Modelling of methane and n-butane sorption, diffusion and permeation in polydimethylsiloxane using PC-SAFT

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Abstract

Published sorption, diffusion and permeation data for methane and n-butane in polydimethylsiloxane (PDMS) from -20 to 50 °C was simulated using a perturbed chain statistical association theory (PC-SAFT) based model. The use of a temperature-dependent interaction parameter within the PC-SAFT model allowed the pure gas sorption data to be very well represented. The mixed gas sorption results were fully predictable from these pure gas parameters, without the introduction of any additional parameters, and agreed well with the experimental data. The model was also able to model the dilation behaviour of PDMS under various gas compositions, making it possible to analyse gas sorption properties using pure gas sorption data only. A diffusion model coupled with the PC-SAFT model was capable of fitting both pure and mixed gas permeation data well by applying an exponential expression to account for such dilation in the diffusivity term. Only two parameters (i.e. infinite dilution mobility coefficient L_0 and plasticization factor β) were used and no coupling effect between the two penetrants was needed. The activation energies of L_0 were 11.7 and 13.4 kJ mol⁻¹ for methane and n-butane. Moreover, the model was also able to calculate the concentration profiles of the penetrants across the membrane thickness. For n-butane, the mass concentration profile changed from linear to non-linear when the feed pressure increased from 4 to 11 atm for 8 mol% n-butane at 25 °C. Conversely, methane showed a linear concentration profile under both conditions.

Keywords: perturbed chain statistical association theory; sorption; diffusion; modeling; PDMS.

Introduction

The sorption and transport behavior of small molecules in dense polymeric materials attracts great interest in many applications, such as membrane separation [1-4], sensors [5] and packing materials [6-8]. Among them, membrane separation provides an alternative to traditional energy-intensive separation methods [9, 10]. Permeability and selectivity are two key parameters to characterize membrane performance. For dense polymeric membranes, the permeability is a product of solubility and diffusivity [11]. Gas sorption and permeation measurement are widely carried out to evaluate membrane performance. However, it is critical to develop a robust mathematical model to describe these transport behaviors, both to facilitate a fundamental understanding of membrane properties, to expand datasets beyond the range of experimental results and to accelerate the development of new membrane materials.

A number of models have been developed to describe the sorption of small molecules in both rubbery and glassy polymers [12-14]. For rubbery polymeric membranes, Flory-Huggins theory is one of the most common models to describe penetrant sorption behavior [14]. Theoretically, only one constant interaction parameter (χ) is needed for a penetrant/polymer binary system. However, many studies have shown that a concentration-dependent interaction parameter is needed to fit the experimental sorption data [1], thus making the model less attractive. Merkel et al. [1] reported that the χ value for n-C₃H₈ in PDMS was highly concentration-dependent and a polynomial expression was applied. Further, the Flory-Huggins model requires the partial molar volume of the gas molecule in the polymer and this can vary significantly with temperature. Hence, a dilation measurement must be carried out to estimate the penetrant's partial molar volume in the polymer [15]. This is particularly important when the temperature range is wide as this partial molar volume can change significantly. Moreover, the Flory Huggins model becomes more complicated for multicomponent sorption in polymers, which plays an important role in understanding practical membrane performance, but for which very limited data is available in the literature due to the complexity of gaseous mixture sorption experiments [16-18]. It has been reported that the sorption of one component can be affected by the presence of the other component. For example, Raharjo et al. showed that methane solubility was enhanced by the presence of n-butane in PDMS [19]. Recently, we reported that the solubility of ethanol was increased by the presence of water in poly (vinyl alcohol) (PVA) [20]. As a result, it is useful to develop a predictive model that can calculate the solubility of gas mixtures in polymers from single gas sorption data alone.

Recently, Equation of State (EoS) based models such as the Sanchez-Lacombe lattice fluid equation and perturbed chain statistical associating fluid theory (PC-SAFT) have provided some successful predictive results of this approach [12, 20-22]. Minelli et al. [21] used the Sanchez-Lacombe lattice fluid equation to model the solubility of CO₂ and C₂H₆ in cross-linked poly (ethylene oxide) (XLPEO) over a wide range of temperatures, pressures and compositions. Bashir et al. [23] also showed that the partial molar volumes of hydrocarbons can be calculated using the Sanchez-Lacombe lattice fluid EoS from pure gas sorption data. Hence, it is practical to predict mixed gas sorption behavior from only pure gas sorption data by using EoS models.

