Permeability of Silicone Polymers to Hydrogen

B. D. BHIDE and S. A. STERN*

Department of Chemical Engineering and Materials Science, Syracuse University, Syracuse, New York 13244

SYNOPSIS

Permeability coefficients, $\bar{P}$, for H_2 in 10 different types of silicone polymer membranes were measured in the temperature range of 10.0–55.0°C and at pressures up to 100 psig ($\sim$ 6.8 atm). The values of $\bar{P}$ decrease slightly with increasing Δp, the pressure difference across the membranes. The permeability of silicone polymers to H_2 increases with an increase in temperature; the values of the energy of activation for permeation are in the range of 1.4–4.3 kcal/mol. The substitution of different functional groups in the backbone and side chains of silicone polymers has similar effects on the permeability of the polymers to H_2 as observed in earlier studies with other light gases. $\bar{P}$ for H_2 decreases with an increase in the bulkiness of the substituted functional groups. The substitution of Si — O bonds with stiffer Si — C bonds in the backbone chains also results in a considerable decrease in permeability.

INTRODUCTION

An extensive study has been in progress for several years in this laboratory on the relationships between the chemical structure of polymers and their gas permeability.[1,2] In the course of the study, the permeability of 11 different types of silicone polymers [poly(organosiloxanes)] to He, N_2, O_2, CO_2, CH_4, C_2H_4, C_2H_6, C_3H_8, NH_3, and H_2S was measured in the temperature range of 10.0–55.0°C, but mostly at 35.0°C, and at pressures up to 115 psig ($\sim$ 7.8 atm). The present study is an extension of the above work to H_2. The general objective is to contribute to the knowledge necessary for the development of new polymer membranes for the separation of industrial gas mixtures.

The present study is also of interest because gas permeation occurs by a "solution-diffusion" mechanism[3-5] and H_2 generally exhibits a high diffusivity but a very low solubility in polymers. This behavior is due to the small molecular size and very low critical temperature of H_2.[1,6] By contrast, gases with larger molecules and higher critical temperatures, such as C_3H_8, H_2S, and NH_3, commonly exhibit low diffusivities and high solubilities.

In the present study, the permeability of 10 different types of silicone polymers to H_2 was measured at temperatures from 10.0 to 55.0°C and at pressures up to 100 psig ($\sim$ 6.8 atm). The polymers are listed in the following section. Their structures were systematically altered by the substitution of selected functional groups in their side and backbone chains. The polymers were used in the form of nonporous, planar (flat sheet) membranes.

EXPERIMENTAL

Apparatus and Procedure

The permeability of silicone polymer membranes to H_2 was characterized by a mean permeability coefficients, $\bar{P}$, which was calculated from the isothermal relation[3-5]

$$\bar{P} = G_s \cdot \delta / A (p_h - p_l) \qquad (1)$$

where G_s is the steady-state rate of H_2 permeation through a membrane of effective area A and mean thickness δ, when the pressures p_h and p_l ($< p_h$) are maintained constant at opposite membrane interfaces. In this study, A was 6.93 in.^{2} (44.7 cm^2). The pressure p_h was varied, whereas p_l was always very close to atmospheric pressure. $\bar{P}$ is reported here in the units of cm^3 (STP)·cm/(s·cm^2·cmHg).

The apparatus and procedure used to measure G_s have been described elsewhere.[1] The rate of H_2 permeation was determined at pressure p_l by means of an electronic mass flowmeter [Type 249B, Range 0–10 cm^3 (STP)/min] and a "readout" (Type 246) obtained from MKS Instruments Co. of Burlington, MA. The flowmeter was calibrated by the manufacturer with N_2, and the H_2 flow rate was determined by setting a factor dial in the readout at a specified value ("correction factor") provided by the manufacturer. The flowmeter was found to be sensitive to temperature variations and had to be heavily insulated.

Polymer Membranes

Ten different silicone polymers were used in the form of 8–12 mil (203—305 μm)-thick membranes. These polymers were synthesized by the Silicone Research Dept. of Dow Corning Corp., Midland, MI, and are listed below.

