

Modification of PVC with 1-Vinylimidazole for CO₂/CH₄ Separation: Sorption, Permeation and DFT Studies

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To improve the gas separation performance of poly (vinyl chloride) membrane, 1-vinyl imidazole was grafted onto the poly (vinyl chloride) by free radical graft copolymerization technique. The synthesized copolymer was characterized by the elemental analysis technique using CHN analyzer. The morphology of the prepared membrane was studied by scanning electron microscope. The thermodynamic properties of CO₂ adsorption was investigated at various temperatures and pressures by quartz crystal microbalance. The experimental data were correlated by the dual-mode model. The calculated thermodynamics parameters of CO₂ adsorption display that CO₂ adsorption has the nature of exothermic. Also, methane and carbon dioxide gas permeability was measured. The effects of temperature variation and feed pressure on the membrane performance were studied. The increase in temperature led to a decrease in selectivity of the membrane for carbon dioxide/methane gases; whereas, the selectivity of the membrane increased by increasing the feed pressure. The outcomes indicate that the permeation selectivity of the grafted copolymer is more than that of the poly (vinyl chloride) membrane for CO₂/CH₄ gasses. Moreover, density functional theory calculations showed that the interaction energy of grafted copolymer with CO₂ is stronger than that with CH₄.

Keywords: PVC, Vinylimidazole, Permeation, Adsorption capacity, DFT

INTRODUCTION

Nowadays, one of the most major environmental issues is global warming arising from the enhancement of carbon dioxide (CO₂) concentration emitted mainly from excessive consumption of fossil fuels burning in industrial applications [1,2]. Various methods have been applied for carbon dioxide capture including amine scrubbing, distillation, cryogenic, membrane-based separation, and sorbent adsorption [3,4]. Membranes separation due to low energy consumption [5,6], high thermal and mechanical stability [7], ease of combination with other existing processes [8], and their environmental-friendly properties have attracted lots of attention in gas separation process [9-11]. Poly (vinyl chloride) (PVC) is a flexible and durable polymer with the useful chemical and mechanical

properties. However, the gas separation performances of PVC membranes are not suitable due to high chain compactness and low segmental movement of polymeric chains [12,13] leading to the low gas permeation of PVC [14,15]. Improving the PVC membrane was performed *via* different methods, including graft polymerization [16], polymer-polymer blending [17,18], optimization spinning conditions in fabrication of membrane and addition of inorganic or organic additives in the solution of dope [19-21]. Graft polymerization is among the significant techniques for modifying the performance of membrane involving two kinds of grafting, one is the surface grafting and the other is graft copolymerization. In surface grafting, just the surface is modified, without modifying the compound and the bulk polymer properties, while graft copolymerization includes the reaction of an already formed homopolymer or copolymer with new monomers which are covalently bound to the polymer chains [22,23]. The PVC

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modified for gas separation processes has been reported in the literature [24-27]. Improving the membrane of PVC has been performed using grafting with 1-vinyl-3-butylimidazolium with different anions (thiocyanate, [SCN]⁻, bromide, [Br]⁻, and tetrafluoroborate, [BF₄]⁻) [28], the nucleophilic substitution of chlorine atoms with 2-thionaphthalene, 4-mercaptophenol, and 4-mercaptopyridine sodium salt [29], 1-[(4-thenylphenyl)methyl]-3-butylimidazolium bis(trifluoromethane) sulfonimide, EBI[Tf₂N] and 1-[(4-ethenylphenyl)methyl]-3-butyl-imidazolium chloride [30,31], EBI[Cl] and modification with pyridinium-based ionic liquids and pyridine [32]. In this work, the membrane of PVC was improved using 1-vinyl imidazole (VIm) which has a good flexibility and high permeability for CO₂/CH₄ separation. The monomers of VIm are grafted to the dehydrochlorination PVC backbone using free radical graft copolymerization. The grafted copolymers and the surface of the synthesized membrane are characterized using CHN elemental analyzer and SEM analysis. In this study, for the first time, the adsorption capacities of CO₂ in the PVC-g-PVIm membrane are studied at different temperatures and pressures by QCM. Then, experimental data are correlated to the dual-mode model. Furthermore, the effects of several operating parameters like membrane thickness, the feed temperature, and feed pressure on the membrane performance are investigated for CO₂/CH₄ separation. The density functional theory (DFT) computations are carried out to study the relative affinity of the PVC-g-PVIm membrane for CH₄ and CO₂ gases.

EXPERIMENTALS

Materials

1-Vinylimidazole (> 99%) was obtained from Germany, Sigma-Aldrich company. PVC with K-value 69-71 was provided from Germany, Sigma-Aldrich company. The viscosity average molecular weight ($M_v = 124000 \text{ g mol}^{-1}$) was determined in tetrahydrofuran (THF) using digital viscometer (Lovis 2000M, Anton Paar). 2,2'-Azobis(2-methylpropionitrile) (AIBN), THF and methanol were provided from Germany, Merck company. The gases of CO₂ ($\geq 99.99\%$) obtained from Farafan Gas Corp., Tehran, Iran. CH₄ ($\geq 99.995\%$) were purchased from Roham Gas Corp., Tehran, Iran.

Synthesis and Characterization of Copolymer

The PVC-g-PVIm grafted copolymer was synthesized and characterized by CHN elemental analyzer (ECS 4010 CHNSO Analyzer). The steps of synthesis are illustrated in Fig. 1. The obtained results of the element analyzer showed that 3.7% of 1-vinylimidazole is grafted to the PVC. The synthesis and characterization of PVC-g-PVIm copolymer have been described in the literature [28].

