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Molecular Dynamics Simulation Study on the Solubility, Diffusion, and Permeation Characteristics of Hydrogen-Blended Natural Gas in Polyvinyl Chloride

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Abstract

Against the backdrop of carbon neutrality goals, blending hydrogen into natural gas to form hydrogen-hydrocarbon mixed fuels has become a crucial pathway for building a clean energy system. However, hydrogen blending imposes specific requirements on pipeline transportation materials: while metal pipelines face risks of hydrogen-induced cracking, non-metallic pipelines, although avoiding this hazard, exhibit high gas permeability due to their polymeric nature, potentially leading to significant energy losses and safety hazards.Therefore, this study focuses on typical operating conditions of urban gas networks (temperatures of 270–310 K and pressures of 0.1–0.7 MPa). Using molecular dynamics simulations combined with Grand Canonical Monte Carlo methods, we systematically investigated the solubility, diffusion, and permeation characteristics of hydrogen and methane in polyvinyl chloride (PVC) at a hydrogen blending ratio of 10%.The results indicate that the solubility coefficients of both hydrogen and methane decrease with increasing temperature. In contrast, their diffusion coefficients increase with rising temperature and pressure. The permeability coefficient increases with temperature, primarily because the enhancing effect of the diffusion coefficient outweighs the reducing effect of the solubility coefficient.This study reveals the permeation mechanism of hydrogen-blended natural gas in PVC at the molecular level, providing a theoretical basis for the selection and safety evaluation of non-metallic pipeline materials for transporting hydrogen-blended gas.

Keywords

Hydrogen-blended Natural Gas; Polyvinyl Chloride (PVC); Permeation Properties; Molecular Dynamics Simulation; Grand Canonical Monte Carlo.

1. Introduction

Against the backdrop of the global energy structure transitioning towards cleanliness and low carbon emissions, hydrogen, as a zero-carbon clean energy source, has become a crucial alternative to traditional fossil fuels [1]. Blending hydrogen into natural gas at specific ratios to form Hydrogen-Blended Natural Gas (HBNG) not only enables the effective utilization of existing natural gas pipeline infrastructure but also significantly reduces carbon emissions, offering both economic and environmental benefits [2-3].However, during transportation, hydrogen can induce safety issues in metal pipelines, such as hydrogen embrittlement and hydrogen-induced cracking [4]. Non-metallic pipelines (Polyvinyl Chloride (PVC), Polyethylene (PE), and Polyvinylidene Fluoride (PVDF)) are increasingly becoming the preferred materials for hydrogen transport due to their advantages in corrosion resistance, lightweight properties, and flexibility [5]. Nevertheless, non-metallic materials generally exhibit high gas permeability. This is particularly concerning when transporting small-molecule hydrogen, where permeation-induced energy losses and safety risks cannot be overlooked

[6].Therefore, conducting in-depth research on the permeation mechanisms and behaviors of hydrogen and its mixed gases within non-metallic pipeline materials is of significant importance for ensuring the safe and efficient transport of hydrogen energy.

Non-metallic pipeline materials such as Polyvinyl Chloride (PVC), Polyethylene (PE), and Polyvinylidene Fluoride (PVDF) hold significant application value in gas transmission systems due to their advantages, including corrosion resistance, lightweight properties, low friction coefficients, and ease of installation [7-9]. Consequently, scholars domestically and internationally have employed microscopic research methods, such as Molecular Dynamics (MD) simulations and Grand Canonical Monte Carlo (GCMC) techniques, to systematically investigate the permeability, diffusivity, and solubility of various gases in PVC, PE, and PVDF. These studies aim to elucidate transport mechanisms and optimize material performance.For instance, Zheng et al. [10] utilized GCMC and MD methods to compare the solubility, diffusion, and permeation behaviors of hydrogen in PVC, PE, and PVDF. They found that the solubility coefficient of hydrogen in PVC decreases with increasing temperature, whereas an opposite trend is observed in PE and PVDF; meanwhile, both diffusion and permeation coefficients increase with rising temperature. YunFeng M et al. [11] investigated the diffusion behavior of Volatile Organic Compounds (VOCs) in PVC via MD simulations, demonstrating that the diffusion coefficient increases with temperature, consistent with the Arrhenius law [12]. V F O et al. [13] examined the effect of chain length on the structural and dynamic properties of PVC, noting that physical properties tend to converge when the chain length reaches 100–120 monomer units, thereby providing a basis for selecting simulation parameters.Regarding PE materials, Li X et al. [14] studied the permeation behavior of hydrogen-rich natural gas (with hydrogen blending ratios of 5%–20%) in polyethylene. They discovered that hydrogen solubility increases with temperature, while methane solubility shows the opposite trend; the diffusion coefficients for both gases increase with rising temperature and pressure. Zheng et al. [15] simulated the permeation characteristics of H_2S in PE and PVF_2, confirming that PVF_2 exhibits superior barrier performance due to stronger intermolecular forces and lower diffusion coefficients.These studies have deepened the understanding of gas transport mechanisms in non-metallic materials at the microscopic scale, laying a theoretical foundation for pipeline material selection. However, although the study by Zheng et al. [15] addressed hydrogen sulfide gases, its scope has not yet extended to the more common and complex scenario in hydrogen-blended natural gas: specifically, the interactions between multiple components, namely hydrogen and methane.

