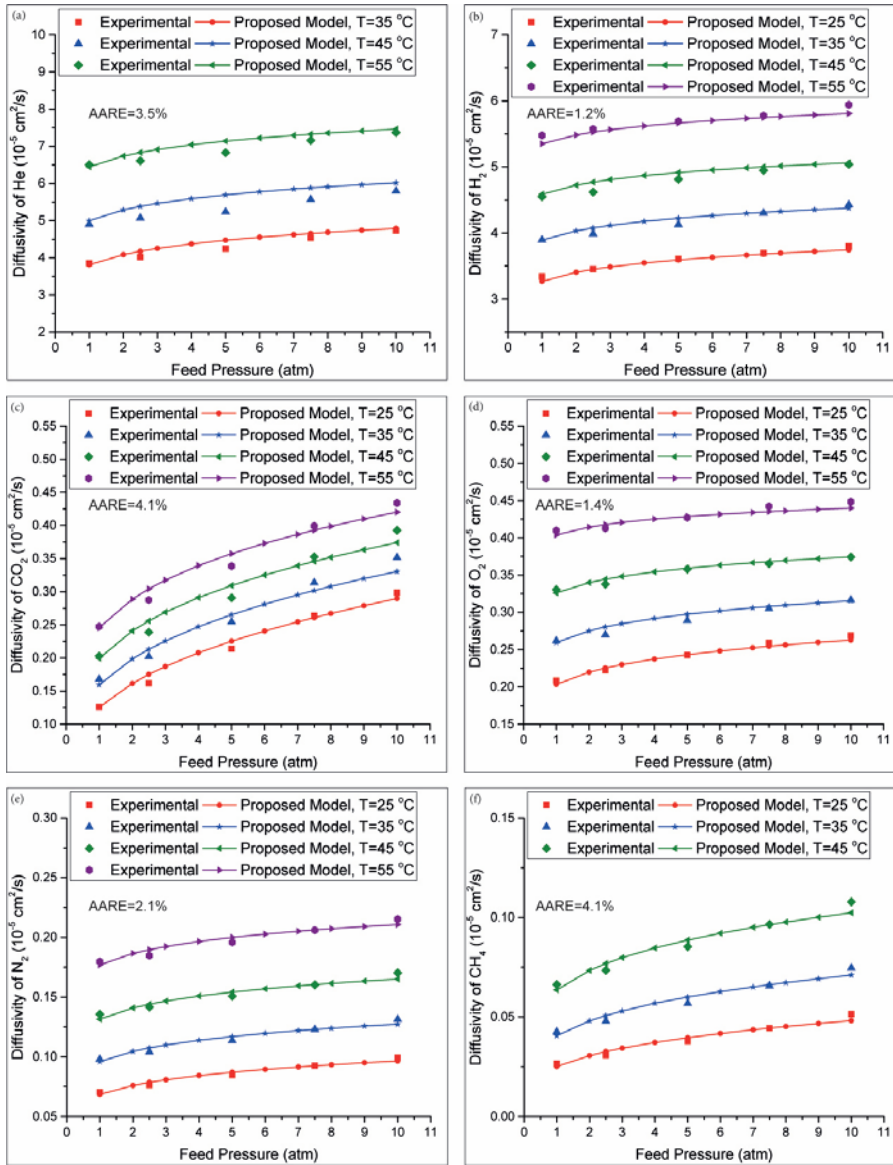


Fig. 6. Comparison of diffusivity predictions of the proposed model and experimental data [27] for He, H₂, CO₂, O₂, N₂ and CH₄ in PIM-1.