Preparation of Membrane

To preparation of membrane, the grafted copolymer solution was dissolved in THF and stirred at 328 K until the perfect dissolution of the components was obtained. After 10 min of degassing with a sonication bath, the prepared solution was poured on a glass plate and evaporated at 303 K for 24 h. The prepared membrane was immersed and washed with generous amount of distilled water several times to make sure about the solvent removal and at last dried at 323 K for 12 h in an oven. The thickness of the prepared membranes was appointed by membranes mass and density. The density of the prepared membranes was determined by the flotation technique at 293.15 K with ZnCl₂ aqueous solution saturated. The solution mixture was adjusted and the prepared membranes remained to hover in solution. The ultrasonic bath was applied to eliminate the bubbles stuck to the membranes. The density of the solution was calculated by a density analyzer (DSA5000, Anton Paar, Austria).

Membrane Characterization

Differential scanning calorimetry. Thermal behavior of graft copolymer of PVC-g-PVIm membrane was estimated by differential scanning calorimetry analysis (DSC) on Thermal Instruments Perkin Elmer, Jade DSC under nitrogen atmosphere at a heating rate of 10 K min⁻¹.

Scanning Electron Microscopy

The cross-sectional morphology of the marked thin film of the PVC-g-PVIm copolymer membrane was studied using a scanning electron microscope (SEM). The membranes of polymer were fractured in liquid nitrogen; samples of the membrane were sputter-coated with a gold thin film. The SEM images of the PVC-g-PVIm copolymer

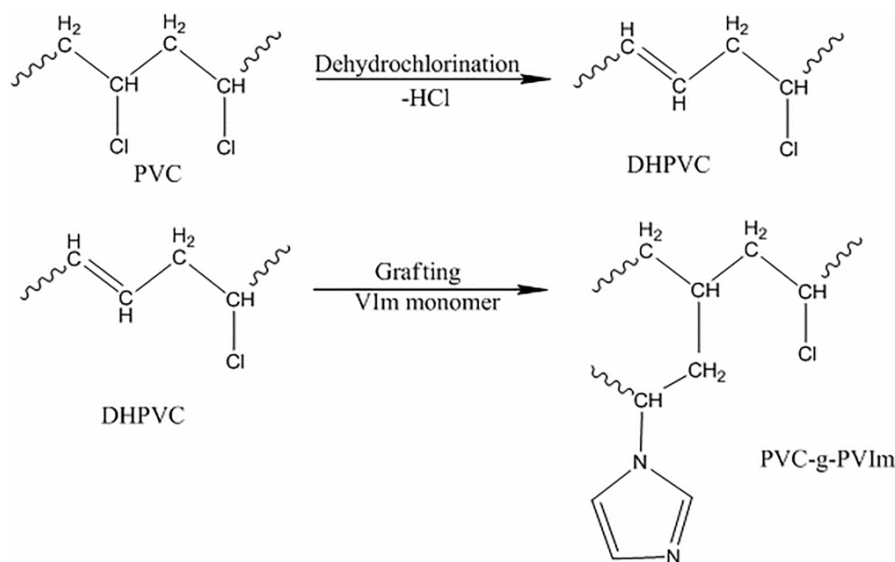


Fig. 1. Steps of synthesis of the grafted copolymer.

membrane were determined with a Cam Scan SEM model (MIRA III, TESCAN, Czech Republic) microscope.

Gas Permeation Apparatus

The permeability of gas was evaluated using the handmade module. The membrane module contains a cylindrical reservoir tank in which the details of a handmade module have been described in previous papers by authors in detail [28]. According to the measured pressure difference among the membranes, membrane thickness, the gas permeability, and effective surface membrane in polymer membranes are computed by solution–diffusion mechanism as follows:

$$P_i = \frac{l}{A\Delta p} \times \frac{dV_i}{dt} \quad (1)$$

where l is the membrane thickness (cm), i indicates the gas penetrant, dV_i/dt is the permeation rate ($\text{m}^3(\text{STP})/\text{s}$), A is the effective membrane area (m^2), and Δp is different pressure of the gas on both sides of the membrane (Pa). The gas permeabilities of membranes were defined in barrer unit. The ideal selectivity of the membrane ($\alpha_{i,j}$) for gases i and j is expressed as the ratio of permeability P_i to P_j as show in Eq. (2):

$$\alpha_{i,j} = \frac{P_i}{P_j} \quad (2)$$

Gas Adsorption Apparatus

The sensor of QCM applied for gas sorption measurements in this study includes the sorption module. This setup is used at temperatures from 288.15 to 308.15 K and pressures up to 0.4 MPa. The solubility cell contains an 8 MHz AT-cut quartz crystal applied in the electrical oscillator circuit. The detailed performance of the sorption module has been demonstrated in our previous articles [33]. The adsorption capacity of adsorbent, Q_e ($\text{kg}_{\text{CO}_2} \cdot \text{kg}_{\text{polymer}}^{-1}$) was computed as follows:

$$Q_e = \frac{\Delta F_s}{\Delta F_c} \times 1000 \quad (3)$$

where ΔF_c is the discrepancy among the uncoated and coated crystal frequencies. ΔF_s is the discrepancy among the coated crystal frequencies in a vacuum and coated crystal after the gas adsorption.