Although experts have conducted certain studies on the gas permeation behavior of non-metallic pipeline materials, most work has focused on PE or PVDF materials, or targeted single gases (such as H_2S), while systematic research on hydrogen-blended natural gas in PVC remains relatively scarce. Furthermore, existing studies often concentrate on the separate analysis of solubility or diffusion coefficients, lacking an integrated investigation of the complete solubility-diffusion-permeation process.Therefore, this paper employs Molecular Dynamics (MD) simulations combined with Grand Canonical Monte Carlo (GCMC) methods to systematically investigate the solubility, diffusion, and permeation characteristics of H_2 and CH_4 in PVC at a hydrogen blending ratio of 10%. This study aims to fill the gap in this field and provide a theoretical basis for the safe transportation of hydrogen-blended natural gas through PVC pipelines.

2. Molecular Dynamics Model

In this study, all simulations were performed using all-atom models. Initial structures were constructed for a single polyvinyl chloride (PVC) chain comprising 100 repeat units, as well as for hydrogen (H_2) and methane (CH_2) molecules. All models underwent geometric optimization for 5000 steps to minimize the system energy.Subsequently, based on the modified rotational isomeric state method proposed by Theodorou and Suter, ten independent three-dimensional periodic amorphous unit cells were generated. Each cell contained five randomly distributed PVC chains to simulate the realistic structure of the polymer's amorphous region. To identify the representative structure closest to equilibrium with the lowest energy, we calculated the energies of all cells and selected the one with the minimum energy for all subsequent simulations. This selected cell was further subjected to 20000 steps of energy minimization to obtain a more stable initial configuration.To achieve a stable equilibrium configuration under room temperature and atmospheric pressure, the optimized cell underwent a series of standard molecular dynamics relaxation steps:

(1) NVT Ensemble Relaxation: The system was run for 500ps at 300 K to allow the density to reach equilibrium.

(2) Annealing Treatment: To enhance the sufficiency of conformational sampling, the PVC cell was heated from 300 K to 600 K in steps of 60 K, and subsequently cooled from 600 K back to 300 K using the same temperature increment.

(3) High-Pressure Relaxation: An NPT simulation was conducted for 500 ps at 300 K and 1 GPa to accelerate the optimization of inter-chain packing.

(4) Final Equilibration: Finally, a 1000 ps NPT simulation was performed under target conditions (298 K, 0.1 MPa) to ensure the system reached complete equilibrium. The initial configuration for subsequent calculations was extracted from this equilibrated trajectory.

Throughout the MD simulations, a cutoff radius of 12.5 Å was employed, utilizing the Consistent Forcefield for Polymers (COMPASSII).

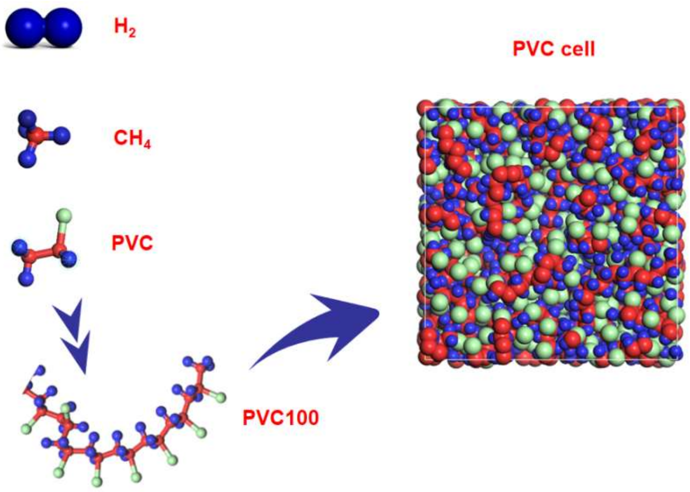


Figure 1. Model schematic. Blue, red, and green spheres denote hydrogen, carbon, and chlorine atoms, respectively

