Concentration and Temperature Dependence on Diffusivities of CO_2 and N_2 for Poly(dimethyl, methylphenyl siloxane)

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Experimental determination of solubility and diffusion coefficients of CO_2 and N_2 in poly(dimethyl, methylphenyl siloxane) (PMPS) for the pressure range 0–150 kPa and the temperature range of $-10°C$ to 45°C is discussed. The absorption isotherms were measured by pressure decay equilibrium. Diffusion coefficients were determined by modeling the transient absorption data by Fickian diffusion. The value of solubility coefficient for CO_2 at 35°C was 1.21 ± 0.02 cm^3 CO_2 (STP)/(cm^3 polymer.atm) and it increased to 2.07 ± 0.01 cm^3 CO_2 (STP)/(cm^3 polymer.atm) at 1°C. The absorption isotherms of CO_2 obtained were linear for the pressure range 0–200 kPa and the enthalpy of sorption value was -10.82 kJ/mole for CO_2. However, the diffusion coefficients of CO_2 changed with feed pressure. The diffusion coefficient of CO_2 in PMPS at 22°C and 128.6 kPa equilibrium pressure was 7.22×10^{-6} cm^2/s and thus the permeability value at these conditions was 1392 Barrers. The diffusion coefficients of CO_2 at 0°C and equilibrium pressures of 125.8 kPa and 10.5 kPa were 5.72×10^{-6} cm^2/s and 4.31×10^{-6} cm^2/s, respectively. Consequently, the CO_2 permeability in PMPS decreases by about 20% when the pressure is reduced from 125.8 to 10.5 kPa at 0°C.

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Introduction

This article describes the experimental determination of absorption and diffusion coefficients of pure CO_2 and N_2 as a function of temperature and pressure for poly(dimethyl, methylphenyl siloxane) (PMPS). An interesting behavior in the pure CO_2 permeability was observed for the experiments performed in the pressure range 0–150 kPa.[1] The CO_2 permeability increased as the membrane temperature was reduced from 22°C to $-20°C$ for feed pressures above 50 kPa, but a reversal in trend was observed for feed pressures below 50 kPa. Consequently, there was a decrease in the CO_2 permeability as the feed pressure was reduced. Also the decrease in the CO_2 permeability with pressure at lower temperatures is larger than at higher temperatures. The possible reasons for this unusual behavior of CO_2 permeability were sought in this study. However, the pure gas N_2 permeability was independent of the feed pressure. This leads to a reduction in the CO_2/N_2 separation factor at low feed pressures. Similar observations were also made for poly(dimethyl siloxane) (PDMS) membrane.[1,2] The increase in CO_2 permeability with decrease in membrane temperature for PBMS membrane at high feed pressures has been reported by Stern et al.[3] The gas separation application, these membranes were tested for, requires separating CO_2 from N_2, Ar and traces of other gases (CH_4, H_2O) on the Martian surface. Therefore, the membranes were tested over the temperature range $-40°C$ to 10°C and feed pressure range of 5–100 kPa as

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these conditions resemble closely to that in the Martian atmosphere.

The permeability of a gas through a polymer membrane can be defined as the product of solubility and diffusivity of the component. From a simplistic point of view, the variation in permeability can result from changes in either solubility or diffusivity of the component with variation in pressure and temperature. The variation in permeability with temperature is well defined by Arrhenius type behavior as shown in Eq. 4 and, therefore, changes in apparent energy of activation (E_p) as a function of pressure can result in different trends in permeability of CO_2 with temperature. The apparent energy of activation is the algebraic sum of energy of activation of diffusion (E_d) and enthalpy of absorption (ΔH_s). For condensable CO_2, the enthalpy of absorption is negative and larger in magnitude than for N_2 and Ar. The reversal in trend is possibly due to a decrease in E_d as the pressure is increased because of increased polymer chain mobility at high concentration of CO_2 in the polymer. This will result in decrease in the value of E_p as the concentration is increased and possibly becoming negative at a certain concentration. Therefore, in order to elucidate the trend reversal, it was necessary to experimentally determine of the values of E_d and ΔH_s as a function of temperature and pressure.