(A) Poly(dimethyl siloxane), [(CH$_3$)$_2$SiO]$_x$

Side-chain Modifications

(B) Poly(ethyl methyl siloxane), (C$_2$H$_5$CH$_3$-SiO)$_x$

(C) Poly(methyl propyl siloxane), (CH$_3$C$_3$H$_7$-SiO)$_x$

(D) Poly(methyl octyl siloxane), (CH$_3$C$_8$H$_{17}$-SiO)$_x$

(E) Poly(methyl trifluoropropyl siloxane), [CH$_3$(CF$_3$CH$_2$CH$_2$)SiO]$_x$

(F) Poly(methyl phenyl siloxane), (CH$_3$C$_6$H$_5$-SiO)$_x$

Backbone Modifications

(G) Poly(dimethyl silmethylene), [(CH$_3$)$_2$-SiCH$_2$]$_x$

(H) Poly(silethylene siloxane), [(CH$_3$)$_2$Si-(CH$_2$)$_2$Si(CH$_3$)$_2$O]$_x$

(I) Poly(silhexylene siloxane), [(CH$_3$)$_2$Si-(CH$_2$)$_6$Si(CH$_3$)$_2$O]$_x$

(K) Poly(meta-silphenylene siloxane), [(CH$_3$)$_2$-Si m-C$_6$H$_4$Si(CH$_3$)$_2$O]$_x$

The above materials will be designated hereafter as polymers A to K (cf. Ref. 1). It should be noted that the structure of polymers B to F can be visualized as having been obtained by replacing one of the methyl groups in the sidechains of the repeating unit of polymer A by different alkyl groups, whereas the structure of the polymers H to L are obtained by replacing alternate oxygen atoms in the backbone chains of polymer A by different alkylene groups. Replacement of all the oxygen atoms in the backbone chains of polymer A by methylene groups yields the structure of polymer G.

Polymers B, C, E, and G to K were filler-free, whereas polymers A, D, and F contained 4.9, 2.0, and 2.9 vol % of a silica filler, respectively. The glass transition temperature, density, and cohesive energy density of the above polymers are listed in Table I.

Gases

Hydrogen was obtained from the Linde Division of Union Carbide Corp. The purity of the gas was reported by the supplier to be 99.99 vol %. Therefore, the gas was used without further purification.

RESULTS

Permeability coefficients, $\bar{P}$, for H_2 in the silicone membranes were measured in the temperature range of 10.0–55.0°C and at pressures up to 100 psig ($\sim$ 6.8 atm). In the case of polymers A, D, and F, which contained an essentially impermeable silica filler, the experimental $\bar{P}$'s were divided by the volume-fraction of the polymers in order to obtain approximate values of $\bar{P}$ for the filler-free membranes. The experimental error in $\bar{P}$ was estimated to be within ±10%, except for polymer F for which the error was of the order of ±13% because of its low permeability.

Typical results of permeability measurements are illustrated in Figures 1 and 2 in the form of semilogarithmic plots of $\bar{P}$ vs Δp for H_2 in polymers B and E, respectively; Δp is the pressure difference across the membranes ($\Delta p = p_h - p_l$). Similar plots were obtained with the other silicone polymers studied. The plots in Figures 1 and 2 are linear under the experimental conditions of this study and can be represented by relations of the form

$$\log \bar{P} = m + n \cdot \Delta p, \qquad (2)$$

where m [= $\log[\bar{P}(\Delta p = 0)]$] and n are constants at a given temperature. Values of m and n for H_2 in the 10 silicone polymer membranes are listed in Table II; these values were obtained from least-squares fits of eq. (2) to the experimental data. Table II shows that $\bar{P}$ is a weak function of Δp and generally tends to decrease slightly with increasing Δp at constant temperature. The values of m for H_2 in a given