Computational Methods

The interaction between PVC-g-PVIm grafted copolymer with CH₄ and CO₂ gases was investigated by the

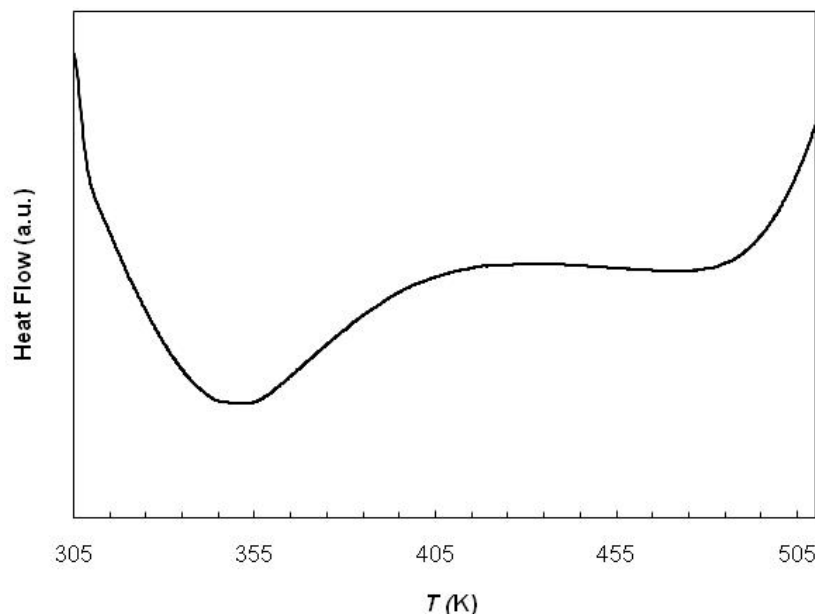


Fig. 2. DSC thermogram of PVC-g-PVIm membrane

Gaussian03 package [34]. The structure of the PVC-g-PVIm grafted copolymers, CO₂, and CH₄ gases were prepared using the Gauss View program, then, the full optimization of structures was performed with the B3LYP-D3/6-311++G*(d,p) level of theory [35,36]. The interaction energies were calculated using the following equation:

$$\Delta E = E_{AB} - (E_A + E_B) \quad (4)$$

where E_{AB} indicates the energy of the PVC-g-PVIm grafted copolymer containing CO₂ or CH₄ gases, E_A is the energy of the grafted copolymer and E_B is the energy of methane or carbon dioxide gases, respectively [37]. The natural bond orbital (NBO) analysis was carried out using the NBO 3.1 program [38] located in the Gaussian 03 package at the B3LYP-D3/6-311++G*(d,p) level of theory.

RESULTS AND DISCUSSION

Membrane Characterization

Differential scanning calorimetry. To determine the glass transition temperature (T_g), the thermal property of the PVC-g-PVIm membrane was investigated using differential

scanning calorimetry (DSC) analysis. Figure 2 presents the DSC thermogram of the PVC-g-PVIm membrane. The DSC thermogram shows that the PVC-g-PVIm has a T_g about 350 K which is lower than the transition temperature of pure PVC [39]. This behavior can be due to plasticizing effect that modifies the flexibility of polymer chains, facilitates the segmental movement, and causes more capability in separating gases.

Scanning Electron Microscopy

The membrane was prepared from synthesized grafted copolymer and then the cross-sectional images of the polymer membranes were provided by SEM. The SEM images of polymer membranes with different magnifications are illustrated in Fig. 3. Figure 3 shows that the cross-sectional SEMs of the grafted copolymer have a dense substructure.

Gas Adsorption

Sorption isotherm. The sorption isotherms of CO₂ for the PVC-g-PVIm membrane are illustrated in Fig. 4 at temperatures from 293.15 to 308.15 K and pressure up to 0.4 MPa. The CO₂ adsorption capacity of the grafted