The equipment design considerations, procedure followed for experimental determination of solubility, and modeling the transient absorption data to determine diffusion coefficients are discussed in this article. The pressure decay method was used to determine the equilibrium absorption of gases in the polymer. The diffusion coefficients were calculated by fitting the transient absorption data, i.e. the mass of gas uptake by the polymer as a function of time, by an appropriate model.[4] The experiments were performed in the temperature range of $-10°C$ to $45°C$ and pressure range of 0–150 kPa.

Experimental

Materials

The copolymer PMPS used in this study was obtained from Dow Corning, product no. 6-3121. NMR analysis of the polymer revealed that there were 90% dimethyl groups and 10% methylphenyl groups on the Si–O backbone of the polymer.[1] The crosslinked density of the polymer was determined to be 4.38×10^{-4} mol/cm^3.

Equipment design for absorption measurements

The equipment design is extensively discussed in literature and this apparatus was designed on similar fundamentals.[5,6] However, for our purposes it was important to be able to accurately measure the pressure decay at pressures in the range 5–100 kPa. The overall schematic of the equipment is shown in the Figure 1. The transducers used have a range of 0–666.6 kPa and a resolution of 0.001% of the full-scale reading. The transducers were obtained from MKS instruments, model Baratron Type 627 B. Both the transducers are connected to a power supply and readout, also obtained from MKS instruments model PDR 4000. All the valves are Swagelok manual bellows valves. The system temperature is controlled using a constant temperature water bath. The calibration of the volumes was performed by helium expansion as described in the literature.[5,6] The calibrated values for the volumes V_A and V_B were 24.67 and 24.90 cm^3, respectively.

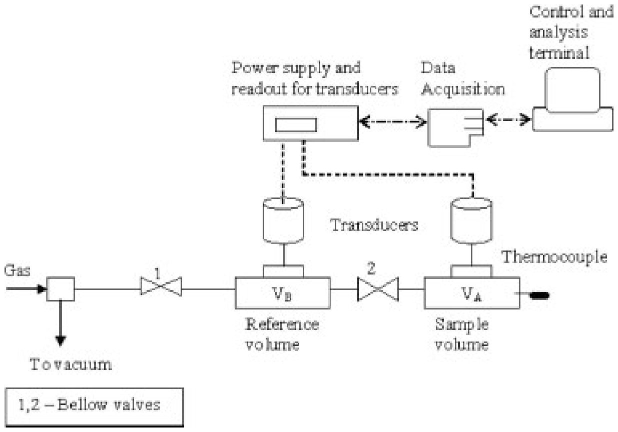

Figure 1. Schematic of the absorption apparatus.

Experimental procedure to determine absorption

The operation of the apparatus to determine the absorption is as follows; the polymer sample is kept in volume V_A and the volumes V_A and V_B are evacuated (5.3×10^{-3} kPa). Pure gas is expanded in V_B to the desired pressure through valve 1. The pressure is measured by the transducer and transferred to the computer interface. The valve 1 is closed at the desired pressure in V_B. Using an appropriate equation of state the number of moles of gas in a given volume can be calculated. The valve 2 is now opened to allow some gas to be expanded into volume V_A. The number of moles of gas expanded can be calculated from the initial and final pressures in the volume, V_B. The pressure then decays in the volume containing the polymer, V_A. By monitoring the pressure decay, the equilibrium pressure can be determined. After pressure equilibrium is reached, the total pressure in V_A can be used to calculate the moles of gas phase in V_A. The difference between the moles in the gas phase and the moles transferred from V_B gives the moles of gas absorbed. The gas compressibility factors (z) were calculated using the Redlich Kwong Soave equation of state and the absorption calculations were performed using the compressibility factor equation of state. The polymer sample used is a membrane of PMPS with a uniform thickness of 140 μm. The volume of the sample is 1.26 cm^3.