Table I   Polymer Characterization[a]

| Polymer	Density at 25.0°C, ρ(g/cm^3)	Glass Transition Temperature,[b] T_g (°C)	Cohesive Energy Density, δ^2 (cal/cm^3)
A. [(CH$_3$)$_2$SiO]$_x$	0.971	−123	53.24
Side-chain modifications			
B. (C$_2$H$_5$CH$_3$SiO)$_x$	0.978	−135	60.15
C. (CH$_3$C$_3$H$_7$SiO)$_x$	0.916	−120	60.15
D. (CH$_3$C$_8$H$_{17}$SiO)$_x$	0.906	−92	63.62
E. [CH$_3$(CF$_3$CH$_2$CH$_2$)SiO]$_x$	1.292	−70	76.36
F. (CH$_3$C$_6$H$_5$SiO)$_x$	1.138	−28	92.88
Backbone modifications			
G. [(CH$_3$)$_2$SiCH$_2$]$_x$	0.917	−92	64.24
H. [(CH$_3$)$_2$Si(CH$_2$)$_2$Si(CH$_3$)$_2$O]$_x$	0.890	−88	64.24
I. [(CH$_3$)$_2$Si(CH$_2$)$_6$Si(CH$_3$)$_2$O]$_x$	—	−90	62.68
K. [(CH$_3$)$_2$Sim-C$_6$H$_4$Si(CH$_3$)$_2$O]$_x$	1.025	−48	75.50

[a] Source: Data from Silicone Research Department, Dow Corning Corp., Midland, MI.

[b] Measured by differential scanning calorimetry.

polymer increase with increasing temperature. The corresponding values of n do not exhibit any systematic trend with temperature, being within the experimental error of the measurements.

Kammermeyer[7] has reported a value of 6.5×10^{-8} cm^3(STP)·cm/(s·cm^2·cmHg) for the permeability coefficient for H$_2$ in a 10 mil (254 μm)-thick poly(dimethyl siloxane) membrane at 28.5°C. The membrane contained an unspecified amount of a silica filler. This value compares with that of 8.9 $\times 10^{-8}$ (in the same units) obtained from the data

of the present study at 28.5°C by interpolation from a plot of log $\bar{P}(\Delta p = 0)$ vs. $1/T$ for a poly(dimethyl siloxane) membrane containing 4.9 vol % of silica filler. Robb[8] has reported that $\bar{P} = 7.92 \times 10^{-8}$ in the above units for H$_2$ in poly(dimethyl siloxane) at 25.0°C and at an unspecified low pressure; this value of $\bar{P}$ is corrected for filler content (33 wt % silica filler). By comparison, a value of $\bar{P}(\Delta p = 0)$ $= 7.9 \times 10^{-8}$ (in the same units) was obtained in this study at 25.0°C by interpolation and correction for filler content. The present results are consistent with those of Kammermeyer and Robb.
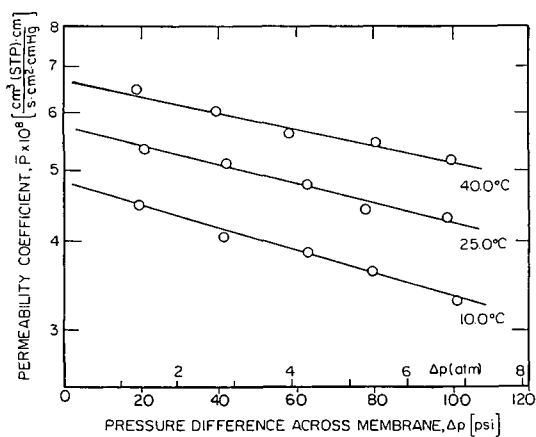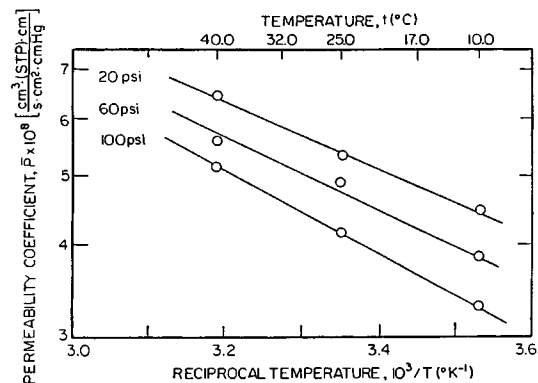

