Permeability of Dense (Homogeneous) Cellulose Acetate Membranes to Methane, Carbon Dioxide, and Their Mixtures at Elevated Pressures

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SYNOPSIS

Mean permeability coefficients for CH_4 and CO_2 ($\bar{P}_{CH_4}$ and $\bar{P}_{CO_2}$) in cellulose acetate (CA, DS = 2.45) were determined at 35°C (95°F) and at pressures up to about 54 atm (800 psia). The measurements were made with pure CH_4 and CO_2 as well as with CH_4/CO_2 mixtures containing 9.7, 24.0, and 46.1 mol % CO_2. In the measurements with the pure gases, $\bar{P}_{CH_4}$ was found to decrease with increasing pressure, as expected from the "dual-mode" sorption model. By contrast, $\bar{P}_{CO_2}$ passes through a minimum and then increases with increasing pressure, probably due to the plasticization (swelling) of CA by CO_2. The values of $\bar{P}_{CH_4}$ and $\bar{P}_{CO_2}$ determined with the mixtures containing 9.7 and 24.0 mol % CO_2 decrease with increasing total pressure; this behavior is adequately described by the extended "dual-mode" sorption model for mixtures. By contrast, the values of $\bar{P}_{CH_4}$ and $\bar{P}_{CO_2}$ obtained with the mixture containing 46.1 mol % CO_2 pass through a minimum and then increase as the total pressure is raised, probably also due to the plasticization of CA by CO_2. The CO_2/CH_4 selectivity ($= \tilde{P}_{CO_2}/\bar{P}_{CH_4}$) of the CA membranes decreases with increasing total pressure and, at constant pressure, decreases with increasing CO_2 concentration in the feed mixture. The effects of exposing the CA membranes to high-pressure CO_2 prior to the permeability measurements ("conditioning" effects) on $\bar{P}_{CH_4}$ and $\bar{P}_{CO_2}$ have also been studied. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

Carbon dioxide can be removed effectively from mixtures with CH_4 and higher hydrocarbons by selective permeation through cellulose acetate (CA) membranes. This membrane separation process is being widely used for the upgrading of "crude" natural gas as well as in enhanced oil recovery operations.[1-16] Another application of this process, albeit on a much smaller scale, is for the upgrading of biogas and landfill gases. The permeability of "dense" (homogeneous) CA membranes to pure CH_4, CO_2, and several other gases has been reported in a comprehensive study by

Puleo and colleagues.[17] By contrast, only limited data have been published on the permeability of CA to mixtures of CH_4 and CO_2.[3,5,8,9,18,19]

The present investigation was aimed at providing additional information on the effects of gas composition and pressure on the permeability of dense CA membranes to CH_4/CO_2 mixtures. This information may prove useful for assessing the performance of CA membranes in the above-mentioned separation processes, at least in cases where the concentration of gases other than CH_4 and CO_2 is relatively small.

Accordingly, the permeability of dense CA membranes to CH_4, CO_2, and three CH_4/CO_2 mixtures containing 9.7, 24.0, and 46.1 mol % CO_2 was measured at 35°C (95°F) and at pressures up to 54.4 atm (800 psia). The effects of membrane "conditioning" by exposure to high-pressure CO_2 on permeability were also studied.
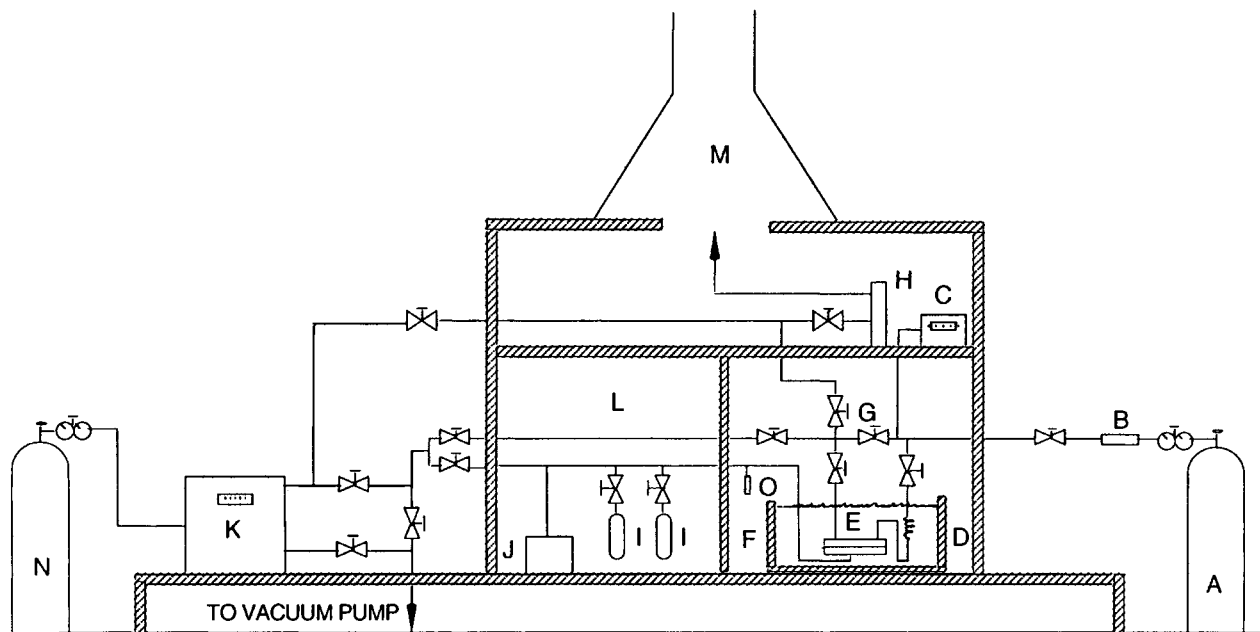

Figure 1 Diagram of apparatus used for studying the permeability of polymer membranes to gas mixtures. (A) feed gas cylinder; (B) filter; (C) digital high-pressure gauge; (D) heat exchanger; (E) permeability cell; (F) constant temperature bath; (G) metering valve; (H) digital bubble flow meter; (I) gas reservoirs; (J) low-pressure transducer; (K) gas chromatograph; (L) constant-temperature air cabinet; (M) fume hood; (N) GC carrier gas cylinder; (O) relief valve.