Experimental procedure to determine diffusion coefficients

The experimental measurement of pressure decay vs. time was performed by incorporating a LabVIEW interface with the pressure transducers. The volume V_B is pressurized to the desired value through valve 1. The valve 1 is closed and pressure is allowed to stabilize in V_B. The gas is expanded in volume V_A through valve 2. The pressure decay is measured as a function of time through the LabVIEW interface. The data are collected in the form of pressure vs. time. The difference in two successive pressure readings is converted to moles of gas at STP conditions by an appropriate equation of state, which accounts for the moles absorbed by the polymer sample at the corresponding time. The plot of total moles uptake with time is fit to a diffusion model to determine the diffusion coefficients. The approach for the model used here is similar to discussed by Crank for diffusion through a stirred solution in limited volume.[7]

Theory

The product of diffusivity (D) and solubility coefficient (S) is defined as the permeability (P) of a component diffusing through a membrane.

$$P = DS \tag{1}$$

The diffusivity and solubility dependence on temperature is shown by Eqs. 2 and 3. ΔH_s is the enthalpy of sorption and E_d is the activation energy for diffusion. Combining Eqs. 1–3, the temperature dependence of permeability can be defined by Eq. 4 with apparent energy of activation (E_p) written as the algebraic sum of activation energy of diffusion and enthalpy of sorption (Eq. 5).

$$S = S_0 \exp\left(\frac{-\Delta H_s}{RT}\right) \tag{2}$$

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

$$P = P_0 \exp\left(-\frac{E_p}{RT}\right) \tag{4}$$

$$E_p = E_d + \Delta H_s \tag{5}$$

The model to determine diffusion coefficients is as follows; an infinite sheet of thickness $2l$ is placed in a finite volume of gas and there is diffusion of gas in the sheet. The sheet occupies the space $-l \leq x \leq l$ and the absorbing gas occupies $-a - l \leq x \leq l + a$. The sheet is initially free of gas and the initial concentration of the gas in the volume is C_0.

The model is given by Eqs. 6 and 7.

$$\frac{M_t}{M_\infty} = 1 - \sum_{n=1}^{\infty} \frac{2\alpha(1+\alpha)}{(1+\alpha+\alpha^2 q_n^2)} \exp\left(-\frac{D q_n^2 t}{l^2}\right) \tag{6}$$

$$\tan \mathrm{q}_n = -\alpha q_n \tag{7}$$

M_t is the total amount of gas dissolved in the polymer at time t and M_∞ is the amount of gas dissolved at infinite time or equilibrium absorption. The q_n's are the real positive roots of Eq. 7 and $\alpha = a/Kl$, which can also be written as $\alpha = V_g/(KV_p)$. V_p and V_g are polymer and gas volumes, respectively, and K is the partition coefficient between the polymer and gas phase.

Equation 6 is used to fit the experimental data to determine diffusion coefficients.

The absorption of gases and vapors in crosslinked rubbery polymer is described by the Flory–Rehner expression shown in Eq. 8,[8] where, p is the pressure of the penetrant, p_s is the saturation pressure of the penetrant at the temperature, χ is the interaction parameter of the penetrant-polymer system, ϕ_2 is the penetrant volume fraction in the polymer, V_2 is the penetrant molar volume and v_e/V_0 is the effective number of crosslinks per unit volume of polymer (moles/volume).

$$\ln\left(\frac{p}{p_s}\right) = \ln \phi_2 + (1-\phi_2) + \chi(1-\phi_2)^2 + V_2\left(\frac{V_e}{V_0}\right)\left[(1-\phi_2)^{1/3} - \left(\frac{1-\phi_2}{2}\right)\right] \tag{8}$$

The volume fraction of the absorbed penetrant is given by Eq. 9, where C is the equilibrium concentration of the penetrant (cm^3 gas(STP)/cm^3 polymer) and $\bar{V}_2$ is the penetrant partial molar volume (cm^3/mol). The interaction parameter could be a function of both temperature and concentration of the penetrant.

$$\phi_2 = \left[1 + \frac{22414}{C\bar{V}_2}\right]^{-1} \tag{9}$$

Results and Discussion

The absorption isotherms were obtained at five different temperatures in the temperature range 0–35°C. As shown in Figure 2, the absorption isotherms are linear in this pressure range (0–150 kPa). This agrees well with the fact that PMPS is a rubbery polymer and should follow Henry's sorption at these pressure conditions. The absorption isotherms are modeled using the Flory–Rehner expression (Eqs. 8 and 9). The value for the crosslinked density for the PMPS membrane determined by rheology experiments is 4.38 × 10^{-4} mol/cm^3. The value for the partial molar volume of CO$_2$ in PMPS used was 45 cm^3/mol.[9] Table 1 shows the solubility values and the interaction parameter (χ) values for CO$_2$ in PMPS as a function of temperature. The interaction parameter values for CO$_2$ in PMPS increase as the temperature is decreased. Kamiya et al. have reported the interaction parameter for CO$_2$ in PDMS to be 0.73 at 25°C, and also observed an increase in the interaction parameter value with decreas-