Figure 1   Mean permeability coefficients as a function of pressure difference across membrane for H$_2$ in poly(ethyl methyl siloxane), (C$_2$H$_5$CH$_3$SiO)$_x$. The polymer was filler-free.
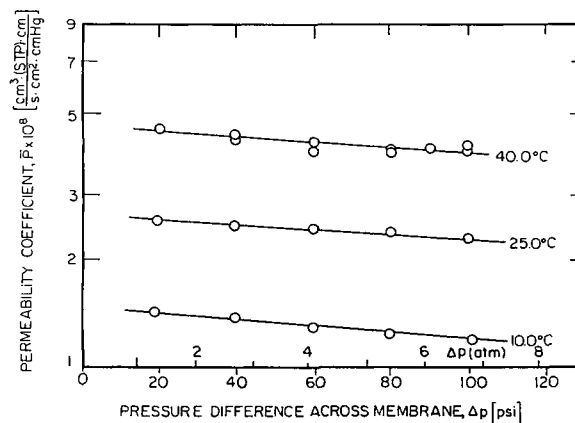
Figure 2   Mean permeability coefficients as a function of pressure difference across membrane for H$_2$ in poly(methyl trifluoropropyl siloxane), [CH$_3$(CF$_3$CH$_2$-CH$_2$)SiO]$_x$. The polymer was filler-free.

Table II Parameters in Eq. (2) for Hydrogen[a]

Temperature, t (°C)	m (dimensionless)	$n_{avg} \times 10^2$ [b] (atm)$^{-1}$
Polymer A [(CH$_3$)$_2$SiO]$_x$		
10.0	0.795	
35.0	0.996	−0.16
55.0	1.130	
Polymer B (C$_2$H$_5$CH$_3$SiO)$_x$		
10.0	0.684	
25.0	0.758	−1.99
40.0	0.825	
Polymer C (CH$_3$C$_3$H$_7$SiO)$_x$		
10.0	0.699	
25.0	0.801	−0.76
40.0	0.893	
Polymer D (CH$_3$C$_8$H$_{17}$SiO)$_x$		
10.0	0.401	
25.0	0.475	−0.82
40.0	0.527	
Polymer E [CH$_3$(CF$_3$CH$_2$CH$_2$)SiO]$_x$		
10.0	0.174	
25.0	0.419	−1.14
40.0	0.663	
Polymer F (CH$_3$C$_6$H$_5$SiO)$_x$		
10.0	−0.180	
25.0	−0.072	−1.88
40.0	−0.022	
Polymer G [(CH$_3$)$_2$SiCH$_2$]$_x$		
10.0	0.309	
25.0	0.438	−3.59
40.0	0.617	
Polymer H [(CH$_3$)$_2$Si(CH$_2$)$_2$Si(CH$_3$)$_2$O]$_x$		
10.0	0.627	
25.0	0.853	−1.79
40.0	0.918	
Polymer I [(CH$_3$)$_2$Si(CH$_2$)$_6$Si(CH$_3$)$_2$O]$_x$		
10.0	0.607	
25.0	0.662	−1.81
40.0	0.712	
Polymer K [(CH$_3$)$_2$Si m-C$_6$H$_4$Si(CH$_3$)$_2$O]$_x$		
10.0	0.122	
17.0	0.331	−2.94
25.0	0.456	

[a] $\log(\bar{P} \times 10^8) = m + n \cdot \Delta p$.
[b] Average of values at three different temperature. Units of $\bar{P}$: [cm^3(STP) cm/(s cm^2 cmHg)].

Figure 3 Arrhenius plots of mean permeability coefficients for H$_2$ in poly(ethyl methyl siloxane), (C$_2$H$_5$CH$_3$SiO)$_x$.