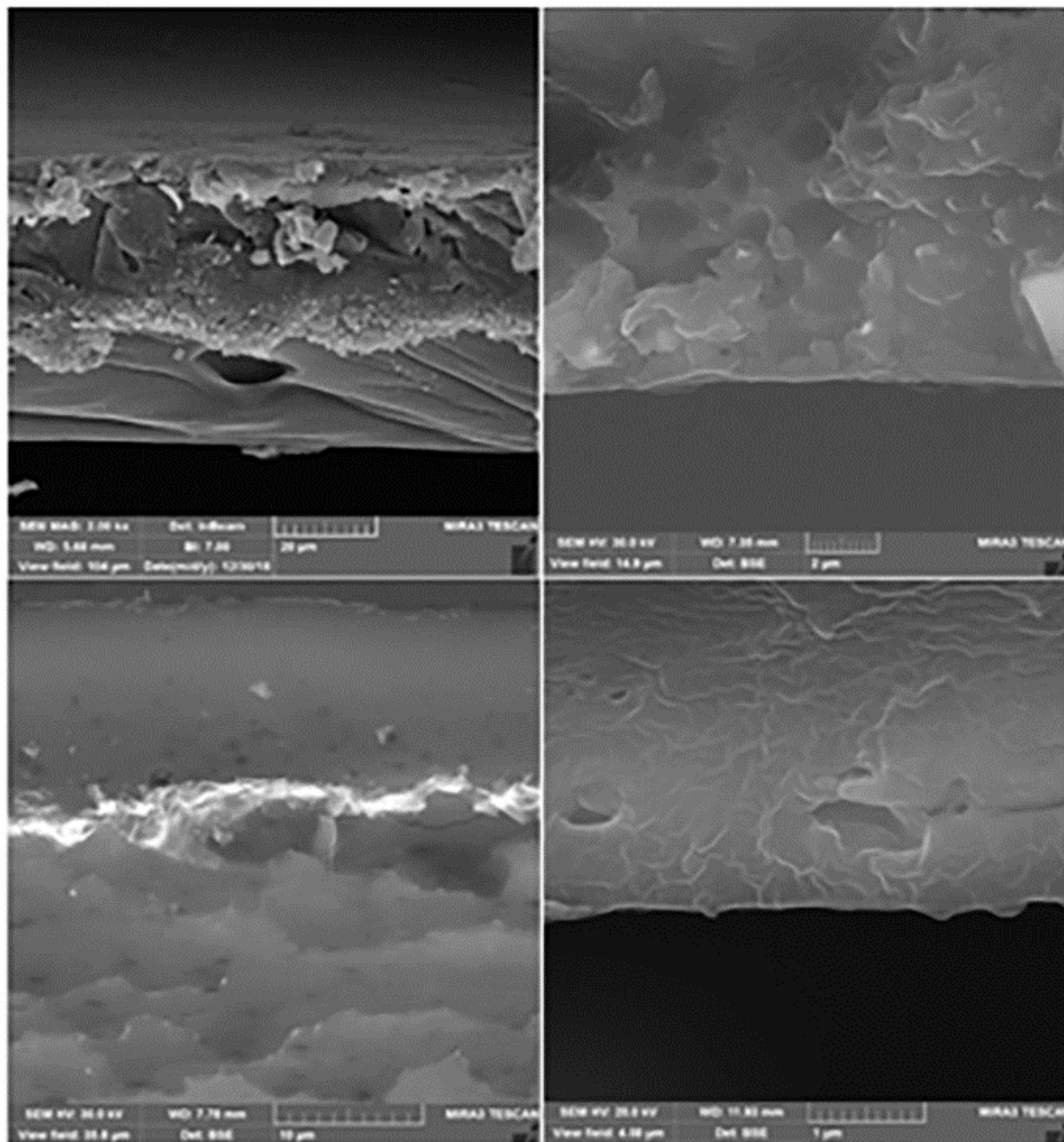


Fig. 3. The SEM images of the cross sections of grafted copolymer of PVC-g-PVIm membrane.

copolymer was decreased by increasing temperature. The experimental data were fitted using a dual-mode adsorption model which was used to express gas adsorption in glassy polymers.

The concept of the dual-mode model, consider two

terms for gas sorption, take place due to two terms: (i) the one term of sorption that is arising from the gas dissolved in the polymer matrix and expressed by Henry's law sorption. (ii) The next term of sorption is attributed to capture into free volumes that can be due to the

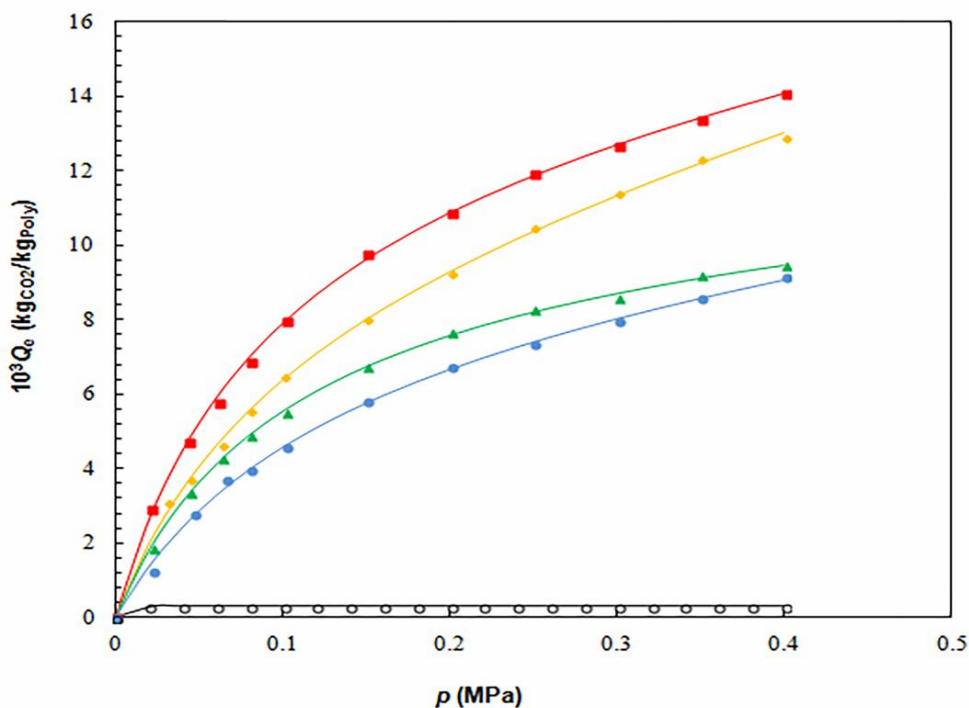


Fig. 4. Adsorption isotherms of PVC-g-PVIm grafted copolymer; (■) CO₂ at 293.15 K, (◆) CO₂ at 298.15 K, (▲) CO₂ at 303.15 K, and (●) CO₂ at 308.15 K, (○) CH₄ at 298.15 K, (–) Fitted to Eq. (5).