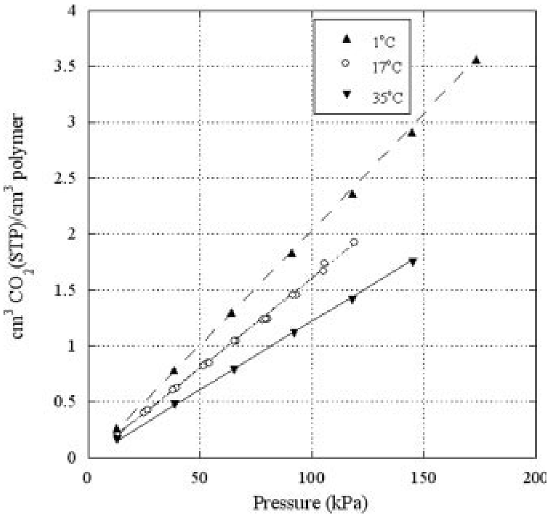

Figure 2. Absorption isotherms for CO$_2$ in poly(dimethyl, methylphenyl siloxane).

The data are modeled using the Flory–Rehner expression for gas absorption in rubbery polymers.

Table 1. Gas Solubilities and Interaction Parameter Values for the PMPS as a Function of Temperature

Gas	Temperature (°C)	Solubility Coefficient (cm^3(STP)/cm^3 Polymer.atm)	Interaction Parameter
CO_2	1	2.07 ± 0.01	0.90
CO_2	17	1.61 ± 0.02	0.76
CO_2	35	1.21 ± 0.02	0.67
N_2	35	0.10 ± 0.01	–

ing temperature.[10] The enthalpy of absorption (ΔH_s) for CO_2 was calculated to be -10.18 kJ/mole.

The permeation results of CO_2 for the pressure range 0–80 kPa and temperature range of -20°C to 20°C for PMPS membrane are shown in Figure 3. Figure 4 represents the N_2 permeance results for the above-mentioned conditions. Comparing the isoperms (equal permeance lines) for CO_2 and N_2, it was observed that the permeance of N_2 remains constant with increase in feed pressure whereas the CO_2 permeance changes significantly with pressure. Also, different trends in the CO_2 permeance can be observed with a variation in membrane temperature. Similar effects have been reported in the literature for the permeability of NH_3 in poly(meta-silphenylene siloxane) and for the permeability of propane in a series of side chain and backbone modified siloxane polymers.[3,11] The permeability of NH_3 increases with increasing temperature for low feed pressures (0–2000 mbar) and a reversal in trend occurs at high pressures (500–700 kPa).[11] This polymer has a phenyl group in the backbone and, therefore, is more rigid than PDMS and PMPS, and NH_3 is more condensable than CO_2. Both these reasons contribute to the fact that the reversal in trend occurs at higher pressures for a more rigid polymer.

The linearity of the absorption isotherms suggests that the change in CO_2 permeability as a function of pressure is due to changes in the diffusion coefficient. Diffusion coefficients were determined by fitting the transient absorption data with the model. The details of the experimental procedure and modeling are discussed earlier in the Experimental procedure to determine absorption sections and Theory section. Equations 6 and 7 were used to fit the data to determine the diffusion coefficients. The value of α was calculated from known volumes of polymer and gas phase, and the partition coefficient of the gas at the particular temperature. The first five terms (n values 1–5) in Eq. 6 were used to fit the data. Figure 5 presents the transient absorption data for an equilibrium pressure of 28.1 kPa at 23°C in which the ordinate represents mass uptake of the gas at any time (t) normalized by equilibrium mass uptake (M_t/M_∞) and abscissa represents the time. The curve representing the model is also depicted in this Figure. The least squares method was used to fit the data to the model. The diffusion coefficient obtained from fitting the data with the model was 6.71×10^{-6} cm^2/s with the permeability value of 1295 Barrers. The value of the diffusion coefficient at 128.6 kPa equilibrium pressure and 23°C was