3. Numerical Simulations

To systematically reveal the transport mechanism of hydrogen-blended natural gas in polyvinyl chloride (PVC), this study integrates Grand Canonical Monte Carlo (GCMC) and Molecular Dynamics (MD) simulation methods to conduct a multi-scale analysis ranging from gas molecule adsorption and motion within the polymer to overall permeation behavior. The research focuses on a mixed gas with a 10% hydrogen blending ratio (H_2/CH_4) under typical urban gas pipeline operating conditions (temperatures of 270–310 K and pressures of 0.1–0.7 MPa), progressively investigating the dynamic processes of dissolution, diffusion, and permeation. Specifically, GCMC simulations are employed to obtain gas adsorption isotherms in PVC and calculate solubility coefficients, while MD simulations track gas molecule trajectories to determine diffusion coefficients based on Mean Square Displacement (MSD). Finally, relying on the "solution-diffusion" coupling theory, the permeation performance is comprehensively evaluated. The following sections will elaborate on the simulation methodologies and theoretical foundations for each stage.

3.1 Simulation of Dissolution and Adsorption Processes

The solubility coefficients of H_2 and CH_4 in polyvinyl chloride (PVC) were investigated using a combined "NPT + GCMC" approach. This methodology accounts for the swelling effect of PVC upon gas adsorption and the subsequent influence of this swelling on further adsorption behavior. Within the Grand Canonical Monte Carlo (GCMC) framework, the Metropolis algorithm was employed to perform insertion, deletion, and displacement moves for hydrogen (H_2) and methane (CH_4) molecules within the PVC simulation cell. The probabilities for these moves were set to 0.4, 0.4, and 0.2, respectively.A total of 2×10^7steps were executed, with the first half dedicated to equilibration and the second half to production runs. Adsorption isotherms for H_2 and CH_4 in PVC were obtained at various temperatures and subsequently fitted using Equation (1). As defined in Equation (2), the solubility coefficient corresponds to the slope of the isotherm as the fugacity (f) approaches zero. To minimize errors, multiple dissolution simulations were conducted for the selected PVC cell until the fitting error at each temperature condition satisfied the criterion specified in Equation (3)

$$C=K\cdot f \tag{1}$$

$$S=\lim_{f\to0}\frac{c}{f}=k \tag{2}$$

$$R^2\geq0.95 \tag{3}$$

3.2 Simulation of the Diffusion Process

The amorphous polyvinyl chloride (PVC) simulation cells containing hydrogen (H_2) and methane (CH_4) molecules were equilibrated via 1000 ps NPT ensemble simulations. Subsequently, 10000 ps NVT ensemble simulations were performed on the equilibrated amorphous cells to generate mean square displacement versus time (MSD-t) curves. In these simulations, the time step was set to 1fs, with trajectory frames recorded every 500 steps. Finally, the diffusion coefficients (D) were derived from the linear regime of the MSD-t plots using the Einstein relation, as expressed in Equation (4).

$$D=\frac{a}{6} \tag{4}$$

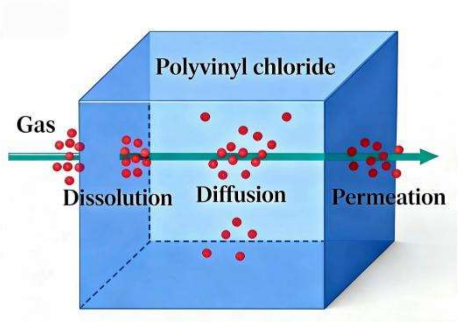


Figure 2. Schematic illustration of the gas permeation process in polymers

3.3 Permeability coefficient

The permeation of gas molecules through polymers is described by the solution-diffusion model, as illustrated in Figure 2. In this process, gas molecules first dissolve into the polymer matrix at the upstream surface, then diffuse through the bulk polymer, and finally desorb from the downstream surface. Consequently, the permeation of H_2 and CH_4 through PVC involves three sequential steps:

dissolution, diffusion, and desorption. The relationship among these parameters is expressed by Equation (5).

$$P=S\cdot D \tag{5}$$

Where P is the permeability coefficient [cm^3(STP)·cm/(cm^2·s·MPa)], S is the solubility coefficient [cm^3(STP)/(cm^3·MPa)], and D is the diffusion coefficient (cm^2/s).