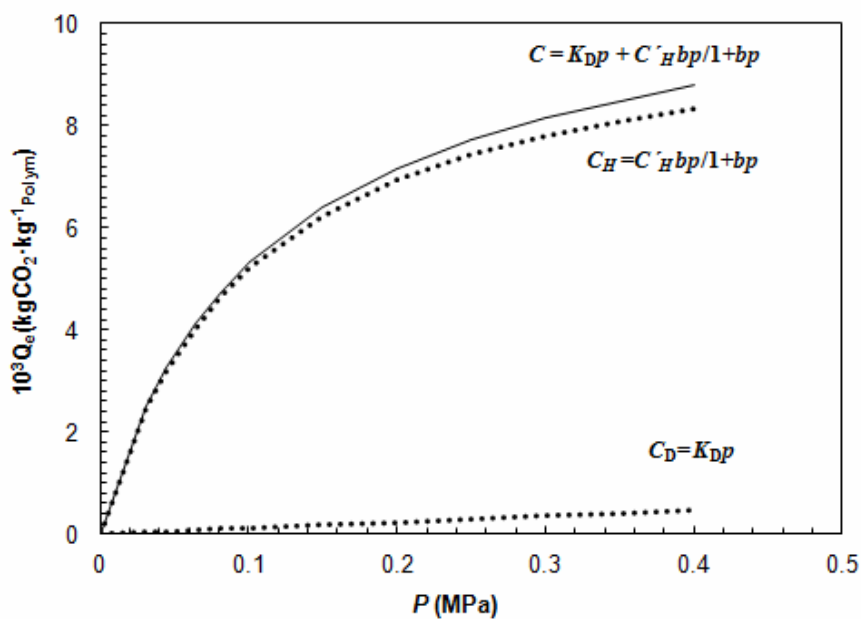


Fig. 5. Schematic representation of a dual-mode adsorption analysis using Eq. (5) for CO₂ adsorption isotherms onto PVC-g-PVIm at $T = 298.15$ K.

nonequilibrium nature of glassy polymers, and is determined using a Langmuir isotherm. Based on the dual-mode sorption model, adsorption capacity is arising from two contributions: the non-specific (Q_D) sorption and the Langmuir adsorption in the polymer fractional free volume (FFV) (Q_H). The total sorption of the gas in a polymer ($kg_{CO_2} kg_{polymer}^{-1}$) is the sum of these two populations described by the following equation [40,41]:

$$Q_e = Q_D + Q_H = k_D p + C'_H K p / (1 + K p) \quad (5)$$

where k_D is Henry's law constant ($kg_{CO_2} kg_{polymer}^{-1} Pa^{-1}$), p is the gas equilibrium pressure in bar, C'_H and K are parameters of the Langmuir isotherm. Henry's law constant is attributed to both polymer-polymer and gas-polymer interactions. C'_H ($kg_{CO_2} kg_{polymer}^{-1}$) explains the sorption into the non-equilibrium excess volume in the glassy polymers. K is the Langmuir sorption equilibrium constant that equals to the ratio of rate constants of the sorption and desorption process in Pa^{-1} . Based on the dual-mode sorption model, the molecules penetrating into the glassy polymers adsorb in the free volume and the non-equilibrium free volume, accordingly. The glassy polymers have more gas sorption in comparison to the rubbery polymers [42,43]. The non-specific (Q_D) sorption and the Langmuir adsorption (Q_H) contributions are illustrated in Fig. 5. Based on Fig. 5, the non-specific sorption was incremented monotonically with pressure, whereas Langmuir adsorption in high pressure approached to the constant value. Figure 5 reveals that the Langmuir adsorption has had a dominant contribution. The dual-mode sorption parameters of CO₂ are listed in Table 1.

The Langmuir saturation constant was decremented with increment in temperature and this tendency is common for glassy polymers. In glassy polymers, the free excluded volume fraction was reduced by incrementing temperature; therefore, the value of C'_H parameter decreases with the enhancement of temperature. The solubility coefficient (S) of gas in glassy polymers is expressed by the following equation

$$S = k_D + \frac{C'_H K}{(1 + K p)} \quad (6)$$

The higher gas solubility of the glassy polymers in comparison with the rubbery polymers can be attributed to the non-equilibrium excess free volume of the glassy polymers. The excess free volume provides higher adsorption sites for the gas adsorption in the glassy polymers. At lower than T_g , the increase in Langmuir sites of the polymer leads to increment the sorption capacity and the gas Langmuir adsorption in the PVC-g-PVIm grafted copolymer. Moreover, the sorption isotherm of CH₄ on PVC-g-PVIm grafted copolymer showed that the non-specific adsorption of methane is negligible for the grafted copolymer, so that the sorption isotherm of methane is a direct line and the quantities of C'_H and K are approximately zero. As discussed, higher CO₂ solubility in comparison to methane is attributed to more CO₂ chemical affinity which has a stronger interaction with the polar polymer functional group [44]. The thermodynamic parameters for the carbon dioxide and methane sorption on grafted copolymer are computed by Vant'Hoff equation at temperatures from 293.15 to 308.15 K. The changes in enthalpy (ΔH°) and entropy (ΔS°) in the adsorption are evaluated as follows [45-47]:

$$\ln K = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \quad (7)$$

where T is the adsorption temperature and R is the universal gas constant. ΔH° and ΔS° of adsorption were determined from the slope and intercept of $\ln K$ against mutual temperature. The computed ΔH° and ΔS° of adsorption were $-15.4 \text{ kJ mol}^{-1}$ and $-51.7 \text{ J mol}^{-1} \text{ K}^{-1}$, respectively. The results showed that ΔH° was negative values and sorption process had the nature of exothermic. ΔS° of adsorption can be expressed by the behavior of the CO₂ molecules in the adsorption process, which undergoes from randomized to a regular form on the adsorbent surface.

Regeneration Efficiency of Copolymer in Gas Sorption

One of the main factors affecting the adsorption performance is regeneration. To measure the reuse capacity, four cycles of CO₂ sorption/desorption on the PVC-g-PVIm grafted copolymer were examined (Fig. 6). The CO₂ sorption was measured at 298.15 K and 0.1 MPa, and the

Table 1. Henry’s Law Constant (k_D), Langmuir Saturation Constant (C'_H), Langmuir Affinity Constant (K), and Absolute Average Relative Deviation ($AARD\%$) for Adsorption of CO_2 onto PVC-g-PVIm at Different Temperatures (T) and Pressures (p) up to 0.4MPa^a