The solution-diffusion model is widely used to describe the transport behavior of penetrants through dense polymeric membranes, and the generalized driving force is the gradient of the chemical potential of penetrants across the membrane [24]. The difficulty comes from the changes to the diffusivity term as the membrane changes in composition [3, 25, 26]. Similar to mixed gas solubility, the permeability of one gas in a gaseous mixture can be different from that in a pure gas permeation measurement. One can combine a proper EoS model with a diffusion model to describe gas transport behavior in membranes for both pure gas and mixed gas permeation [27-30]. However, a concentration-averaged diffusivity is widely used. This means that little information about the penetrant concentration profile across the membrane has been reported [31, 32].

In this work, the PC-SAFT EoS [33] is employed to investigate both pure and mixed gas sorption data of CH₄ and n-C₄H₁₀ in PDMS from -20 to 50 °C adapted from the work of Raharjo et al. [19]. The interaction parameters between the penetrants and PDMS were retrieved from the pure gas sorption data and the model was then used to model the mixed gas sorption data in a predictive manner. Then, a concentration dependent diffusivity was coupled with the thermodynamic model to describe both pure and mixed gas permeation data simultaneously. The model allowed the concentration profiles of both penetrants across the membrane width to be determined, revealing non-linear behaviour. The model is expected to have better predictive ability and requires fewer fitting parameters than other approaches.

Model description

Thermodynamic model

The PC-SAFT EoS [33] was used as the thermodynamic model to analyze the sorption and dilation data of methane and n-butane in PDMS. In brief, the residual Helmholtz free energy

(A^{res}) is used, which consists of a hard chain contribution (A^{hc}) and a dispersion contribution (A^{disp}) as shown in Eq. (1).

$$A^{res} = A^{hc} + A^{disp} \quad (1)$$

Three pure-component parameters (i.e. the segment diameter (σ_i), the segment number (m_i) and the dispersion energy parameter (ϵ/k)) are used to represent a substance, which can be retrieved from pressure-volume-temperature (PVT) and/or vapor-liquid equilibrium (VLE) data. A major advantage of the PC-SAFT model is that there are a larger number of pure-component parameters available in the literature. Table 1 shows the pure-component parameters of PDMS, CH_4 and $\text{n-C}_4\text{H}_{10}$.

Table 1: Pure-component PC-SAFT parameters.

	M (g/mol)	m_i/M (mol/g)	σ_i (Å)	ϵ/k (K)	Ref.
PDMS	*	0.03481	3.4557	204.58	[34]
CH_4	16.043	0.06233	3.7039	150.03	[33]
$\text{n-C}_4\text{H}_{10}$	58.123	0.04011	3.7086	222.88	[33]

*: a molecular weight of 100 kg/mol was assumed for PDMS. However, the variation in the predicted sorption was less than 1% across a molecular weight range from 10 to 1,000,000 kg/mol.

For a binary mixture, an interaction parameter (k_{ij}) is needed. The segment diameter (σ_{ij}) and dispersion energy (ϵ_{ij}/k) of the mixture can be calculated by:

$$\sigma_{ij} = 1/2 (\sigma_i + \sigma_j) \quad (2)$$

$$\epsilon_{ij} = \sqrt{\epsilon_i \epsilon_j} (1 - k_{ij}) \quad (3)$$

The penetrant concentration in the membrane can be solved by applying phase equilibrium criteria (Eq. 4) once k_{ij} is known:

$$\mu_i^{gas}(T, P, x_i^{gas}) = \mu_i^{pol}(T, P, x_i^{pol}) \quad (4)$$

where T and P are the experimental temperature and pressure. μ_i^{gas} and μ_i^{pol} are the chemical potentials of penetrant i (*i.e.* methane or n-butane) in the gas and polymer phase, respectively. x_i^{gas} and x_i^{pol} are the molar fraction of penetrant i in the gas and polymer phase, respectively.