4. Results and Discussion

4.1 Model Validation

4.1.1 Temperature Control Accuracy Verification

To validate the reliability of the molecular dynamics simulations, we first assessed the temperature control stability of the system. As detailed in Table 1, precise temperature regulation was achieved for both diffusion and solubility simulations within the 270–310 K interval.

Table 1. Verification of Temperature Control Accuracy in Simulations

Simulation Type	Set Temperature (K)	Simulation Temperature (K)	Absolute Error (K)	Relative Error (%)
Diffusion	270	268.691	-1.309	-0.487
	280	282.990	2.990	1.068
	290	291.880	1.880	0.648
	300	302.253	2.253	0.751
	310	311.821	1.821	0.587
Dissolution	270	275.510	5.510	2.041
	280	278.036	-1.964	-0.701
	290	289.713	-0.287	-0.099
	300	295.916	-4.084	-1.361
	310	307.283	-2.717	-0.876

The analysis results indicate that the maximum absolute error for the diffusion simulations was 2.990 K (at 280 K), with a corresponding maximum relative error of 1.068%. For the dissolution simulations, the maximum absolute error reached 5.510 K (at 270 K), yielding a maximum relative error of 2.041%. Notably, the relative errors for all simulations remained within 2.1%. This level of accuracy satisfies the temperature control requirements for molecular dynamics (MD) simulations, thereby ensuring the reliability of subsequent calculations for dissolution and diffusion coefficients.

4.1.2 Assessment of System Density Accuracy

Bai et al. [16] reported that the experimental apparent density of poly(vinyl chloride) (PVC) resin typically ranges from 1.35 to 1.46g/cm^3. To validate our model, the equilibrium densities of the amorphous PVC unit cells constructed in this work were calculated at various temperatures, as summarized in Table 2.

Table 2. Validation Results of PVC System Density

Simulation Type	Temperature(K)	Simulated Density(g/cm³)	Validation
Diffusion	**270**	**1.406**	**Yes**
	280	**1.390**	
	290	**1.386**	
	300	**1.381**	
	310	**1.376**	
Dissolution	**270**	**1.402**	
	280	**1.401**	
	290	**1.389**	
	300	**1.395**	
	310	**1.408**	

The densities of the PVC systems under all simulated conditions fall within the range of 1.376–1.408 g/cm³, which is in excellent agreement with the actual density characteristics of PVC materials (1.35–1.46 g/cm³). These results demonstrate that the amorphous PVC unit cell model constructed in this study possesses a reasonable packing structure and physical properties, accurately reflecting the microstructural features of real PVC materials.

4.1.3 Comprehensive Evaluation of Model Reliability

Based on the dual validation of temperature control precision and system density reasonableness, it is confirmed that the PVC gas system model established in this molecular dynamics (MD) study possesses high reliability and physical fidelity. With a temperature control error of less than 2.1% and a system density that shows excellent agreement with experimental values, this model provides a solid theoretical foundation for the accurate prediction of hydrogen and methane solubility, diffusion, and permeability characteristics in PVC materials.

The validation results confirm that the combination of the COMPASSII force field, periodic boundary conditions, and the adopted relaxation protocol effectively captures both the microstructural and thermodynamic characteristics of PVC. Consequently, this methodological framework guarantees the reliability and scientific validity of our simulation findings.

4.2 Study on Gas Solubility

For an HBR of 10%, the adsorption isotherms of H_2 and CH_4 in PVC were investigated, as shown in Figure 3. The data were fitted using the least-squares method to calculate the solubility coefficients, with the results presented in Figure 4. As indicated by these results, the solubility coefficients of both H_2 and CH_4 in PVC decrease with increasing temperature.Within the investigated temperature range (270–310 K), PVC remains in the glassy state (given its glass transition temperature,

Tg, of approximately 77–90 °C). In this state, the motion of polymer chain segments is frozen, and the free volume within the material is essentially fixed. Upon heating, the volumetric expansion of PVC is primarily attributed to the increase in occupied volume caused by molecular bond vibrations and atomic amplitude variations, while the fraction of free volume available for gas dissolution remains nearly constant or may even decrease relatively.Specifically for CH_4 , the increase in temperature leads to a higher diffusion rate, which reduces the residence amount (or retention) of CH_4 within the PVC matrix. This kinetic effect contributes to the observed decline in the solubility coefficient of CH_4 as temperature rises.