EXPERIMENTAL TECHNIQUES

Materials

Polymer

CA with a degree of acetyl substitution (DS) of 2.45 (39.8% acetyl content) was obtained from Tennessee Eastman Co. of Kingsport, TN. The glass-transition temperature (T_g) of this polymer was found to be 195°C by differential scanning calorimetry (DSC). Puleo and coworkers[17] have reported a T_g of 200°C for CA with the same DS. The CA was used in the form of dense (homogeneous) membranes, which were prepared as described below.

Gases

Pure CH_4 and CO_2 were supplied by Union Carbide Industrial Gases (now Praxair, Inc., Tonawanda, NY), and were represented to have a purity of at least 99.5 mol %. Certified mixtures of CH_4 and CO_2 were obtained from Matheson Gases, Buffalo, NY. Three different mixtures containing 9.7, 24.0, and 46.1 mol % CO_2 were used in this study.

Membrane Preparation

Dense (homogeneous) CA membranes were prepared by casting from a 5 wt % solution of the polymer in acetone onto a Petri dish in a controlled environment. The polymer solution was filtered through a microfilter prior to casting. The Petri dish was inserted into a plastic bag which was purged with dry nitrogen; the bag was then sealed in order to allow for slow solvent evaporation and to prevent contact with atmospheric moisture. The membrane thus obtained was stripped from the Petri dish and dried for 3 to 4 days in a vacuum oven, first at ambient temperature and then for 48 h at 150°C, to ensure solvent removal. After gradual cooling to room temperature, the membrane was stored in a vacuum desiccator. The thickness of the dry membrane was about 76 μm (3 mil).

Two CA membranes, designated "Samples 1 and 2," were used in this study and both were prepared by the procedure described above.

Experimental Technique

Apparatus

The permeability and selectivity of CA membranes to the pure gases and gas mixtures mentioned above were

measured by the variable-pressure method.[20–22] A diagram of the apparatus is shown in Figure 1. The gas being studied (the "feed"), which was stored in a high-pressure cylinder A, was passed through a filter B which had a nominal pore size of 7 μm. The feed pressure was measured by means of a digital pressure transducer C (Heise Series 9, Dresser Industries, Newtown, CT). The feed then flowed through a heat exchanger D, where it attained the desired temperature before entering a high-pressure permeability cell E which housed a CA membrane. The effective area of the membrane was 43 cm^2. The heat exchanger and the permeability cell were immersed in a constant-temperature water bath F which maintained the desired experimental temperature to within $\pm 0.1°C$.

In the permeability cell, the feed was allowed to flow over one side of the membrane at a desired elevated pressure. The opposite side of the membrane was maintained at a low pressure by means of a vacuum pump O. A specified fraction of the feed (the "stage cut"), which depended on the feed flow rate and pressure, permeated through the membrane into the low-pressure side of the permeability cell and was collected in two stainless steel reservoirs I. The volumes of these reservoirs were measured by the helium expansion technique. The flow rate of the permeating gas (the "permeate") was determined by measuring the rate of pressure increase in reservoirs I. The permeate pressure was monitored with a low-pressure transducer J (Model 390 HA-00100, MKS Instruments, Andover, MA). The flow rate of the fraction of feed that did not permeate through the membrane (the "retentate") was controlled with metering valve G and was measured with a digital bubble flow meter H (Model 650, Fisher Scientific, Pittsburgh, PA). The stage cut was obtained from the ratio of permeate flow rate to feed flow rate.

The feed, retentate, and permeate compositions were analyzed by means of a gas chromatograph (GC) K (Model 3700, Varian Associates, Inc., Palo Alto, CA) equipped with a stainless steel column (I.D. = $\frac{1}{8}$ in.) which contained HayeSep Q, 80/100 packing (Alltech Associates, Inc., Deerfield, IL). Injection of the low-pressure permeate into the GC required that the pressure in the GC sample loop be lower than in reservoirs I. This was achieved by evacuating the GC sample loop prior to permeate injection. The GC was calibrated with certified standard gas mixtures provided by MG Industries of Valley Forge, PA.

The entire permeability apparatus was enclosed in a fume hood M (Fig. 1). The permeate reservoirs I and the low-pressure transducer J were enclosed in a constant-temperature chamber L inside the fume hood. The temperature of this chamber was also controlled to within $\pm 0.1°C$.

Experimental Procedure

All measurements were made at 35°C (95°F). The pressure on the feed side was varied from 4 to 54.4 atm (59 to 800 psia) whereas the pressure on the permeate side was always maintained at less than 30 Torr. Mean permeability coefficients for CH$_4$ and CO$_2$, $\bar{P}_{CH_4}$ and $\bar{P}_{CO_2}$, respectively, were determined both with pure CH$_4$ and CO$_2$ and with CH$_4$/CO$_2$ mixtures. The maximum experimental error in the permeability coefficients was estimated to be $\pm 8\%$, the largest source of error being the membrane thickness.

The permeability of a CA membrane (sample 1) was determined using pure CH$_4$ first, followed in order by the CH$_4$/CO$_2$ mixtures containing 9.7, 24.0, and 46.1 mol % CO$_2$, and finally by pure CO$_2$. This is the order of increasing CO$_2$ concentration, and hence of increasing plasticization (swelling) of the CA membrane by CO$_2$, since CO$_2$ is much more soluble in CA than CH$_4$. Permeability measurements with a second CA membrane (sample 2) were made with CH$_4$ and CO$_2$ only, in the stated order, to test the reproducibility of the measurements with pure gases.