In this work, k_{ij} was set as a fitting parameter at each temperature to minimize the objective function below:

$$Obj = \sum_{l=1}^{N^{exp}} \left(\frac{C_l^{exp} - C_l^{calc}}{C_l^{exp}} \right)^2 \quad (5)$$

where C_l^{exp} and C_l^{calc} are the experimental pure gas sorption data at one temperature from Raharjo et al. [19] and calculated data from the PC-SAFT model. The PC-SAFT model was coded using Matlab R2018b [20, 35].

Transport model

The driving force for permeation of a single penetrant through a membrane is the negative chemical potential gradient of the penetrating species at constant T and P [36, 37]:

$$J_i = -\rho w_i L_i \nabla \left(\frac{\mu_i}{RT} \right)_{T,P} \quad (6)$$

where J_i is the mass diffusion flux of penetrant i , ρ is the density of the mixture, w_i , L_i and μ_i are the mass fraction, mobility coefficient and chemical potential of penetrant i in the polymer matrix, respectively. L_i is a kinetic parameter, reflecting the resistance encountered in the polymer matrix. The above equation can also hold true for mixed gas transport through membranes if the mutual interaction between penetrants in the membrane are negligible. Since the membrane is stationary, the diffusion equations for the ternary mixture (penetrant 1, 2 and the membrane) can be simplified as [36]:

$$J_1 \approx -\rho w_1 L_1 \nabla \left(\frac{\mu_1}{RT} \right)_{T,P} \quad (7)$$

$$J_2 \approx -\rho w_2 L_2 \nabla \left(\frac{\mu_2}{RT} \right)_{T,P}$$

ρ , w_i , and μ_i ($i = 1, 2$) can be easily calculated by the PC-SAFT EoS as described above. L_i is concentration dependent and an exponential correlation with penetrant mass or molar concentration fraction is widely used [3, 38, 39]. The pure CH₄ permeability is nearly constant across the feed pressure range (*i.e.* ~4-15 bar) and the influence of CH₄ on the permeability of

n-C₄H₁₀ is also marginal [16] due to the low concentration of CH₄ in the polymer [19]. Hence in this work, the mobility coefficients of CH₄ (L_1) and n-C₄H₁₀ (L_2) are considered to be a function of only of the n-C₄H₁₀ mass fraction (w_2) in the polymer:

$$L_1 = L_1^0 \exp(\beta_1 w_2) \quad (8)$$

$$L_2 = L_2^0 \exp(\beta_2 w_2)$$

where L_1^0 and L_2^0 are the infinite dilution mobility coefficients of CH₄ and n-C₄H₁₀, while β_1 and β_2 are the plasticization factors. These four fitting parameters (L_1^0 , L_2^0 , β_1 , β_2) can be estimated by fitting both pure and mixed gas permeability data simultaneously through solving Eq. 7 and 8 together with boundary conditions at each experimental temperature. The boundary conditions apply on both the feed and permeate side of the membrane interface. The chemical potential of a penetrant in the membrane at the feed surface equals its chemical potential in the gas on this side. It is similar for the permeate side.

$$z = 0, \quad \mu_{10}^m(T, P^{feed}, x_{10}^m) = \mu_1^{feed}(T, P^{feed}, x_1^{feed});$$

$$\mu_{20}^m(T, P^{feed}, x_{20}^m) = \mu_2^{feed}(T, P^{feed}, x_2^{feed})$$

$$z = L, \quad \mu_{1L}^m(T, P^{feed}, x_{1L}^m) = \mu_1^{perm}(T, P^{perm}, x_1^{perm});$$

$$\mu_{2L}^m(T, P^{feed}, x_{2L}^m) = \mu_2^{perm}(T, P^{perm}, x_2^{perm}) \quad (9)$$

where x is the molar fraction of the species 1 or 2. Superscripts *m*, *feed* and *perm* represent the membrane, feed and permeate fluid phases; while the subscripts 0 and *L* indicate the feed and permeate sides of the membrane phase. It is worthwhile noting that the pressure across the membrane is the same as the feed pressure as the solution-diffusion model applies [24]. Eq. 7 and 8 can then be numerically solved when these boundary conditions are applied. All codes were implemented in Matlab 2018b.