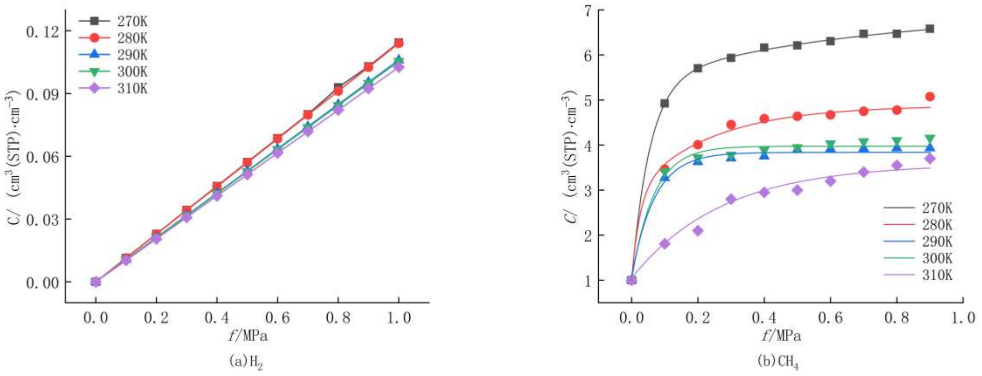


Figure 3. Adsorption isotherms of H_2 and CH_4 in PVC at an HBR of 10%

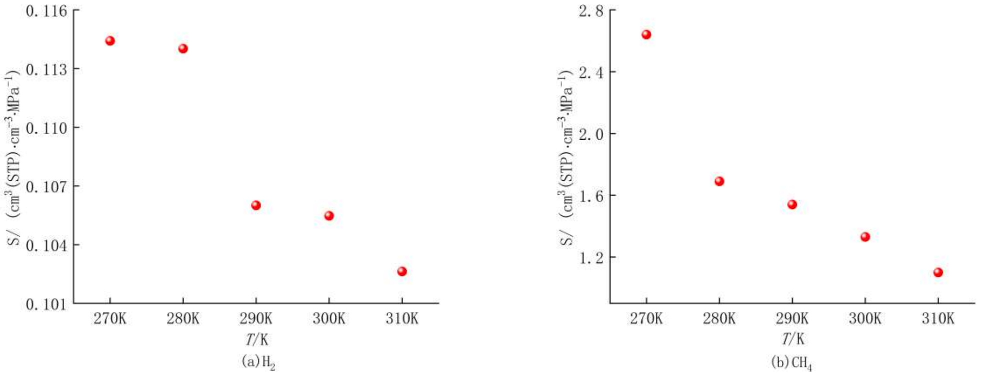


Figure 4. Effect of temperature (270–310 K) on the solubility coefficients of H_2 and CH_4 in PVC at an HBR of 10%

4.3 Study on Gas Diffusion

The effect of temperature (270–310 K) on the diffusion coefficients of H_2 and CH_4 was investigated at a pressure of 0.1 MPa and an HBR of 10%, as shown in Figure 5. The results indicate that the diffusion coefficients of both gases increase with rising temperature. This trend is attributed to the enhanced kinetic energy of the gas molecules and the increased segmental mobility of the PVC chains at higher temperatures. These factors accelerate the diffusion rate of the gas molecules. Furthermore, the thermal expansion leads to an increase in the free volume within the PVC matrix, providing more space for gas diffusion.