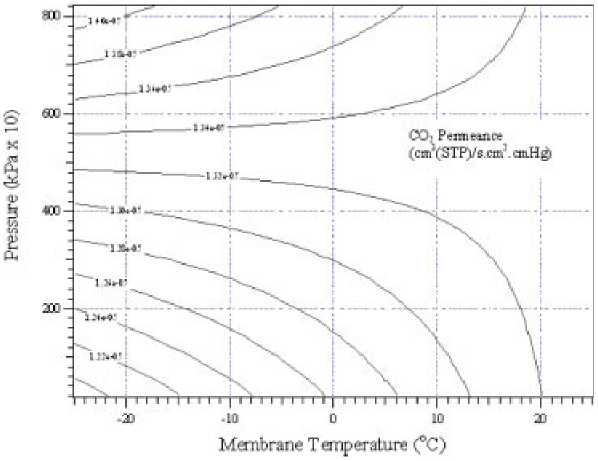

Figure 3. Effect of pressure and temperature on CO_2 permeance for PMPS membrane at low pressure conditions.

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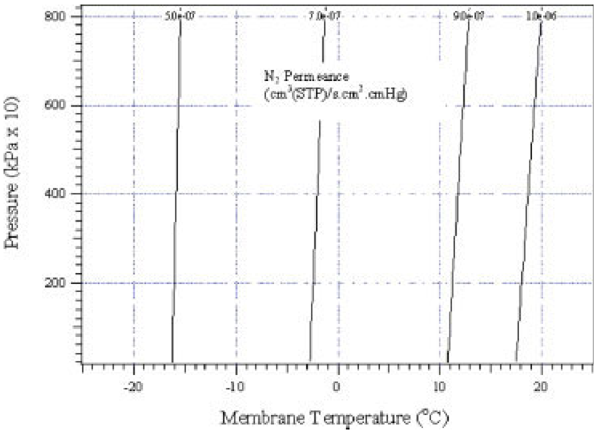

Figure 4. Effect of pressure and temperature on N_2 permeance for PMPS membrane at low pressure conditions.

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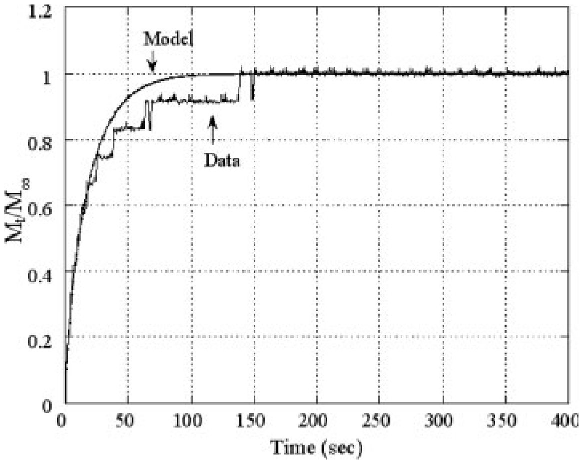

Figure 5. CO_2 transient absorption data and model in poly(dimethyl, methylphenyl siloxane) at 28.1 kPa equilibrium pressure and 22°C.

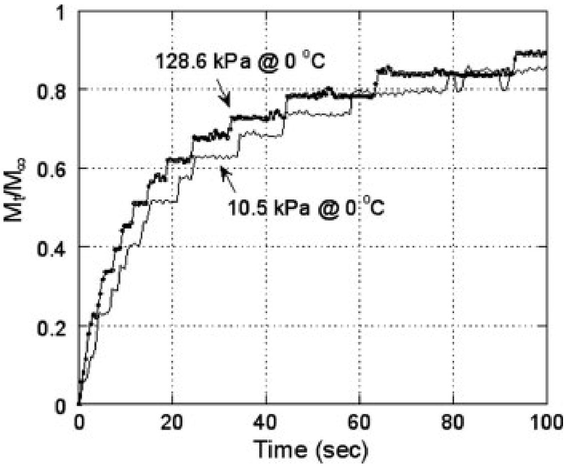

Figure 6. CO_2 transient absorption data at 0°C and equilibrium pressures of 10.5 kPa and 125.8 kPa.