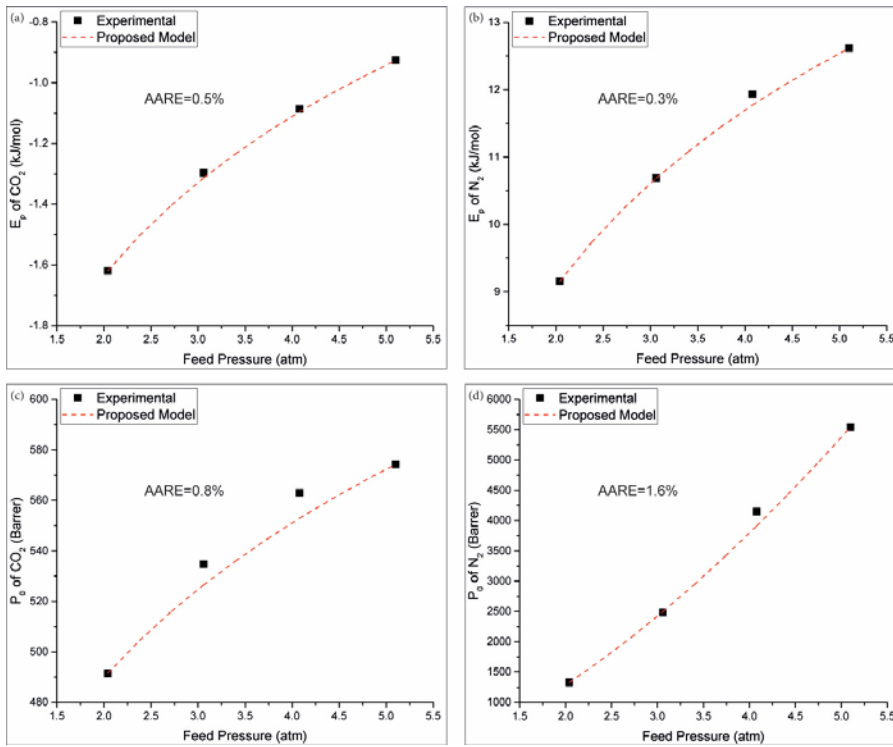


Fig. 7. Comparison of predictions of the Two-point modified van't Hoff-Arrhenius model and obtained Arrhenius model parameters (P_0 and E_p) by experimental data through 6FDA-DAM for CO₂ and N₂.

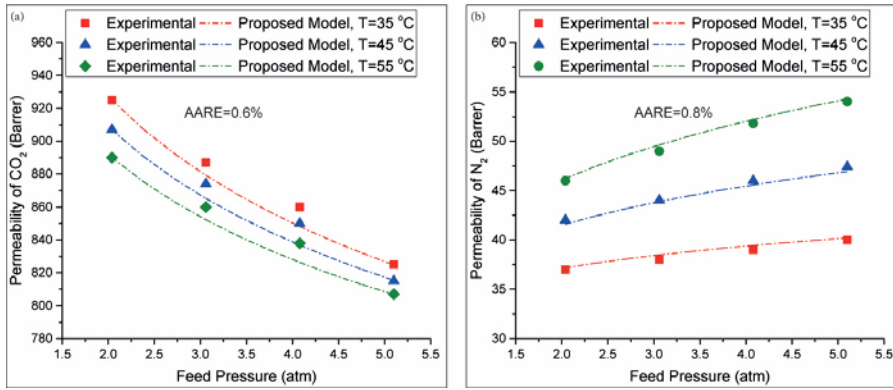


Fig. 8. Comparison of permeability predictions of the Two-point modified van't Hoff-Arrhenius model and experimental data for binary mixture of CO₂ and N₂ containing 10 vol.% CO₂ in 6FDA-DAM.

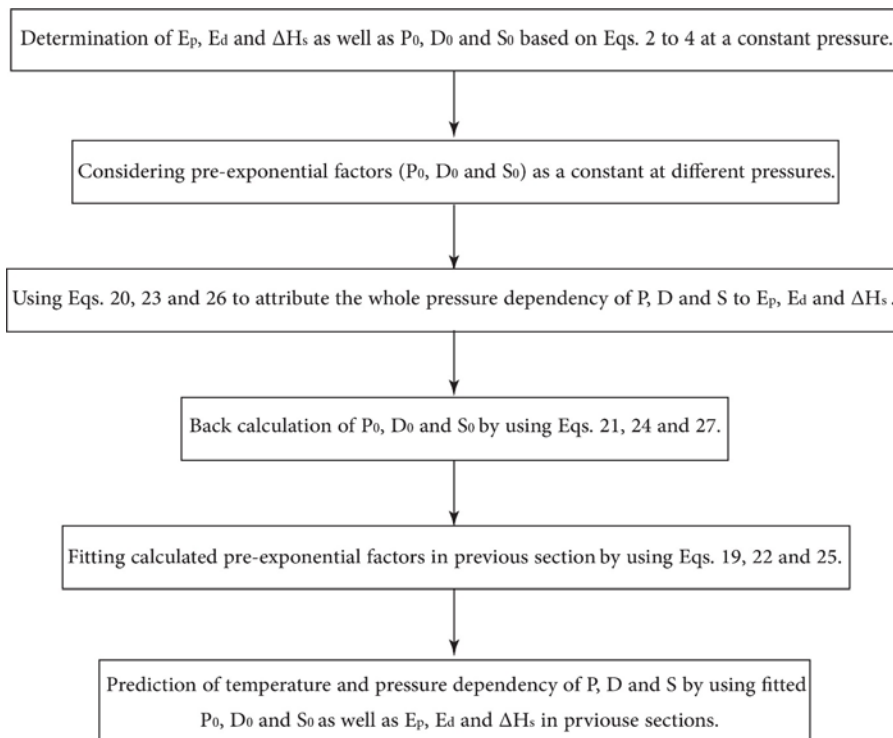


Fig. 9. A schematic diagram of the proposed approach for validation of the proposed models based on related experimental data to different temperatures/single pressure and different pressures/single temperature.