The temperature dependence of $\bar{P}$ for the H$_2$/silicone polymer systems studied is illustrated in Figures 3 and 4, where semilogarithmic plots of $\bar{P}$ vs. $1/T$ are shown for H$_2$ in polymers B and E. The plots are linear at constant values of Δp, and the data can be represented by Arrhenius-type relations of the form

$$\bar{P} = P_0 \cdot \exp(-E_p/RT), \qquad \Delta p = \text{const}, \quad (3)$$

where P_0 is a constant; E_p is the energy of activation for the permeation process; R is the universal gas constant; and T is the absolute temperature. The values of E_p, extrapolated to $\Delta p = 0$, were found to be in the range of 1.4 to 4.3 kcal/mole for most of the polymers studied. These values were determined from those of $\bar{P}(\Delta p = 0)$ at only three different temperatures, and therefore only indicate the order of magnitude of E_p.
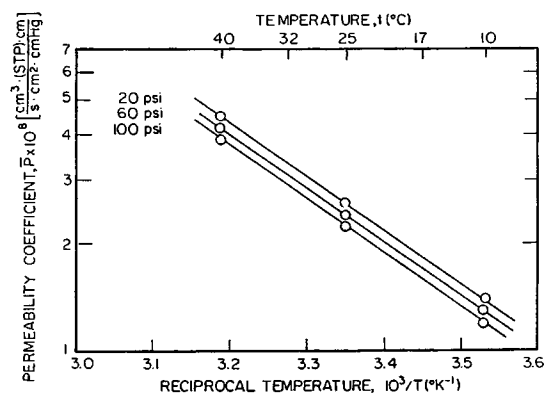
Figure 4 Arrhenius plots of mean permeability coefficients for H$_2$ in poly(methyl trifluoropropyl siloxane), [CH$_3$(CF$_3$CH$_2$CH$_2$)SiO]$_x$.

DISCUSSION

The pressure and temperature dependence of $\bar{P}$ described above may be attributed to the following factors. It can be shown that the mean permeability coefficient, $\bar{P}$, is a product of a mean diffusion coefficient, $\bar{D}$, and a solubility coefficient, S^{3-5}:

$$\bar{P} = \bar{D} \cdot S, \qquad (4)$$

where $\bar{D}$ and S have been defined elsewhere. When $p_h \gg p_l$, S is evaluated at the "upstream" pressure p_h on a membrane.

The solubility of H_2 in rubbery polymers is very low, as expected from its low critical temperature, T_c, and commonly obeys Henry's law, i.e., S is independent of the penetrant gas pressure (or concentration in polymers). In such cases, $\bar{D}$ is often also independent of pressure (or concentration). According to eq. (4), $\bar{P}$ for H_2 in silicone polymers should then also be independent of pressure. However, Table II indicates that $\bar{P}$ actually decreases slightly as the applied pressure p_h (or Δp) is increased. This probably is due to the fact that the polymer free-volume is decreased by the hydrostatic pressure of H_2.[3,4,9] Similar arguments can be made for the other H_2/silicone polymer systems studied.

The positive temperature dependence of $\bar{P}$ for H_2

in silicone polymers ($E_p > 0$) has been observed for this gas also in other polymers. E_p is the sum of the energy of activation for diffusion, E_d, and the partial molar heat of solution, $\Delta H_s^{3,4}$:

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

E_d is always positive, whereas ΔH_s can be either positive or negative. It has been observed that ΔH_s is slightly positive for the quantum gases (H_2, He, and Ne) in polyethylene,[10] i.e., the solubility increases with increasing temperature, and this is probably also the case for the H_2/silicone systems studied. Consequently, E_p should also be positive, as has been observed experimentally.