7.22×10^{-6} cm^2/s with the permeability value of 1392 Barrers. The value of the permeability calculated from steady state permeation experiment is 1470 Barrers at 137.8 kPa differential pressure and 21°C,[1] which is within 10% of the value obtained from the absorption measurement. A more significant reduction in the diffusion coefficient with a decrease in pressure was observed at lower membrane temperatures. Figure 6 shows M_t/M_∞ vs. time at 0°C for equilibrium pressures of 10.5 kPa and 125.8 kPa. The value of the diffusion coefficients at 125.8 kPa and 10.5 kPa were 5.72×10^{-6} cm^2/s and 4.31×10^{-6} cm^2/s, respectively; a significant difference in values. These diffusion coefficient values are lower than the value obtained at 23°C, which is expected as the diffusion coefficients of gases in polymers decrease with a decrease in temperature. Table 2 shows the diffusion coefficients of CO_2 in PMPS at various temperatures and pressures.

Table 2. Diffusion Coefficients of CO_2 in PMPS at Various Temperatures and Pressures

Temperature (°C)	Pressure (mbar)	Diffusion Coefficient × 10^6 (cm^2/s)	R^2
0	105.00	4.31	0.95
	149.00	4.52	0.94
	151.00	4.59	0.94
	629.00	5.11	0.93
	1258.0	5.72	0.92
	1919.0	5.75	0.92
23	281.00	6.71	0.93
	544.00	6.79	0.92
	1286.0	7.22	0.93
	2000.0	7.22	0.91
35	203.00	7.73	0.93
	1310.0	7.80	0.94
45	490.00	8.52	0.95
	1306.0	8.51	0.92
	1882.0	8.52	0.92

R^2 values are from the least sum of squares regression fit of the model to the transient absorption data.

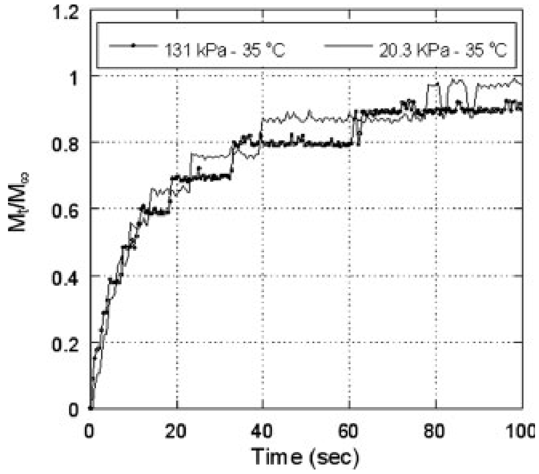

Figure 7. CO_2 transient absorption data at 0°C – 125.8 kPa and 45°C – 130.6 kPa.

As the membrane temperature is increased further, i.e. at 35°C, the diffusion coefficients become independent of pressure. Figure 7 represents the transient absorption data at 35°C for equilibrium pressures of 20.3 and 131.0 kPa, and the diffusion coefficient value in both cases is $\sim 7.8 \times 10^{-6}$ cm^2/s. Figure 8 depicts the diffusion coefficients of CO_2 calculated from transient absorption data vs. equilibrium pressure at different temperatures. In general, the diffusion coefficients decrease as the membrane temperature is reduced at all pressures. At lower membrane temperatures, the diffusion coefficients also decrease as the pressure is reduced. The reduction in the diffusion coefficient with feed pressure was larger at 0°C than at 23°C.

The changes in CO_2 permeability and diffusion coefficient as a function of pressure can be related to CO_2 induced structural changes in the polymer as the concentration of the gas in the polymer increases with increasing pressures. It is important to note that only the diffusion coefficients are affected with pressure and not the absorption isotherms that