The measurements with CH$_4$/CO$_2$ mixtures were made at very low stage cuts (≤ 0.001) in order to determine the permeability coefficients for CH$_4$ and CO$_2$ in the mixtures. At such low stage cuts the composition of the feed mixture flowing across the membrane remains essentially unchanged because of the very small amount of gas removed as permeate.

Measurements with a given gas or gas mixture at different "upstream" pressures were made by increasing the pressure in a stepwise manner. Before exposure to a different gas or gas mixture, both sides of the membrane in the permeability cell were evacuated for about 12 to 16 h. However, prior to measurements with pure CO$_2$, membrane sample 1 was kept in a vacuum oven for 2 days at 150°C, and was then further evacuated in the permeability cell for 8 days at 35°C. This procedure was necessary in order to thoroughly remove the CO$_2$ dissolved in the membrane during prior measurements with CH$_4$/CO$_2$ mixtures.

The effects of "conditioning" of a CA membrane by preexposure to pure CO$_2$ on the permeability of the membrane to CH$_4$ and CO$_2$ were also investigated. The permeability and selectivity of the CA membrane to CH$_4$ and CO$_2$ before and after exposure to high-pressure CO$_2$ are also reported and discussed below.

Treatment of Experimental Data

The permeability measurements with CH_4/CO_2 mixtures were made at very low stage cuts (≤ 0.001). Under these conditions the feed and retentate have, for all practical purposes, the same composition.[22-25] Mean permeability coefficients, $\bar{P}$, for the components of the feed gases, CH_4 and CO_2, were determined from the following relations[22-25]:

$$\bar{P}_{CO_2} = \frac{y_{CO_2} \cdot G \cdot \delta}{A(p_h x_{CO_2} - p_1 y_{CO_2})} \quad (1)$$

and

$$\bar{P}_{CH_4} = \frac{y_{CH_4} \cdot G \cdot \delta}{A(p_h x_{CH_4} - p_1 y_{CH_4})} \quad (2)$$

where x and y are the mole-fraction concentrations of CO_2 or CH_4 in the feed and permeate, respectively; A is the effective membrane area, in cm^2; δ is the membrane thickness, in cm; G is the total steady-state rate of gas permeation at a given temperature and feed pressure, in $cm^3(STP)/s$; and p_h and p_1 ($\ll p_h$) are the total pressures, in cmHg, on the feed and permeate sides of the membrane, respectively. The values of the mean permeability coefficient, $\bar{P}$, are reported here in units of $cm^3(STP)$ cm (s cm^2 cmHg)$^{-1}$. Equations (1) and (2) were also used to calculate $\bar{P}_{CO_2}$ and $\bar{P}_{CH_4}$ for the pure gases, but in these cases $x_{CO_2} = y_{CO_2} = 1$ and $x_{CH_4} = y_{CH_4} = 1$.

The selectivity of CA for CO_2 relative to CH_4 is characterized here by an "ideal" separation factor, $\alpha^*(CO_2/CH_4)$, defined by the relation[22-25]

$$\alpha^*(CO_2/CH_4) \equiv \bar{P}_{CO_2}/\bar{P}_{CH_4} \quad (3)$$

where $\bar{P}_{CO_2}$ and $\bar{P}_{CH_4}$ are the permeability coefficients for CO_2 and CH_4, respectively, in CA.

RESULTS AND DISCUSSION

Measurements with Pure CH₄ and CO₂

The permeability of dense (homogeneous) CA (DS = 2.45) membranes to pure CH_4 and CO_2 was measured at 35°C (95°F) in the pressure ranges from 4 to 54.4 atm (59 to 800 psia) and 1.4 to 54.4 atm (20 to 800 psia), respectively. The results of these measurements with membrane samples 1 and 2 are shown in Figure 2 in the form of plots of the mean permeability coefficients $\bar{P}_{CO_2}$ and $\bar{P}_{CH_4}$ versus the "upstream" pressure p_h. CA is much more permeable
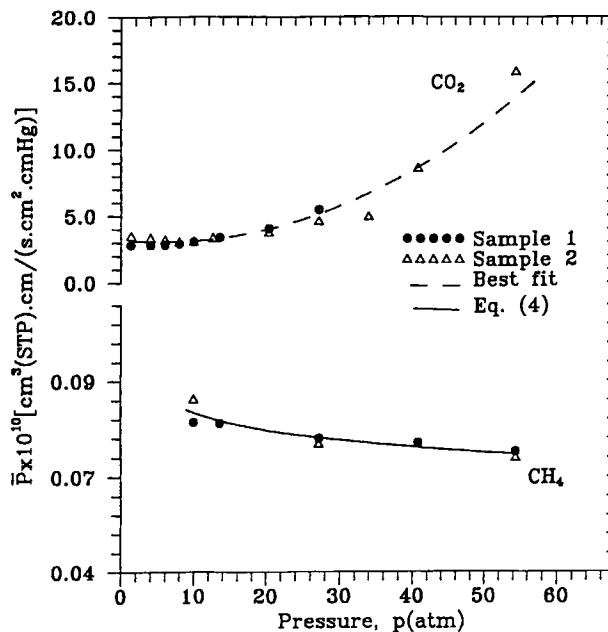

Figure 2   Mean permeability coefficients for pure CH_4 and CO_2 in cellulose acetate (DS = 2.45) as a function of total feed pressure at 35°C. The measurements were made with two membranes, designated as Samples 1 and 2. The solid curve was calculated from eq. (4) while the dashed curve is a least-squares fit to the experimental data.

to CO_2 than to CH_4 because both the diffusivity and the solubility of CO_2 in this polymer are higher than the corresponding properties of CH_4. The higher diffusivity of CO_2 is due to the smaller "kinetic" diameter of CO_2 molecules,[26] whereas the higher solubility of CO_2 is expected from its higher critical temperature; the critical temperature is a "scaling factor" for the solubility of different gases in a polymer under comparable conditions.