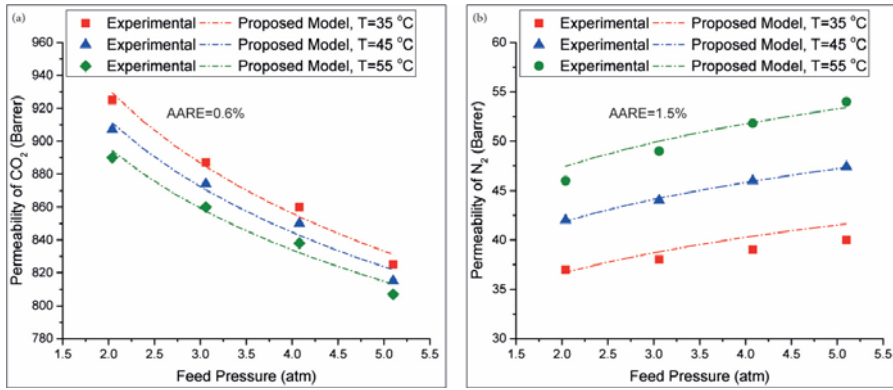


Fig. 10. Permeability predictions of the proposed model over a wide range of temperature and pressure by using corresponding experimental data for binary mixture of CO₂ and N₂ containing 10 vol.% CO₂ in 6FDA-DAM at 45 °C from 2 to 5 atm and at 3 atm from 35 to 55 °C.

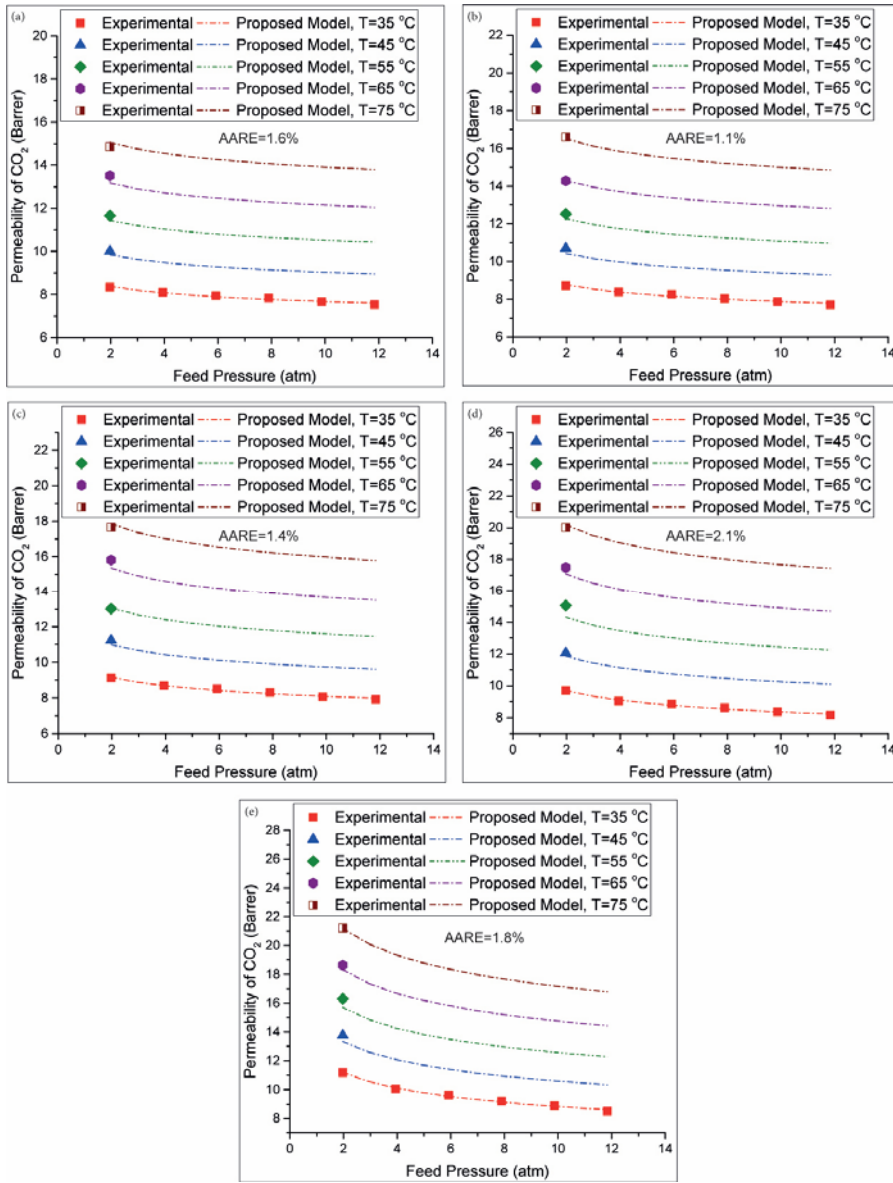


Fig. 11. Predictions of the proposed model over a wide range of operational conditions by using corresponding experimental data [19] at 35 °C in the feed pressure range from 2 to 12 bar and at 2 bar from 35 to 75 °C for CO₂ in (a) Matrimid₅, (b) Matrimid₅/NaY (5 wt.%), (c) Matrimid₅/NaY (10 wt.%), (d) Matrimid₅/NaY (15 wt.%), and (e) Matrimid₅/NaY (20 wt.%).