Results and Discussion

The validity of the pure component parameters for PDMS (Table 1) was first investigated by comparing model predictions for the thermal expansion of the polymer (Figure 2) and experimental data from Raharjo et al. [19], who use a polymer of crosslink density 3.15×10^{-4} mol/cm³. The model results agree well with the experimental data. Moreover, the calculated

density is also very close to the experimental value. The simulation provides a value of 1.0 g/cm³ at 25 °C, while the experimental value is 0.98 ± 0.01 g/cm³. It should be noted that large deviations in the crosslink density beyond those typical of the PDMS polymers considered here may have some impact on these simulations.

Figure 1: Thermal expansion of PDMS under vacuum as a function of temperature. The experimental data are from Raharjo et al. [19] and the model prediction is from the PC-SAFT model.

The interaction parameters for CH₄/PDMS and n-C₄H₁₀/PDMS at each temperature (k_{ij}) were then obtained by fitting the pure gas sorption isotherms. A linear relationship with temperature was observed for the fitted k_{ij} . As a result, the following equation was used to further reduce the number of fitting parameters:

$$k_{ij} = a * T + b \quad (10)$$

where a (K⁻¹) and b are two fitting parameters (see Table 2).

Such a temperature-dependent k_{ij} is widely used for other penetrant/polymer systems [38]. Simulations were also conducted with a constant k_{ij} , but significant deviations from experimental data were observed in this case. Figure 2 shows CH₄ and n-C₄H₁₀ pure gas sorption isotherms taken from [19] along with the PC-SAFT model predictions using the parameters in Tables 1 and 2. It is clear that the model represents the sorption isotherms

accurately across the entire pressure and temperature range. This is not surprising as PDMS is a rubbery polymer, which is in an equilibrium state.

Table 2: Binary interaction parameters for the PC-SAFT EoS derived from gas sorption isotherms [19] as a function of the temperature (T) in Kelvin (K) from -253.15 to 323.15 K.

k_{ij}		
CH ₄ /PDMS	$0.149 + 3.53 \times 10^{-4} T \text{ (K)}$	This work
n-C ₄ H ₁₀ /PDMS	$0.0131 + 5.25 \times 10^{-5} T \text{ (K)}$	This work
CH ₄ /n-C ₄ H ₁₀	0.022	[33]

Figure 2: n-C₄H₁₀ and CH₄ sorption isotherms as a function of temperature. The experimental data are from Raharjo et al. [19] and the predictions are from the PC-SAFT model.

Once the interaction parameters are determined, the mixed gas sorption performance can be directly predicted by the PC-SAFT model and no other fitting parameters are needed. Figure 3 shows both experimental and predicted CH₄ sorption isotherms at constant n-C₄H₁₀ fugacity from -20 to 50 °C as a function of CH₄ fugacity. Overall, the model results represent well the experimental data without any adjustable parameters. This a significant improvement

198 compared with the widely used Flory-Huggins model, where concentration-dependent
 199 interaction parameters must be used [1, 17] to fit the experimental data.

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201 Figure 3: The impact of n-C₄H₁₀ on the CH₄ sorption isotherms at various temperatures. The
 202 experimental data are from Raharjo et al.[19] and the predictions are from the PC-SAFT
 203 model.

204 Having shown that the PC-SAFT model can be successfully applied to predict CH₄/n-C₄H₁₀
 205 mixture sorption behavior in PDMS, the model was used to investigate the effect of the second
 206 component across a broader range of conditions, as shown in Figure 4. For n-C₄H₁₀, activity is
 207 used on the x-axis, which is the ratio of fugacity to the saturation fugacity at a given temperature.
 208 Raharjo et al. [19] show that the sorption of n-C₄H₁₀ follows a master curve with respect to
 209 activity, regardless of fugacity or temperature. As found experimentally by Raharjo et al. [19],
 210 the solubility of CH₄ is enhanced by the presence of n-C₄H₁₀ (Figure 4a and 4b). The CH₄
 211 fugacity plays a marginal role up to 25 atm. However, the ratio of solubility increases from 2.2
 212 to 3 as the CH₄ fugacity increases from 25 to 50 atm at 0°C and an n-C₄H₁₀ activity of 0.8
 213 (Figure 4a). This probably reflects the strong solubility of CH₄ in n-C₄H₁₀ [19]. This effect is
 214 much less significant at 35 °C (Figure 4b).

215 Raharjo et al. [19] find that the presence of CH₄ has no measurable impact on the solubility of
 216 n-C₄H₁₀. Conversely, these simulations allow us to show that there is a measurable impact
 217 when n-C₄H₁₀ activity is 0.8 at 0 °C (Fig. 4c).