According to the "partial immobilization" version of the dual-mode sorption model of gas permeation through glassy polymers, the pressure dependence of the permeability coefficient can be represented by the following relation[21,22,27-30]:

$$\bar{P} = k_D D_D \left(1 + \frac{FK}{1 + bp_h}\right) \quad (4)$$

where $F = D_H/D_D$; $K = c'_H b/k_D$; k_D is the solubility coefficient for the penetrant gas population dissolved in the polymer by the Henry's law mode; c'_H is a "Langmuir capacity" constant, which represents the maximum concentration of the penetrant populations dissolved by the Langmuir mode; b is a "Langmuir affinity" constant (a kinetic factor); D_D and D_H are the mutual diffusion coefficients for the pen-

etrant gas populations dissolved in the polymer by the Henry's law and the Langmuir modes, respectively. Equation (4) is based on the assumption that the polymer is not significantly plasticized by the penetrant gas and that D_D and D_H are constants.

Figure 2 shows that $\bar{P}_{CH_4}$ decreases with increasing pressure, in accordance with eq. (4), the decrease being more marked at lower pressures. The pressure dependence of $\bar{P}_{CH_4}$ is satisfactorily represented by eq. (4). The values of the parameters k_D, c'_H, and b for CH_4 in eq. (4) at 35°C were taken from the study of Puleo and coworkers[17] and are listed in Table I. Similar values reported by Sada and coworkers[18,19] and by Stern and coworkers[31,32] were not used in the present investigation because of the differences in the degree of acetyl substitution of their CA membranes, in membrane "history," and in the experimental temperature. D_D and D_H in eq. (4) were determined for CH_4 from nonlinear least-squares fits of eq. (4) to the experimental $\bar{P}_{CH_4}/p_h$ data, using the above-mentioned dual-sorption parameters k_D, c'_H, and b. Values of D_D and D_H are listed in Table II. It is seen that $D_D > D_H$, as has also been reported for the transport of CH_4 and of other light gases in a variety of glassy polymers.

By contrast to the decrease of $\bar{P}_{CH_4}$ with pressure, the value of $\bar{P}_{CO_2}$ appears to pass through a slight minimum at low pressures and then increases rapidly as the pressure is raised (Fig. 2). A similar behavior has also been observed by Puleo and colleagues.[17] This behavior is probably due to the fact that $\bar{P}_{CO_2}$ first decreases with increasing pressure, as predicted by the dual-mode sorption model [eq. (4)], and then increases because the polymer is strongly plasticized (swelled) by CO_2. The minimum in the plot of $\bar{P}_{CO_2}$ versus p_h would probably have been more marked if data were available at lower pressures. Therefore, the pressure dependence of $\bar{P}_{CO_2}$ cannot be represented by eq. (4), which is based on the assumption that the polymer is not significantly plasticized and that D_D and D_H are constants. Equation (4) could possibly be applied in cases where

the concentration of CO_2 in CA is very low, but no data were obtained in this study for such conditions.

Zhou and Stern[33] have extended the dual-mode sorption model with "partial immobilization" by assuming that D_D and D_H are exponential functions of the penetrant gas concentration. Such a behavior could occur when the polymer is strongly plasticized by the penetrant. An expression for $\bar{P}$ as a function of p_h was derived for such cases.[33] This expression also could not be used to represent the permeability of *pure* CO_2 in CA determined in this study because of the large number of parameters required (four parameters in addition to k_D, c'_H, and b) and the limited number and scatter of the permeability data obtained at higher pressures. However, values of D_D and D_H for CO_2 could be obtained from permeability measurements with CH_4/CO_2 mixtures, as is shown in the following section.

Values of $\bar{P}_{CH_4}$ and $\bar{P}_{CO_2}$ at 35°C and 10 atm (147 psia) obtained with the pure gases are listed in Table III, together with the selectivity of CA for CO_2 relative to CH_4 expressed in terms of the "ideal" separation factor $\alpha^*(CO_2/CH_4)$ [$\equiv \bar{P}_{CO_2}/\bar{P}_{CH_4}$]. Table III also lists the corresponding values reported by Puleo and colleagues[17] and by Sada and coworkers.[18] The values of $\bar{P}_{CH_4}$ and $\bar{P}_{CO_2}$ determined in the present study prior to exposing the CA membranes to high-pressure CO_2 are significantly lower than the values reported by these investigators (Table III), possibly due to differences in sample "history." However, the CO_2/CH_4 selectivity values are consistent with the values reported by these authors.

Permeability Measurements with CH_4/CO_2 Mixtures

Effect of Applied Pressure on Permeability

The permeability coefficients $\bar{P}_{CH_4}$ and $\bar{P}_{CO_2}$ as well as the CO_2/CH_4 selectivity of the CA membranes, determined at 35°C with CH_4/CO_2 mixtures containing 9.7, 24.0, and 46.1 mol % CO_2, are plotted

Table I Dual-Mode Sorption Parameters for CO_2 and CH_4 in Cellulose Acetate (DS = 2.45) at 35°C

Gas	k_D	c'_H	b	K ($c'_H b/k_D$)	Reference
CO_2	1.572[a]	14.62[a]	0.303[a]	2.82[a]	Puleo, Paul, and Kelley[17]
	1.362[b]	22.58[b]	0.248[b]	4.11[b]	
CH_4	0.190	2.504	0.132	1.74	

Units: k_D [cm³(STP)/cm³ polym·atm]; c'_H [cm³(STP)/cm³ Polym]; b (atm⁻¹)

[a] Parameters for a CA membrane not exposed to CO_2.

[b] Parameters for a CA membrane exposed to CO_2 at pressures up to 30 atm (441 psia) ("conditioned").