T (K)	$10^2 k_D$ ($kg_{CO_2} \cdot kg_{polymer}^{-1} \cdot MPa^{-1}$)	$10^3 C'_H$ ($kg_{CO_2} \cdot kg_{polymer}^{-1}$)	K (MPa^{-1})	$AARD$ (%) ^b
293.15	0.734	13.658	11.01	1.3
298.15	1.170	10.411	9.95	1.6
303.15	0.197	10.959	9.51	1.0
308.15	0.531	9.126	7.93	2.9

^aStandard uncertainties is $u(T) = 0.05$ K and $u_r(p) = 0.01$ MPa. ^b $AARD\% = \frac{100}{n} \sum \left| \frac{Q_e^{cal} - Q_e^{exp}}{Q_e^{exp}} \right|$

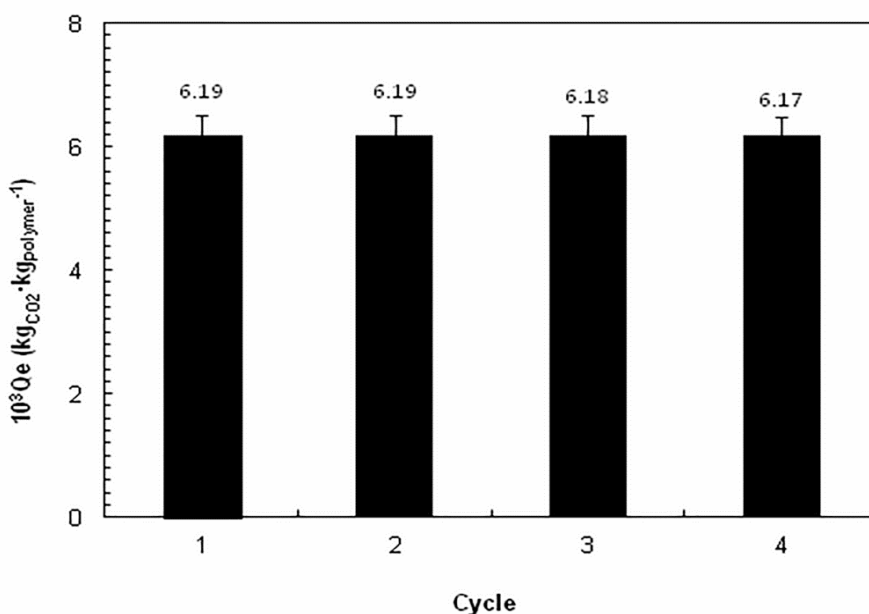


Fig. 6. CO_2 adsorption capability on PVC-g-PVIm at $T = 298.15$ K and $p = 0.1$ MPa after multiple regenerations.

CO_2 desorption was performed under vacuum at the same temperature for 1 h. The Sorption/desorption quantities show that CO_2 has been fully eliminated in 1 h, and that the sorption quantity was stable in four cycles. The CO_2 adsorption quantities on grafted copolymer are 6.19, 6.19, 6.18 and 6.17 $kg_{CO_2} \cdot kg_{polymer}^{-1}$ in four consecutive cycles of sorption/desorption, and the regeneration yield for the

grafted copolymer is 99.80% after four sequential cycles of sorption/desorption. The slightly decrement in CO_2 absorption ability after five sequential cycles of regeneration may be due to defective desorption of CO_2 .

Gas Permeation

Effect of thickness membrane. The permeability of CH_4 and CO_2 gases into an asymmetric membrane is related

to the membrane morphology, thickness, solubility and diffusivity of the gas. The permeability of CO₂ and CH₄ gases in PVC-g-PVIm membranes was determined at constant pressure (0.2MPa) and temperature (298.15 K) as depicted in Fig. 7.

As seen in Fig. 7, the permeability of methane and carbon dioxide gases on PVC-g-PVIm membranes is reduced by increasing the membrane thickness. The effect of the membrane thickness on the permeation properties indicates that with the increase in thickness of membrane, the CO₂/CH₄ selectivity is approximately incremented. On the bases Fick's laws, the thickness of membrane has an important efficacy on permeation of gas and more gas permeation occurs in the thinner membrane.

Effect of Temperature

The enhancement of temperature has a significant effect on the permeation of gas molecules in polymer membranes. The permeability of studied gases in various temperatures at constant pressure is reported in Table 2. The gas permeation in the membrane increases with increasing the temperature from 293.15 to 308.15 K. Enhancement of temperature causes an enhancement in mobility of the penetrant gases in the membrane, leading to increment the diffusion in the membrane. Rising temperature leads to more flexibility of the polymer membrane and enhances the mobility of polymer chains. Moreover, this behavior can be explained due to the available fractional free volume which is often a linear function of temperature in polymer membranes. Table 2 indicates that the permeation selectivity of PVC is improved with grafting 1-vinylimidazole. This improvement can be due to the strong interactions between 1-vinylimidazole and CO₂ with respect to CH₄. However, CO₂/CH₄ permeation selectivity is reduced by increasing temperature. This phenomenon can be attributed to the decrease of CO₂ solubility at elevated temperatures. Hence, the permeation is controlled *via* diffusion phenomena more than solubility phenomena.

The relationship between permeation and temperature was expressed via the Arrhenius equation as follows:

$$P = P_0 \exp\left(-\frac{E_p}{RT}\right) \quad (8)$$

where P_0 is pre-exponential factors, T is the temperature, R

is the gas constant, and E_p is the activation energy of permeation process. The activation energy of the permeation is computed from the slopes of $\ln P$ versus reciprocal temperature. The computed permeation activation energies of PVC are 38.4 and 57.7 kJ mol⁻¹ for CO₂ and CH₄, respectively, and those of PVC-g-PVIm are 32.8 and 68.3 kJ mol⁻¹ for CO₂ and CH₄, respectively. The more value of activation energy of permeation corresponds to a stronger temperature dependency of permeation phenomena. The results show that the CO₂ permeation has a high-temperature dependency compared with CH₄. This phenomenon displays solubility phenomena rather than a diffusion phenomenon.