Table III lists the values of the critical temperature, T_c, and the Lennard–Jones molecular-size parameter of the penetrants, σ_v, determined from viscosity data.[11] Table III also lists the ratios of $\bar{P}(\Delta p = 0)$ for different gases in polymer A relative to those in polymers K, F, and L at 35.0°C. Values of $\bar{P}$ at $\Delta p = 0$ are useful for comparison purposes because the plasticizing effects of the more highly permeable gases on the polymers are minimized. The data for NH_3, H_2S, and H_2 at 35.0°C were obtained by interpolation from data at other temperatures, and therefore are less accurate than indicated by the experimental error in the measurement of $\bar{P}$.

Table III shows that $\bar{P}(\Delta p = 0)$ for different gases

Table III Effect of Critical Temperature and Molecular Size of Penetrant Gases on Their Permeability Coefficients in Different Silicone Polymers at 35°C

| Gas | Critical Temperature, T_c (K) | Molecular Diameter, σ_v (Å)[a] | Permeability Coefficients, $\bar{P}(A) \times 10^8$ [b] | Ratios of $\bar{P}$ | | |
				$\dfrac{\bar{P}(A)}{\bar{P}(K)}$	$\dfrac{\bar{P}(A)}{\bar{P}(F)}$	$\dfrac{\bar{P}(A)^c}{\bar{P}(L)}$
NH_3 [d]	405.6	2.900	126.2	5.9	11.5	43.0
H_2S [d]	373.2	3.623	89.9	4.3	10.3	47.9
C_3H_8 [e]	369.8	5.118	84.5	14.3	60.9	325.0
C_2H_6 [e]	305.6	4.443	42.0	13.9	46.2	280.0
CO_2 [e]	304.2	3.941	47.5	9.8	21.0	93.1
C_2H_4 [e]	282.4	4.163	36.5	13.3	39.3	182.5
CH_4 [e]	190.6	3.758	13.2	12.4	36.7	129.4
O_2 [e]	154.6	3.467	9.6	11.7	29.9	88.1
N_2 [e]	126.2	3.798	4.7	15.0	45.7	146.9
H_2 [f]	33.2	2.827	9.9	3.8	8.6	—
He [e]	5.2	2.551	5.6	6.7	16.0	17.3

[a] σ_v = Lennard–Jones diameter determined from viscosity data (Ref. 11).
[b] Units of $\bar{P}$: cm^3 (STP) $\cdot$ cm/(s $\cdot$ cm^2 $\cdot$ cmHg); all $\bar{P}$ values are at $\Delta p = 0$;
[c] Polymer L: Poly(para-silphenylene siloxane), $[(CH_3)_2Si \ p\text{-}C_6H_4Si(CH_3)_2O]_x$.
[d] Ref. 2.
[e] Ref. 1.
[f] Present study.

in polymer A increases with increasing T_c of the penetrant gas, i.e., with increasing gas solubility in the polymer (cf. Refs. 6 and 12). H_2 and He are exceptions because of their small molecular sizes and high diffusivities in polymers. Similar trends were observed for the permeability of the above gases in other silicone polymers studied. By contrast, no particular correlation is obtained between $\bar{P}(\Delta p = 0)$ and the molecular size, σ_v, of the penetrants.

The effect of the chemical structure of silicone polymers on their gas permeability is illustrated in Figure 5. The substitution of increasingly bulkier functional groups in the side or backbone chains of the polymers decreases their permeability to H_2 as well as to other gases.[1,2] Such substitutions increase the stiffness of the polymer chains by impeding the rotational mobility of chain segments, as indicated by a rise in the glass transition temperature, T_g. Figure 5 shows that the H_2 permeability of the polymers decreases (roughly) with increasing T_g as has been observed also with other gases.[1,2] A similar result is obtained by replacing the flexible Si—O bonds in the polymer backbone chains with shorter and stiffer Si—C bonds, as is evident from a comparison of the H_2 permeability of polymer A, $[(CH_3)_2SiO]_x$, and polymer G, $[(CH_3)_2SiCH_2]_x$.