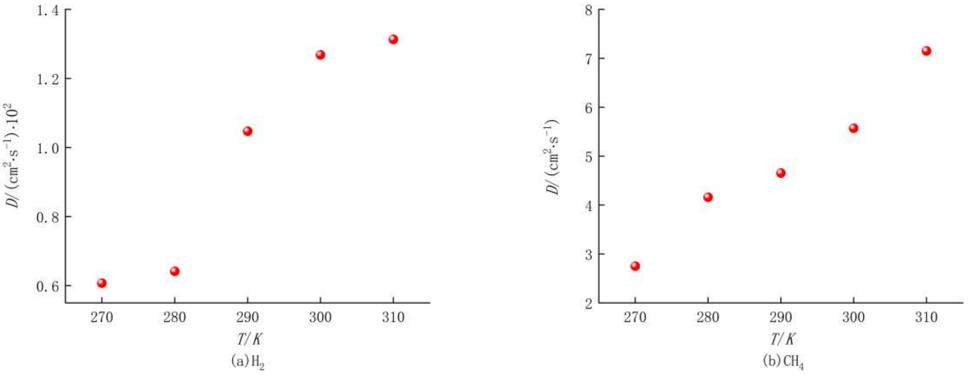
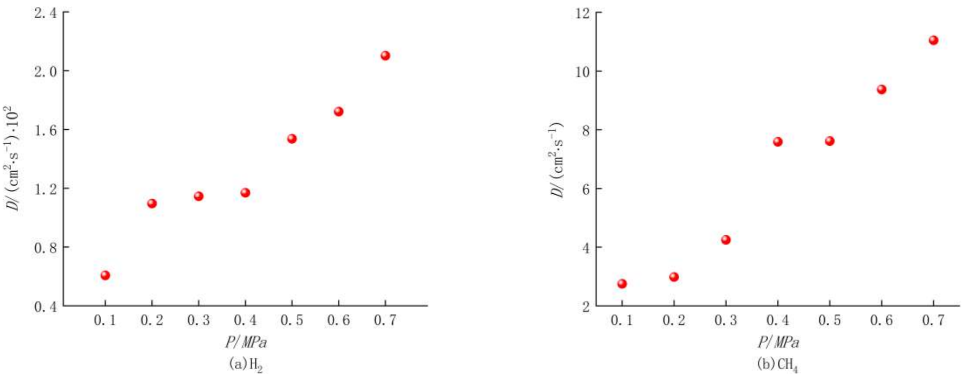


Figure 5. Effect of temperature (270–310 K) on the diffusion coefficients of H_2 and CH_4 in PVC at 0.1 MPa and an HBR of 10%

Similarly, the effect of pressure (0.1–0.7 MPa) on the diffusion coefficient was investigated at 270 K and an HBR of 10%, as illustrated in the Figure 6. It can be observed that the diffusion coefficient increases with increasing pressure. This is attributed to the fact that the mass of gas adsorbed by the PVC increases with pressure. Consequently, the PVC volume expands due to this swelling effect, providing more free volume for the diffusion of gas molecules.

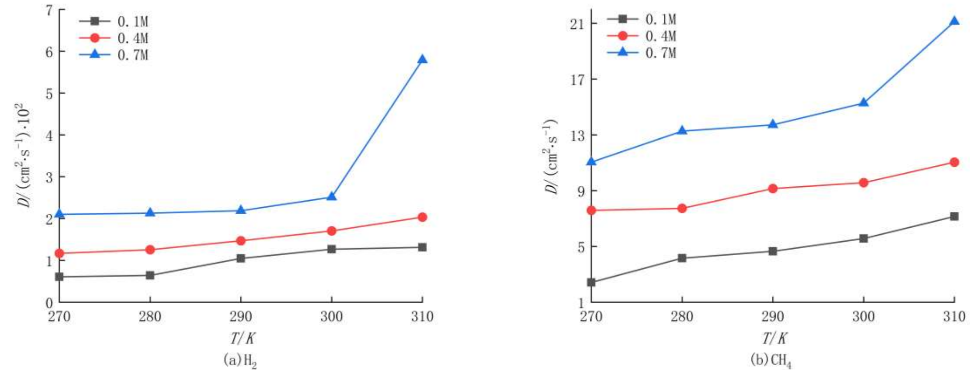


(a) H_2

(b) CH_4

Figure 6. Effect of pressure (0.1–0.7 MPa) on the diffusion coefficients of H_2 and CH_4 in PVC at 270 K and an HBR of 10%

To investigate the temperature-dependent characteristics of this behavior, a systematic simulation study was conducted. The simulations covered a wide range of temperature and pressure conditions for polyvinyl chloride (PVC). As shown in Figure 7,the simulation results indicate that at a constant pressure, the diffusion coefficients of both H_2 and CH_4 in PVC increase with rising temperature; conversely, at a constant temperature, the diffusion coefficients also increase with increasing pressure. The obtained data consistently support the validity of the aforementioned trend under varying temperature conditions, further corroborating the reliability of the theoretical model.