Figure 4: The second component effects on methane/n-butane solubility in PDMS, calculated from the PC-SAFT model.

The swelling induced by the gas mixture was also analyzed by the PC-SAFT model and the comparison between the experimental data and the model at 25 °C is shown in Figure 5. In general, the model represents the volumetric behavior of the mixture reasonably well without the adjustment of any further parameters. The maximum deviation is within 15%.

Figure 5: The influence of gas composition on the dilation of PDMS at 25 °C. The experimental data are from Raharjo et al. [19] and the predictions are from the PC-SAFT model.

The discussion above has shown that the PC-SAFT model can be successfully applied to CH₄/n-C₄H₁₀/PDMS ternary systems. Hence, it was next coupled with the transport model in Eq. 3 to investigate the transport behavior of pure and mixed gases through a PDMS membrane, using experimental data again provided by Raharjo et al. [16]. As this paper provides only limited data points for pure CH₄ and n-C₄H₁₀ permeabilities (i.e. 4 points at each temperature), it is impossible to retrieve reliable mobility coefficients (L^o and β) from pure gas permeation data as reported by Toni et. al [36]. Rather, the entire set of pure and mixed gas permeability data is fitted to Equations 7 and 8 at each temperature (a total of 17-22 points at each of the six temperatures). Figure 6 shows the comparison of model results and experimental data [16] while the fitted parameters are shown in Table 3. It is clear that the transport model coupled with the PC-SAFT model can describe CH₄ and n-C₄H₁₀ permeability data very well from -20 to 50 °C and up to 16 bar under both pure and mixed gas testing conditions. It is worthwhile noting that the models presented in Raharjo et al. [16] can also fit the permeation data well, however, at least 6 parameters are needed to achieve best-fit values for this Maxwell-Stefan model at any given temperature, whereas in the present case, four are sufficient. In particular, we can achieve a very good fit to the data without the need to include coupling effects (*i.e.* the coupling mobility coefficient L_{12}/L_{21}) between the two penetrants in the transport model.

Figure 6: The permeability of CH₄ and n-butane at various temperature and pressure: comparison between experimental data [16] and model fitting using Eq. 7 and 8.

Both infinite dilution mobility coefficients (L^o) increase with temperature (Table 3). The values for CH₄ are larger than that of n-C₄H₁₀, as CH₄ has a smaller kinetic diameter. They are orders of magnitudes larger than those in glassy polymeric membrane[36, 37]. The values of both gases are consistent with infinite dilution coefficients calculated from pure gas permeation data shown in Raharjo et al.[16]. For example, Raharjo et al. give values of $18, 22$ and $27 \times 10^{-6} \text{ cm}^2/\text{s}$ for CH₄ at 25, 35 and 50 °C. Within error, the impact of plasticization by n-C₄H₁₀ on CH₄ is constant at $\beta = 5.3 \pm 0.6$ across the entire temperature range, Conversely, the impact of plasticization by n-C₄H₁₀ on its own mobility shows a slight temperature dependence, increasing slightly from ~ 9 to 12 when the temperature increased from -20 to 50 °C. Again, these data are consistent with the estimate provided by Raharjo et al. [16] of 7.6 ± 0.1 for both penetrants. It is worth noting that the assumptions for the plasticization factor here are different from that used Toni et al. [5], where they used the plasticization factor taken from single gas permeation data to account for the influence of one penetrant on the other. This might cause the variations between their predictions and experimental data.

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Table 3: Transport model parameters for CH₄ and n-C₄H₁₀ at different temperatures.