Effect of Feed Pressure

Permeability and selectivity of CO₂ and CH₄ gases on the PVC-g-PVIm membrane were investigated in various pressures at 298.15 K. The permeability and selectivity of CO₂ and CH₄ gases on the PVC-g-PVIm membrane are listed in Table 2. As seen in Table 2, the permeation of CO₂ and CH₄ gases is reduced considerably with the increase of feed pressure from 0.2 to 0.4 MPa, while the CO₂/CH₄ selectivity is increased with increasing the feed pressure. This tendency may be due to the two main effects containing the membrane compaction and gas solubility. The reduction of the membrane's free volume in the compression processes causes the reduction in the membrane permeability, whereas increment the solubility of CO₂ compared with that of CH₄ leads to an enhancement in selectivity of the membrane. Therefore, it can be concluded that the contribution of solubility in permeation of CO₂ is more than that of CH₄. According to the dual-mode sorption model [48], an increase in membrane solubility in a higher feed pressure leads to a higher gas permeability of the membrane. However, for the glassy membranes contain PVC, with increasing the feed pressure, the compaction is the most dominant factor in decrease the gas permeability of the PVC-g-PVIm membrane. Nevertheless the CO₂/CH₄ selectivity increase with increasing pressure. Moreover, this model describes the reduction of permeability on the basis of a site-saturation mechanism. So, permeation and sorption will be performed even at low levels of microvoid environment. At higher penetrant concentrations, the microvoid saturation decreases the accessible

Table 2. Permeability Coefficient (P) and Permeability Selectivity (α) of PVC and PVC-g-PVIm Membranes at Different Temperatures (T) and Pressures (p)^a

P (MPa)	T/K	$10^{17}P$ ($\text{m}^3(\text{STP}) \text{m}^{-1} \text{s}^{-1} \text{Pa}^{-1}$)		$\alpha_{\text{CO}_2/\text{CH}_4}$
		CO_2	CH_4	
PVC				
0.2	293.15	0.59	0.17	3.47
0.2	298.15	0.84	0.34	2.47
0.2	303.15	1.09	0.44	2.48
0.2	308.15	1.25	0.55	2.27
PVC-g-PVIm				
0.2	293.15	3.91	0.34	11.50
0.2	298.15	6.06	0.74	8.19
0.2	303.15	7.21	1.08	6.68
0.2	308.15	7.61	1.34	5.68
0.3	298.15	5.84	0.67	8.72
0.4	298.15	5.12	0.57	8.98

^aStandard uncertainties are $u(T) = 0.05 \text{ K}$, $u(p) = 0.01 \text{ MPa}$, $u_r(P) = 2\%$.

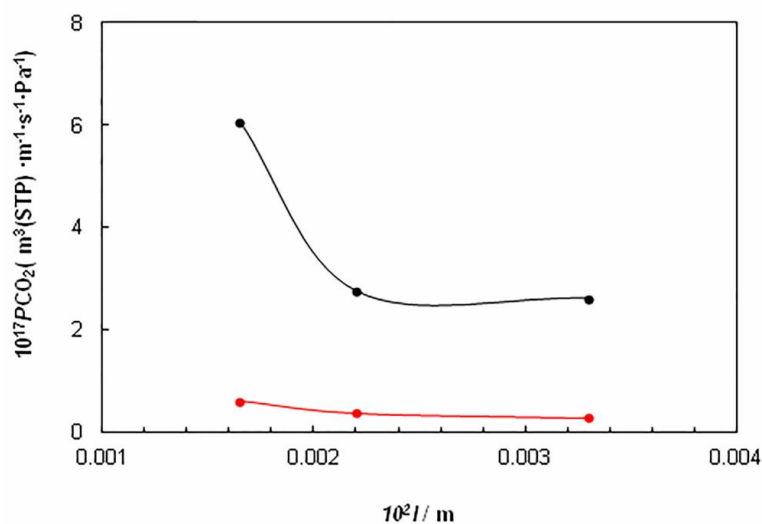


Fig. 7. Effect of membrane thickness on permeability of methane (●) and carbon dioxide (●).