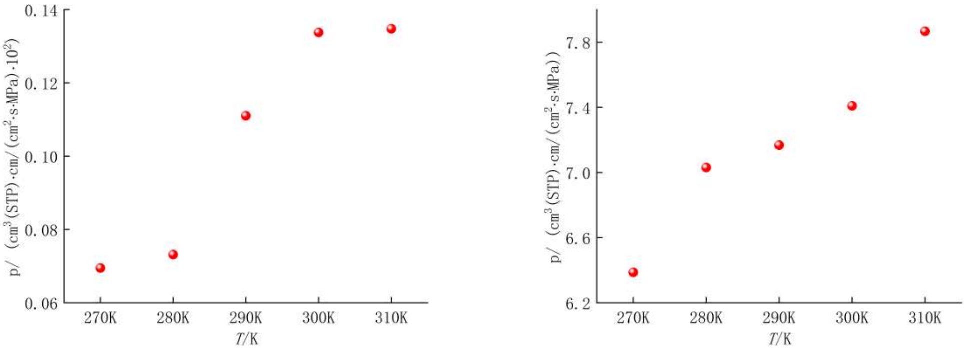
(a) H_2

(b) CH_4

Figure 7. Diffusion coefficients of H_2 and CH_4 in PVC at different pressures (0.1, 0.4, 0.7 MPa) and temperatures (270–310 K) with an HBR of 10%

4.4 Permeability

The temperature dependence of H_2 and CH_4 permeation in PVC was investigated over the range of 270–310 K by analyzing the data from Figures 4 and 5, as summarized in Figure 8. Both gases exhibit increased permeability with rising temperature. According to the solution-diffusion model, this trend arises because the increase in diffusion coefficient (D) with temperature outweighs the decrease in solubility coefficient (S). Molecular dynamics simulations support this finding, revealing enhanced chain mobility and free volume at higher temperatures, which promote gas diffusion. The results highlight the dominant role of diffusivity in governing permeation behavior under thermal variation.



(a) H_2 (b) CH_4

Figure 8. Effect of temperature (270–310 K) on the permeation coefficients of H_2 and CH_4 in PVC at 0.1 MPa and an HBR of 10%

5. Conclusion

In this work, the transport behaviors (solubility, diffusion, and permeation) of hydrogen (H_2) and methane (CH_4) in polyvinyl chloride (PVC) were systematically investigated under a hydrogen blending ratio (HBR) of 10% by employing combined Grand Canonical Monte Carlo (GCMC) and Molecular Dynamics (MD) simulations. The study focused on the effects of temperature (270–310 K) and pressure (0.1–0.7 MPa). The main conclusions are as follows:

The solubility coefficients of both H_2 and CH_4 decrease with increasing temperature. This phenomenon is primarily attributed to the glassy state of PVC within the 270–310 K temperature range, where polymer chain segmental motion is effectively frozen, and the fractional free volume within the material remains relatively constant. The volumetric expansion induced by rising temperature mainly stems from the increased vibration of molecular bond lengths and angles, leading to an increase in "occupied volume." Consequently, the proportion of "free volume," which is critical for gas dissolution, is relatively reduced. Furthermore, elevated temperatures enhance the kinetic energy of gas molecules, making them less susceptible to adsorption and fixation, thereby reducing the equilibrium adsorption capacity.

The diffusion coefficients of both H_2 and CH_4 increase with rising temperature and pressure. Simulations conducted under three distinct pressure conditions demonstrate that this positive correlation holds for both gases. The dominant effect of elevated temperature is the significant enhancement of the thermal kinetic energy of gas molecules and the increased local mobility of polymer segments. These factors collectively accelerate the diffusion rate, a trend that follows the Arrhenius relationship. Conversely, the increase in pressure promotes the swelling of the PVC matrix, which expands the free volume of the system and provides additional pathways for gas diffusion.

The permeability coefficients of H_2 and CH_4 increase with rising temperature. Permeation is a synergistic outcome of solubility and diffusion. Although the solubility coefficient decreases with increasing temperature, the diffusion coefficient increases more significantly due to intensified molecular thermal motion. Consequently, diffusion behavior plays a dominant role in the permeation process, leading to an overall increase in the permeability coefficient with rising temperature.

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