Table II Mutual Diffusion Coefficients for CH$_4$ in Cellulose Acetate (DS = 2.45) at 35°C

CH$_4$/CO$_2$ Composition (mole %)	D_{D,CH_4}	D_{H,CH_4}	$F = D_H/D_D$	Reference
Pure CH$_4$	0.28	0.057	0.21	This work
(90.3/9.7)	0.37	0.044	0.12	
(76.0/24.0)	0.41	0.063	0.15	

Units: D_D (cm^2/s); D_H (cm^2/s).

as functions of the total "upstream" pressure p_h in Figures 3–5. Values of $\bar{P}_{CH_4}$ and $\bar{P}_{CO_2}$ obtained with these mixtures at 10.0 atm (147 psia) and 54.4 atm (800 psia) are also listed in Table IV. Figures 3 and 4 show that, in the measurements with CH$_4$/CO$_2$ mixtures containing 9.7 and 24.0 mol % CO$_2$, the values of both $\bar{P}_{CH_4}$ and $\bar{P}_{CO_2}$ decrease with increasing total pressure p_h. This behavior is similar to that observed in the measurements with pure CH$_4$ and is predicted by an extension of the "dual-mode" sorption model to gas mixtures.[34] According to this extension, the permeability coefficients $\bar{P}_{CH_4}$ and $\bar{P}_{CO_2}$ for CH$_4$/CO$_2$ mixtures can be represented as a function of the applied pressure p_h by the following relations:

$$\bar{P}_{CH_4} = k_{D,CH_4}D_{D,CH_4}$$
$$\times \left[1 + \frac{F_{CH_4}K_{CH_4}}{1 + b_{CH_4}p_h + y_{CO_2}p_h(b_{CO_2} - b_{CH_4})}\right] \quad (5)$$

and

$$\bar{P}_{CO_2} = k_{D,CO_2}D_{D,CO_2}$$
$$\times \left[1 + \frac{F_{CO_2}K_{CO_2}}{1 + b_{CH_4}p_h + y_{CO_2}p_h(b_{CO_2} - b_{CH_4})}\right], \quad (6)$$

where all the parameters are as defined previously. As in the dual-mode sorption model for pure gases, it is assumed in eqs. (5) and (6) that the polymer is not significantly plasticized by the permeating gas mixture. It is also assumed that the mutual diffusion coefficients D_D and D_H for the components of the mixture are constant at a given temperature, and hence are independent of the composition of the mixture. The values of the parameters in eqs. (5) and (6) are commonly taken to be the same as those determined for the (pure) components of the mixture under comparable conditions.

Equations (5) and (6) were found to represent adequately the decrease in $\bar{P}_{CH_4}$ and $\bar{P}_{CO_2}$ with increasing p_h observed experimentally with CH$_4$/CO$_2$ mixtures containing 9.7 and 24.0 mol % CO$_2$, provided that D_D and D_H are not taken as constant

Table III Permeability and Selectivity of Cellulose Acetate to Pure CH$_4$ and CO$_2$

Temperature (°C)	Degree of Acetylation (DS)	Permeability Coefficient, $\bar{P} \times 10^{10}$		Selectivity, $\bar{P}_{CO_2}/\bar{P}_{CH_4}$	Reference
		CO$_2$	CH$_4$		
35.0	2.45	3.04[a]	0.079[a]	38.0[a]	This work
		3.11[b]	0.085[b]	36.6[b]	This work
		4.57[c]	0.180[c]	25.4[c]	This work
35.0	2.45	4.75	0.130	36.5	Puleo, Paul, and Kelley[17]
30.0	2.40	4.15	0.153	27.1	Sada, Kumazawa, Xu, and Wang[19]

Units: $\bar{P}$: [cm^3(STP)·cm/(s·cm^2·cmHg)]; Pressure: 10.0 atm (147.0 psia)
[a] Membrane sample 1, prior to conditioning with CO$_2$.
[b] Membrane sample 2, prior to conditioning with CO$_2$.
[c] Membrane sample 1, exposed to CO$_2$ at 27.2 atm (400 psia) for 5 days ("conditioned"). See text for details.
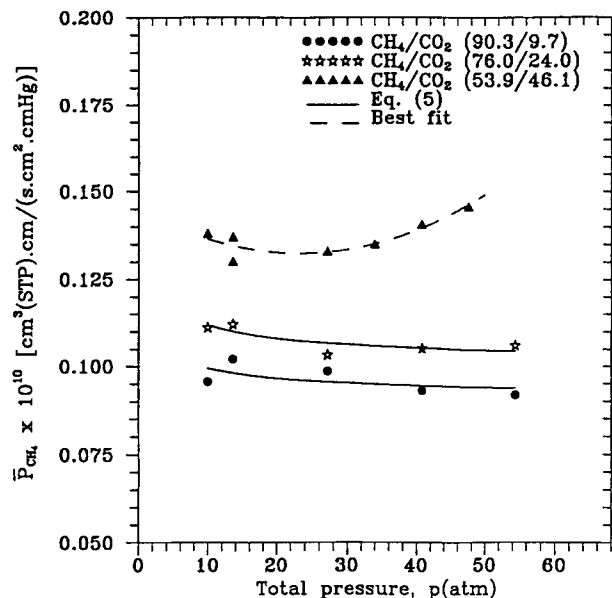
Figure 3 Mean permeability coefficients for CH_4 in cellulose acetate (DS = 2.45) as a function of total feed pressure measured with CH_4/CO_2 mixtures of various compositions at 35°C. The solid lines were calculated using eq. (5) and the parameters in Tables I and II. The dashed line is a "best fit." All the measurements were made with membrane sample 1.

(Figs. 3 and 4). The values of the parameters k_D, c'_H, and b for pure CH_4 and CO_2 in CA (DS = 2.45) at 35°C were taken from the study of Puleo and coworkers[17] and are listed in Table I; these values are for CA not previously "conditioned" by exposure to CO_2 at elevated pressures.