Temperature (°C)	L^o ($\times 10^6$ cm ² /s)		β	
	CH ₄	n-C ₄ H ₁₀	CH ₄	n-C ₄ H ₁₀
-20	8.4 $\pm$ 1.5	1.93 $\pm$ 0.06	4.7 $\pm$ 0.6	9.1 $\pm$ 0.5
-10	9.7 $\pm$ 1.5	2.30 $\pm$ 0.09	5.9 $\pm$ 0.7	10.7 $\pm$ 0.7
0	12.1 $\pm$ 0.9	2.92 $\pm$ 0.08	5.3 $\pm$ 0.7	10.9 $\pm$ 0.7
25	18.4 $\pm$ 1.3	4.84 $\pm$ 0.13	6.1 $\pm$ 1.0	11.6 $\pm$ 0.5
35	21.8 $\pm$ 1.3	5.73 $\pm$ 0.08	4.9 $\pm$ 0.6	11.8 $\pm$ 0.4
50	27.3 $\pm$ 1.8	7.54 $\pm$ 0.06	5.2 $\pm$ 0.4	12.1 $\pm$ 0.4

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The activation energies for L^o of both CH₄ and n-C₄H₁₀ were analyzed by fitting the Arrhenius plot shown in Figure 7. The lines represent linear fittings with $R^2 > 0.99$. The activation energies were 11.7 and 13.4 kJ mol⁻¹ for CH₄ and n-C₄H₁₀, respectively. It is reasonable that n-C₄H₁₀ has a larger value as it is larger than CH₄, hence more sensitive to temperature. There are small deviations from the values reported by Raharjo et al. [16]. The values here are calculated based on both single and mixed gas permeation data from -20 to 50 °C, while the values in [16] are from pure permeation data only from 25 to 35 °C.

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Figure 7: Arrhenius plot of infinite dilution mobility coefficients of CH₄ and n-C₄H₁₀ in PDMS. Lines are linear fittings.

By solving Eq. 7 and 8, one can also investigate the concentration profiles of gases across the membrane thickness, providing more insights into the transport behavior. Figure 8 shows the mass concentration profiles of n-C₄H₁₀ under 8 mol% n-C₄H₁₀ at 4 and 11 atm total pressure. The mass fraction at the interface of the feed side ($x=0$) increased from 2.4 to 6.1 wt% when the total feed pressure increased from 4 to 11 atm. A linear profile was observed when the total feed pressure is 4 atm. However, when the pressure increased to 11 atm, a visible deviation from a linear profile is observed. Indeed, similar results have been reported for the permeation water/ethanol mixture through polyimide membranes [28] and for cyclohexanone through a gum rubber membrane [40]. This non-linear concentration profile is an outcome of the solution diffusion model for swollen membranes at high feed pressures [40]. Linear concentration profiles were observed for methane for both conditions, reflective of the lower mass fractions of this component in the membrane.

Figure 8: Calculated concentration profile of n- C₄H₁₀ across the membrane at 25 °C at different total feed pressures (feed composition: 8 mol% n-C₄H₁₀, balance CH₄). Dashed lines are linear for guidance.

Conclusions

The PC-SAFT model was successfully applied to describe the pure gas sorption data of CH₄ and n-C₄H₁₀ in PDMS from -20 to 50 °C with a temperature-dependent penetrant/polymer interaction parameter. It was then able to predict CH₄/n-C₄H₁₀ mixture sorption behavior in PDMS without the addition of any further parameters. The sorption of CH₄ in the mixture is largely affected by the presence of n-C₄H₁₀, i.e. the higher n-butane activity, the higher CH₄ sorption. On the other hand, the model showed that the influence of CH₄ on the sorption of n-C₄H₁₀ was marginal when the activity of n-C₄H₁₀ was less than 0.8. The n-C₄H₁₀ sorption increased monotonously with CH₄ partial pressure when its activity was fixed at 0.8 at 0 °C but this effect was less prominent at 35 °C. Moreover, the model can also represent dilation data well, which can significantly reduce the experimental work required when the partial molar volume varies with temperature.

A simple exponential expression of diffusivity coupled with the PC-SAFT Equation of State can be used within the solution diffusion model to represent both pure and mixed gas permeation data very well. No coupling effects between methane and n-butane were needed. The plasticization factor for methane was constant within the testing temperature range from -

20 to 50 °C, while it increased slightly from ~9 to 12 for n-butane. Both infinite dilution mobility coefficients increased with temperature and followed an Arrhenius relationship. CH₄ had a slightly lower activation energy (11.7 kJ mol⁻¹) than that of n-C₄H₁₀ (13.4 kJ mol⁻¹) as it has a smaller kinetic diameter. The concentration profile of n-butane across the membrane was non-linear when the total pressure increased from 4 to 11 atm for 8 mol% n-butane mixture at 25 °C, while a linear concentration profile was observed for CH₄ under both conditions.

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