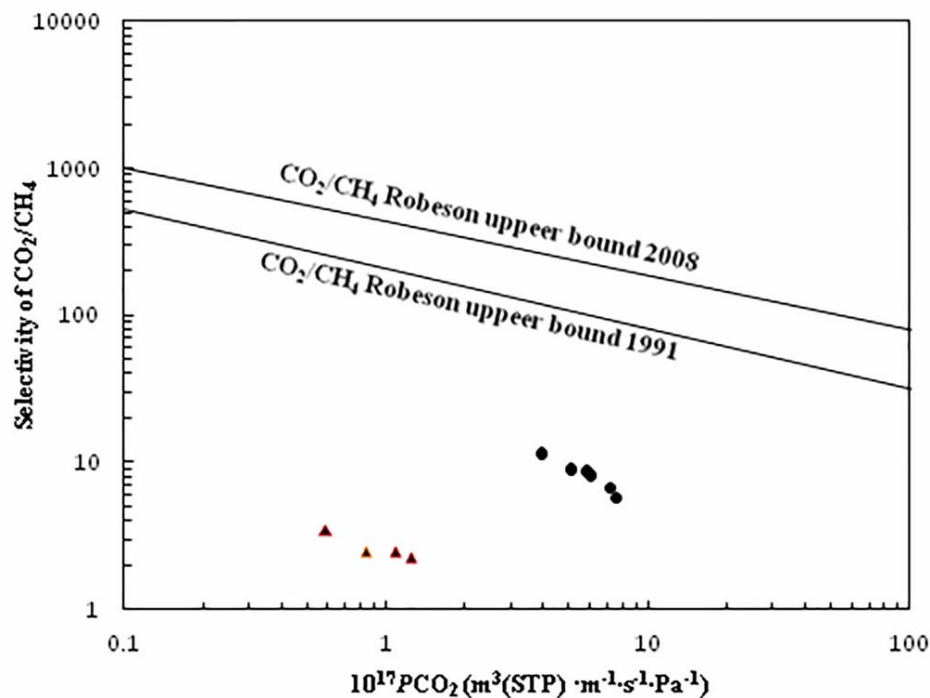


Fig. 8. The CO₂/CH₄ separation performance of the prepared membranes in comparison to Robeson upper bounds for (▲) PVC and (●) PVC-g-PVIm.

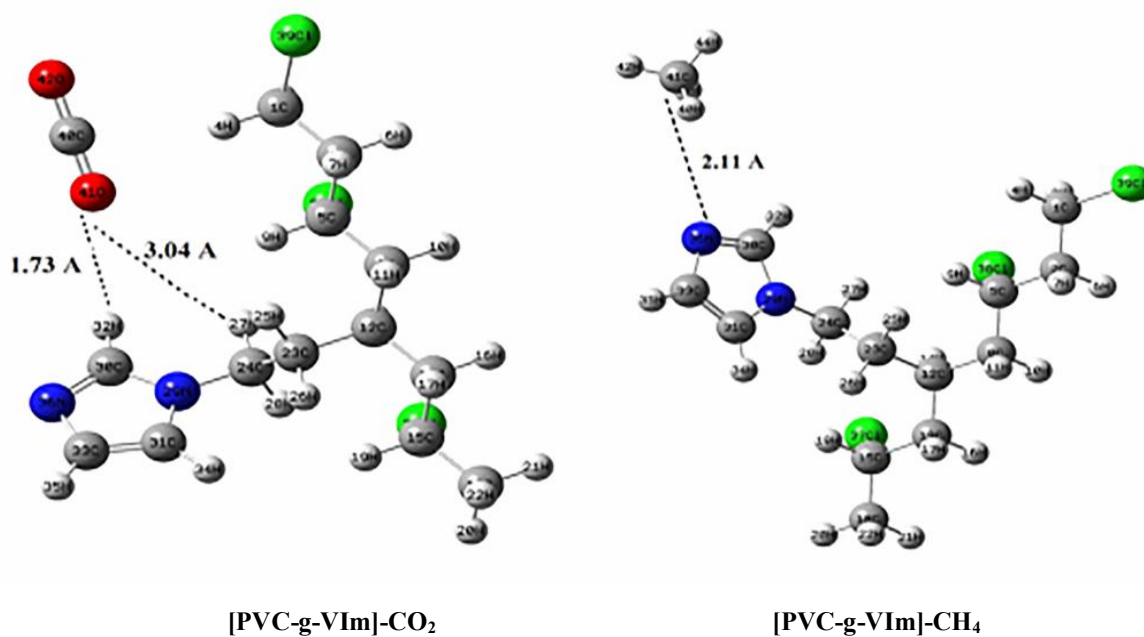


Fig. 9. Optimized structures of the grafted copolymers of [PVC-g-VIm]-gas.

Table 3. Interaction Energies and Charge Transfer of CO₂ and CH₄ with PVC-g-VIm

Polymer-gas system	Interaction energy (kJ mol ⁻¹)	Charge transfer
[PVC-g-VIm]-CO ₂	-5.62	-0.023
[PVC-g-VIm]-CH ₄	-0.50	0.003

pathways for permeation leading to a reduced permeability [49].

Evaluation of Gas Permeation Performance

To assess the effect of grafted VIm monomer on enhancement the gas separation properties of PVC-g-PVIm membrane, the selectivity of PVC and PVC-g-PVIm membranes for CO₂/CH₄ gases were calculated. The outcomes were compared to the Robeson upper bounds [50]. The selectivity of CO₂/CH₄ versus CO₂ permeability is shown in Fig. 8. The results of Fig. 6 reveal that the PVC-g-PVIm membrane performs better than the PVC membrane in the separation of CO₂/CH₄.

DFT Calculations

To corroborate the experimental data, stable energy was computed using the density functional theory (DFT) method. The DFT calculations was carried out to calculate the relative affinity of the PVC-g-VIm grafted copolymer to interact with molecules CH₄ or CO₂. The optimized structure of the PVC-g-VIm and its complex with CO₂ and CH₄ are shown in Fig. 9. The interaction energies and the charge transfer of the composite at B3LYP-D3/6-311++G* (d,p) are tabulated in Table 3.

The interaction energy between PVC-g-VIm and carbon dioxide or methane gas shows that PVC-g-VIm membrane with carbon dioxide gas is more stable than PVC-g-VIm membrane with methane. Analysis of the outcomes reveals that CO₂ solubility is more than CH₄ solubility. This phenomenon can be due to more chemical affinity of CO₂ compared to CH₄; moreover, CO₂ has a stronger interaction with the functional group of polar PVC-g-VIm membrane because of its quadrupole moment.

CONCLUSIONS

The modification of PVC with 1-vinylimidazole was performed. The PVC-g-PVIm membranes were prepared and their ability for CO₂ separation from CH₄ was investigated. The CO₂ adsorption capacities in PVC-g-PVIm grafted copolymer were calculated by the dual-mode model. The experimental data reveal that the pseudo-second-order model is convenient for the CO₂ adsorption isotherms. The DFT investigations reveal the interaction of grafted copolymer with CO₂ is more than that with CH₄.

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