By contrast with the results obtained with CH_4/CO_2 mixtures containing 9.7 and 24.0 mol % CO_2, in measurements with the CH_4/CO_2 mixture containing the highest concentration of CO_2 (46.1 mol %) the values of both $\bar{P}_{CH_4}$ and $\bar{P}_{CO_2}$ were found to pass through a minimum. This is probably due to a combination of dual-mode sorption behavior at lower pressures and strong plasticization (swelling) of CA by CO_2 at higher pressures, as found in this study also with pure CO_2. Plasticization of CA by pure CO_2 and by CH_4/CO_2 mixtures has been reported previously by other investigators.[9,17-19] Consequently, eqs. (5) and (6) could not be used to represent the dependence of $\bar{P}_{CH_4}$ and $\bar{P}_{CO_2}$ on p_h for the CH_4/CO_2 mixture containing 46.1 mol % CO_2.

Values of D_D and D_H for CH_4 obtained for CH_4/CO_2 mixtures containing 9.7 and 24.0 mol % CO_2 are listed in Table II. These values were determined from nonlinear least-squares fits of eq. (5) to the experimental $\bar{P}_{CH_4}/p_h$ data for the above two mixtures. Similar data for pure CH_4 are also listed in

Table II for comparison. Table II shows that the mutual diffusion coefficient D_D for CH_4 in CA tends to increase with increasing CO_2 concentration in the feed mixture. This behavior may indicate that the presence of highly soluble CO_2 increases the mobility of CH_4 dissolved in CA by the Henry's law mode. The mutual diffusion coefficient D_H for CH_4 dissolved in CA by the Langmuir mode does not show any clear dependence on the CO_2 content of the feed (the values of D_H do not vary by more than ±0.02 cm^2/s). Hence, it would appear that the Henry's law domains in glassy CA are more strongly plasticized by CO_2 than the "unrelaxed" Langmuir domains.

Values of D_D and D_H for CO_2 in CA were obtained from eq. (6) and the experimental $\bar{P}_{CO_2}/p_h$ data for the CH_4/CO_2 mixtures containing 9.7 and 24.0 mol % CO_2. These values of D_D and D_H, which are listed in Table V, are seen to be much higher than those for CH_4, as expected from the smaller "kinetic" diameter of CO_2 molecules [$\sigma_K(CO_2)$ = 0.33 nm; $\sigma_K(CH_4)$ = 0.38 nm]. D_D and D_H for CO_2 do not appear to be significantly dependent on the CO_2 concentration in the feed, at least for the conditions of the present study and considering the errors in the determination of these parameters. No D_D and D_H values for CO_2 could be obtained from measure-
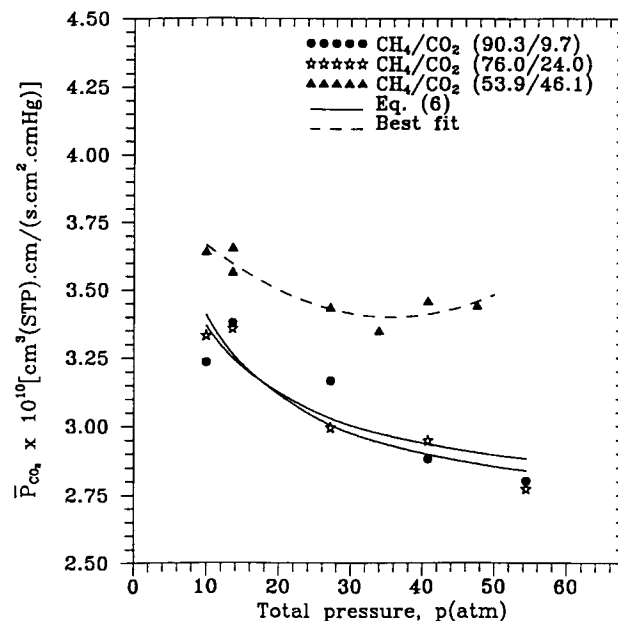

Figure 4 Mean permeability coefficients for CO_2 in cellulose acetate (DS = 2.45) as a function of total feed pressure measured with CH_4/CO_2 mixtures of various compositions at 35°C. The solid lines were calculated from eq. (6) and the parameters in Tables I and V. The dashed line is a "best fit." All the measurements were made with membrane sample 1.
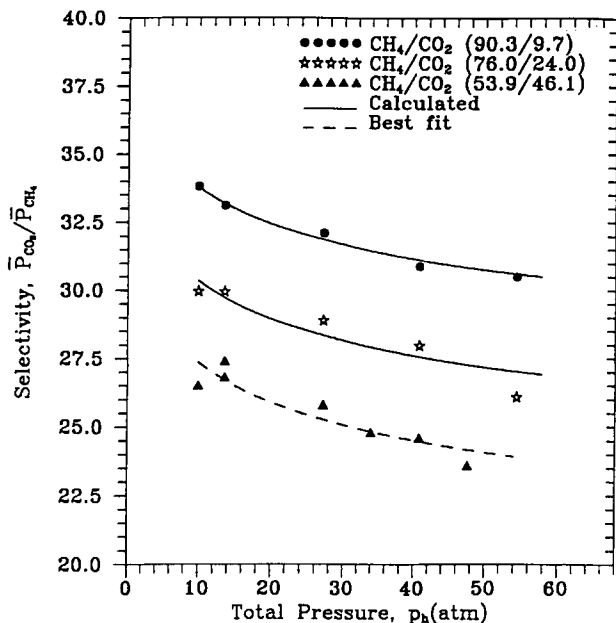
Figure 5 Selectivity of dense (homogeneous) cellulose acetate (DS = 2.45) membranes to CH_4/CO_2 mixtures of various compositions as a function of total feed pressure at 35°C. The solid lines were calculated from values of $\bar{P}_{CH_4}$ and $\bar{P}_{CO_2}$ determined from eqs. (5) and (6), respectively, in conjunction with the parameters k_D, c'_H and b for the pure gases. The dashed line is a "best fit." All the measurements were made with membrane sample 1.

ments with the CH_4/CO_2 mixture with the highest CO_2 content (46.1 mol %) for the reasons mentioned above.