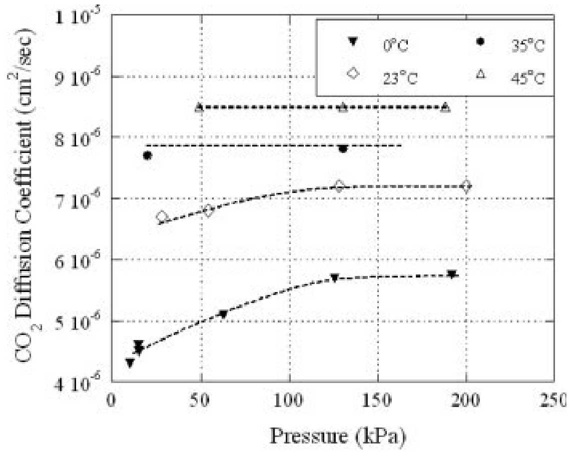

Figure 8. Diffusion coefficients of CO_2 in PMPS calculated from transient absorption data vs. equilibrium pressure at different temperatures.

are observed to be linear for this pressure range. As the feed pressure was increased at 0°C, the diffusion coefficient approached a constant value of $\sim$5.75 × 10^{-6} cm^2/s. As the membrane temperature was increased, apparently the effect of CO_2 induced structural changes leading to an effect on the diffusion coefficient diminishes. It was observed that the diffusion coefficients (CO_2) were independent of pressure above 35°C. The diffusion coefficients becoming independent of the pressure at high temperature is a condition that can be thought to be analogous to the observation where the diffusion coefficients approach a constant value at higher pressures for 0°C. The free volume of the polymer is increased at higher temperatures due to increased chain motions. This may be the reason that the dissolved CO_2 does not cause significant structural changes to the polymer, which is already in an expanded state. Also, at temperatures 0 and 23°C, the polymer reaches a limit where further increment in the concentration of CO_2 in the polymer does not lead to an increase in the diffusion coefficient. Moreover, the amount of gas dissolved in the polymer at a particular pressure increases as the polymer temperature is reduced which further supports plasticization of polymer at lower temperatures that affects the diffusion coefficient. This effect becomes more prominent at lower temperatures and high pressures. For low feed pressures, the amount of gas dissolved in the polymer is low and doesn't produce significant effects on the diffusion coefficient of CO_2.

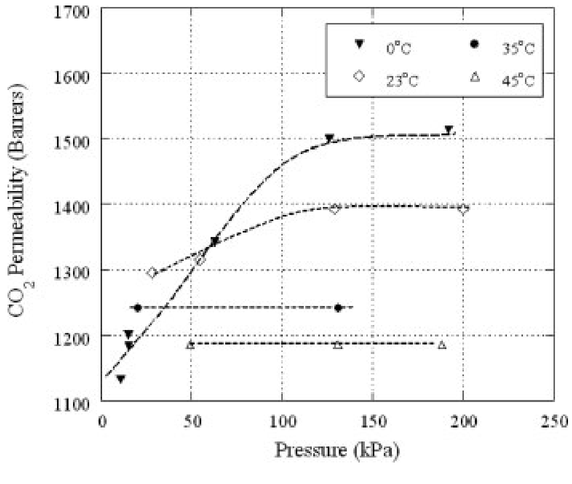

Figure 9. CO_2 permeability in PMPS calculated from transient absorption data vs. equilibrium pressure at different temperatures.

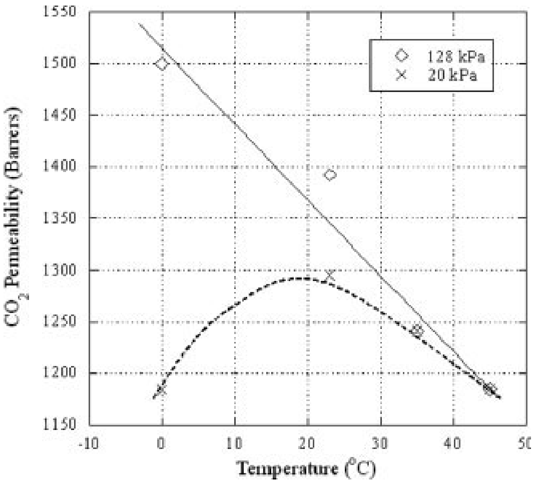

Figure 10. CO_2 permeability in PMPS calculated from transient absorption data vs. temperature at 128 and 20 kPa equilibrium pressures.