It is interesting to note that the values of $\bar{P}(\Delta p = 0)$ for polymer B, $[CH_3C_2H_5SiO]_x$, are lower than those for polymer C, $[CH_3C_3H_7SiO]_x$, although the

propyl group in polymer C is bulkier than is the ethyl group in polymer B. This behavior has also been observed with many other gases.[1,2] However, the T_g of polymer B is also lower than that of polymer C, possibly due to configurational factors that remain to be elucidated.

The effect of chain stiffness on gas permeability is also illustrated in Table III, which shows that, for a given penetrant gas, the ratios of $\bar{P}(\Delta p = 0)$ increase in the order

$$\frac{\bar{P}(A)}{\bar{P}(K)} < \frac{\bar{P}(A)}{\bar{P}(F)} < \frac{\bar{P}(A)}{\bar{P}(L)}$$

Since the chain stiffness of polymers K, F, and L increases in the order K < F < L, the order of the above ratios indicates that increasing stiffness decreases the permeability of silicone polymers to a given penetrant. Moreover, the decrease in permeability is more pronounced the larger the penetrant molecules. Thus, the permeability ratios $\bar{P}(A)/\bar{P}(K)$, $\bar{P}(A)/\bar{P}(F)$, and $\bar{P}(A)/\bar{P}(L)$ are higher for a large penetrant molecule, such as C_2H_6 ($\sigma_v = 4.443$ Å), than are the respective ratios for a small penetrant molecule, such as NH_3 ($\sigma_v = 2.900$ Å).

In previous studies, values of $\bar{P}$, $\bar{D}$, and S have been determined for CO_2, CH_4, and C_3H_8 in the same silicone polymers.[1,6] These studies have shown that the observed decrease in $\bar{P}$ for a given penetrant as increasingly bulkier functional groups are substituted in the polymers, and as the chain stiffness is increased, is mainly due to a decrease in $\bar{D}$. By comparison, S decreases to a much lesser extent. $\bar{D}$ appears to be much more sensitive than is S to even small modifications in the structure of the polymers.

CONCLUSIONS

The values of $\bar{P}$ for H_2 in the silicone polymers studied decrease slightly with increasing pressure difference across the membranes and increase with increasing temperature ($E_p > 0$). The substitution of different functional groups in the backbone and side chains of silicone polymers has the same general effects on the permeability of these polymers to H_2 as has been observed with other light gases.[1] $\bar{P}$ for H_2 decreases with an increase in the bulkiness of the substituted functional groups, i.e., with an increase in the stiffness of the polymer chains. The substitution of Si—O bonds with stiffer Si—C bonds in the backbone chains also results in a considerable decrease in permeability.
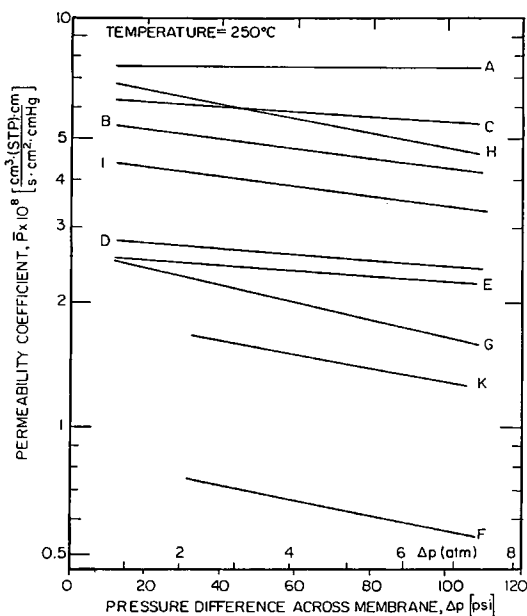
Figure 5 Mean permeability coefficients as a function of pressure difference across membrane for H_2 in different silicone polymers at 25.0°C.

Direct measurements of $\bar{D}$ and/or S for H_2 in different silicone polymers are necessary to quantify the relative contributions of these coefficients to the observed dependence of $\bar{P}$ on Δp, on the temperature, on the nature of penetrant gas, and on polymer structure.

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