Effect of CH_4/CO_2 Composition on Permeability

Figure 3 shows that, at a given total pressure, the value of $\bar{P}_{CH_4}$ increases as the CO_2 concentration in the feed is increased from 9.7 to 46.1 mol %. By contrast, the value of $\bar{P}_{CO_2}$ is essentially unaffected

by an increase in the CO_2 concentration from 9.7 to 24.0 mol %, but increases when the CO_2 concentration is further raised to 46.1 mol % (Fig. 4). This could also be a consequence of the plasticization of CA by CO_2; a plasticization-induced increase in permeability is commonly more pronounced for the slower-permeating components of a gas mixture.[22,35]

Similar observations have been made by Donohue and colleagues,[9] who have measured the permeability and selectivity of "asymmetric" CA membranes to CH_4/CO_2 mixtures containing 2.04, 30.6, and 70.6 mol % CO_2. The measurements were made at ambient temperature and at pressures up to about 60 atm (882 psia). In these studies, $\bar{P}_{CH_4}$ increased at constant total pressure with increasing CO_2 concentration in the feed, whereas $\bar{P}_{CO_2}$ remained relatively unchanged as the CO_2 concentration was increased from 2.04 to 30.6 mol %. However, a significant increase in $\bar{P}_{CO_2}$ was observed in the measurements with a CH_4/CO_2 mixture containing 70.6 mol % CO_2.

According to eqs. (5) and (6), the values of $\bar{P}_{CH_4}$ and $\bar{P}_{CO_2}$ at a given total pressure should *decrease* with increasing CO_2 concentration in the CH_4/CO_2 mixture. However, the unusual behavior observed with CA (DS = 2.45) is believed to be due to a gradual "conditioning" of the membranes by CO_2 during the the permeability measurements with CH_4/CO_2 mixtures. These results are further discussed in the following sections.

CO_2/CH_4 Selectivity of Cellulose Acetate Membranes

The CO_2/CH_4 selectivity of the dense (homogeneous) CA membranes determined with the three CH_4/CO_2 mixtures used in this study is plotted as a function of the total pressure in Figure 5. It can be seen from this figure that the CO_2/CH_4 selectivity of CA decreases with increasing pressure as well as with in-

Table IV   Permeability and Selectivity of Cellulose Acetate (DS = 2.45) to CH_4/CO_2 Mixtures

Feed Composition: CH_4/CO_2 (mole %)	Feed Pressure, p_h (atm)	Permeability Coefficient, $\bar{P} \times 10^{10}$		Selectivity, $\bar{P}_{CO_2}/\bar{P}_{CH_4}$
		CO₂	CH₄	
91.3/9.7	10.0	3.23	0.096	33.8
	54.4	2.80	0.092	30.5
76.0/24.0	10.0	3.33	0.111	30.0
	54.4	2.77	0.106	26.1
53.9/46.1	10.0	3.64	0.138	26.5
	54.4	3.44	0.146	23.6

Units: $\bar{P}$: [cm^3(STP) · cm/(s · cm^2 · cmHg)]; Temperature: 35°C.

Table V Mutual Diffusion Coefficients for CO_2 in Cellulose Acetate (DS = 2.45) at 35°C

CH_4/CO_2 Composition (mole %)	D_{D,CO_4}	D_{H,CO_4}	$F = D_H/D_D$	Reference
(90.3/9.7)	1.31	0.29	0.22	This work
(76.0/24.0)	1.28	0.36	0.28	

Units: D_D (cm²/s); D_H (cm²/s).

creasing CO_2 concentration in the feed. In the measurements with mixtures containing 9.7 and 24.0 mol % CO_2, the decrease in the CO_2/CH_4 selectivity with increasing feed pressure is due to a greater decrease in the permeability to CO_2 than in that to CH_4 (Figs. 3 and 4). This behavior is predicted by eqs. (5) and (6) since $F_{CO_2}K_{CO_2} > F_{CH_4}K_{CH_4}$.[22,36]

The decrease in the CO_2/CH_4 selectivity of CA membranes with increasing pressure observed with the gas mixture containing 46.1 mol % CO_2 is due to a combination of factors. At pressures up to about 30 atm (441 psia), the decrease in the selectivity is due to a steeper decrease in the CA permeability to CO_2 than to CH_4, as was also observed with the mixtures containing 9.7 and 24.0 mol % CO_2 (Fig. 4). At higher pressures, however, the permeability of the CA membrane to CH_4 and CO_2 increases as the pressure is raised, and the decrease in the CO_2/CH_4 selectivity is then due to a greater *increase* in the permeability of CA to CH_4 than in that to CO_2. This behavior is probably also a consequence of the plasticization (swelling) of CA by the CO_2 at higher pressures.

Sada and coworkers[19] have measured the CO_2/CH_4 selectivity of dense (homogeneous) cellulose triacetate (DS = 3.0) membranes using a binary mixture containing 50 mol % CO_2. The measurements were made in the pressure range from 5 to 25 atm (74 to 367 psia) at 30 and 40°C. The CO_2/CH_4 selectivity of these CA membranes was in the range from 20 to 30, and was shown to decrease with increasing pressure and temperature.[19] The CO_2/CH_4 selectivity at 35°C of the CA (DS = 2.45) membranes used in the present study with a binary mixture containing 46.1 mol % CO_2 is consistent with the value reported by Sada and coworkers at 30°C.

It should be noted that a number of investigators have reported values of the CO_2/CH_4 selectivity of "asymmetric" CA membranes determined with binary and multicomponent gas mixtures.[3,5,8–12,16,19] However, it was not possible to compare the CO_2/CH_4 selectivity of the asymmetric CA membranes with the values determined in the present study because the measurements with the asymmetric membranes were made under different experimental conditions and the degree of acetyl substitution was not stated.