Figure 9 shows the variation in permeability vs. the pressure at different temperatures calculated from absorption measurements. The permeability of CO_2 decreased with an increase in temperature for pressures above 70 kPa and for all temperatures (0–45°C). The permeability was observed to increase with increase in temperature for pressures below 50 kPa for the temperature range of 0 to 25°C. At temperatures above 25°C, there was not any significant pressure dependence on CO_2 permeability and the permeability decreased with an increase in the membrane temperature. The CO_2 permeability as a function of temperature for feed pressures of 128 and 20 kPa is shown in Figure 10. This Figure depicts the CO_2 permeability reaching a maximum for low pressure whereas there is a constant decline in permeability at high pressures. The CO_2 permeability at 0°C increases from about 1200 Barrers at 15 kPa to 1500 Barrers at 126 kPa. Figure 5 represents the gas permeation results with the PMPS membrane obtained at Lockheed Martin under simulated Martian atmospheric conditions. In this Figure, the CO_2 permeance at 0°C and 15 kPa feed pressure is approximately 1.25 × 10^{-6} cm^3(STP)/cm^{2}s.cm Hg which increases to 1.37 × 10^{-6} cm^3(STP)/cm^2 s cm Hg at 80 kPa. This is about a 10% increase in permeance as the feed pressure. The increase in CO_2 permeability determined by absorption experiments from 15 to 80 kPa at 0°C computed from Figure 9 is $\sim$15%, which agrees closely with the increase in permeance at these conditions discussed earlier. The nitrogen absorption isotherm at 23°C was obtained in the pressure range 0–200 kPa and was found to be linear. The solubility coefficient value at 23°C for N_2 in PMPS was calculated to be 0.12 cm^3(STP)/(cm^3 polymer.atm). The diffusion coefficient of N_2 computed from the transient absorption data at 23°C and 211 kPa equilibrium pressure was 9.10 × 10^{-6} cm^2/s. This value is higher than the diffusion coefficient of CO_2 in PMPS, which is 7.22 × 10^{-6} cm^2/s at 23°C and 126 kPa equilibrium pressure. Merkel et al., have reported diffusion coefficients of CO_2 and N_2 in PDMS. The diffusion coefficient values of CO_2 and N_2 reported were 22 × 10^{-6} cm^2/s and 34 × 10^{-6} cm^2/s, respectively at 35°C.[8] PMPS has 90% dimethyl groups and 10% methylphenyl groups on the backbone, so the polymer could have similar gas transport properties as PDMS, as seen in this case where the diffusion coefficient of N_2 is higher than CO_2 in both polymers. However, PMPS has 10% methylphenyl groups that make the structure of the polymer more rigid than PDMS and could be the primary reason for the lower diffusion coefficients of CO_2 and N_2 in PMPS as compared with PDMS. Also, a more rigid structure would favor diffusivity selectivity of CO_2 over N_2 as more energy would be required for diffusional jump for N_2 in PMPS than in PDMS because of its larger kinetic diameter. In essence, if the structural rigidity of the polymer is increased, the diffusion coefficient of N_2 could become less than CO_2. The diffusion coefficient was found to be independent of pressure for N_2 in PMPS and absorption isotherms were linear with pressure; this observation is in good agreement with that seen in Figure 4 where the N_2 permeances are constant with pressure.

Conclusions

This study was intended to explain the transport behavior of CO_2 through rubbery PMPS at low temperature and low pressure conditions. The absorption isotherms were measured by pressure decay equilibrium and the diffusion coefficients were determined by model fits to the transient absorption data for CO_2 and N_2. The absorption isotherms were found to be linear for both gases in the pressure range 0–200 kPa and for temperatures in the range 0–35°C. However, the diffusion coefficient of CO_2 was found to be a function of feed pressure for temperatures below 25°C. The CO_2 diffusion coefficient increased from 4.52×10^{-6} cm^2/s at 15 kPa to 5.72×10^{-6} cm^2/s at 125.8 kPa for the sample temperature of 0°C. Therefore, it is primarily the reason for change in permeability of CO_2 with pressure. The change in CO_2 permeability is larger at lower temperatures. The reversal in the trend of CO_2 permeability with temperature as the feed pressure is increased is also explained. The increase in diffusion coefficients as the pressure is increased at low temperature is larger than at high temperature. Because of this effect on the diffusion coefficient, the permeability shows varying trends with temperature at different feed pressures. In contrast, the N_2 permeability is not affected by feed pressure.

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