Conditioning of Cellulose Acetate Membranes by Carbon Dioxide

General Considerations

A number of investigators have reported that exposure of polymer membranes to high-pressure CO_2 ("conditioning") causes an increase in their gas permeability.[17,34–43] Stern and Kulkarni[32] have found an increase in the solubility coefficient of CH_4 in CA (DS = 2.4) after conditioning with CO_2. The conditioning effect was found to be time-dependent.[17,31,39–43] These studies have shown that the diffusion of gases in, and permeation through, CA membranes conditioned with CO_2 are also "history-dependent." The following work was performed in order to investigate in more detail some of the "conditioning" effects observed in the course of the studies described in the previous sections.

Effect of Conditioning on Permeability to Carbon Dioxide

The permeability of a CA membrane (DS = 2.45) to pure CO_2 was found to be dependent on time as well as on pressure (Figs. 6 and 7). The numbers in Figures 6 and 7 indicate the order in which the permeability measurements were made. In measurements 1–8, the *apparent* steady-state permeation of CO_2 was determined after exposing the CA membrane to pure CO_2 for a period of 2 to 3 h at each experimental pressure. However, the permeability measurements at 27.2 atm (400 psia) (measurements 9–15 in Fig. 6) were continued for up to 120 h (5 days). The value of $\bar{P}_{CO_2}$ at a pressure of 27.2 atm increased by about 35% (from 5.45×10^{-10} to 7.34 $\times 10^{-10}$ cm³(STP) cm (s cm² cmHg)⁻¹ in 5 days (Fig. 7). However, the rate of $\bar{P}_{CO_2}$ increase diminished rapidly with time and $\bar{P}_{CO_2}$ tended toward a constant value.
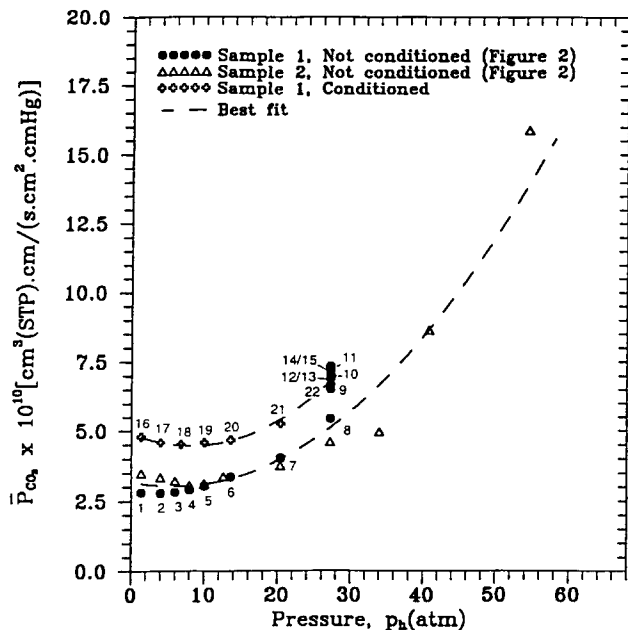
Figure 6 Mean permeability coefficient for CO_2 in cellulose acetate (DS = 2.45) measured with pure CO_2 as a function of pressure at 35°C. The measurements were made with "conditioned" (exposed to CO_2 at 30 atm for 5 days) (Sample 1) and not-conditioned membranes (Samples 1 and 2). The dashed lines are "best fits." Numbers 1–22 indicate the sequence of measurements. Values of $\bar{P}_{CO_2}$ for a not-conditioned membrane are reproduced from Figure 2.

In the study by Puleo and colleagues[17] the value of $\bar{P}_{CO_2}$ in CA (DS = 2.84) determined at 30 atm (441 psia) and 35°C also increased significantly ($\sim$ 31%) for up to about 120 h. However, $\bar{P}_{CO_2}$ did not change significantly with further increases in the period of exposure to CO_2 to 500 h (21 days). The increase in $\bar{P}_{CO_2}$ could be attributed to the conditioning effect of CO_2.[17]

After conditioning, i.e., exposure to CO_2 at 27.2 atm (400 psia) for 5 days, both sides of the CA membrane were evacuated in the permeability cell for 24 h at the experimental temperature (35°C). The permeability of the "conditioned" CA membrane to pure CO_2 was then measured in the order of increasing pressure (measurements 16–22 in Fig. 6). The value of $\bar{P}_{CO_2}$ was found to pass through a slight minimum at low pressures and then to increase steeply as the pressure was raised (Fig. 6). This behavior was probably due to the fact that, as mentioned previously, $\bar{P}_{CO_2}$ first decreased with increasing pressure, as predicted by the dual-mode sorption model, and then increased because the polymer was strongly plasticized (swelled) by CO_2.

As can be seen in Figure 6, the value of $\bar{P}_{CO_2}$ ob-

tained with the "conditioned" CA membrane is significantly higher than that obtained with the same membrane prior to prolonged exposure to CO_2. This behavior is believed to be due also to the plasticization of the CA membrane by CO_2, which increases the free volume and the segmental mobility of CA and consequently increases the permeability of the polymer. The value of $\bar{P}_{CO_2}$ may revert after a sufficiently long time to that obtained with the CA membrane before conditioning, depending on the relaxation times of CA under the experimental conditions used. An increase in the permeability of a polymer to gases on exposure to high-pressure CO_2 at a constant pressure and temperature was also observed with polycarbonate[38–40] and polysulfone[41,42] membranes.

Effect of Conditioning on Permeability to Methane

The value of $\bar{P}_{CH_4}$ obtained from measurements with pure CH_4 with the "conditioned" and not-conditioned CA membranes are compared in Figure 8. The values of $\bar{P}_{CH_4}$ for the not-conditioned CA membrane are reproduced from Figure 2. Prior to the measurements with pure CH_4, the "conditioned" membrane was evacuated for 24 h at 35°C, and the permeability measurements were made by increasing the CH_4
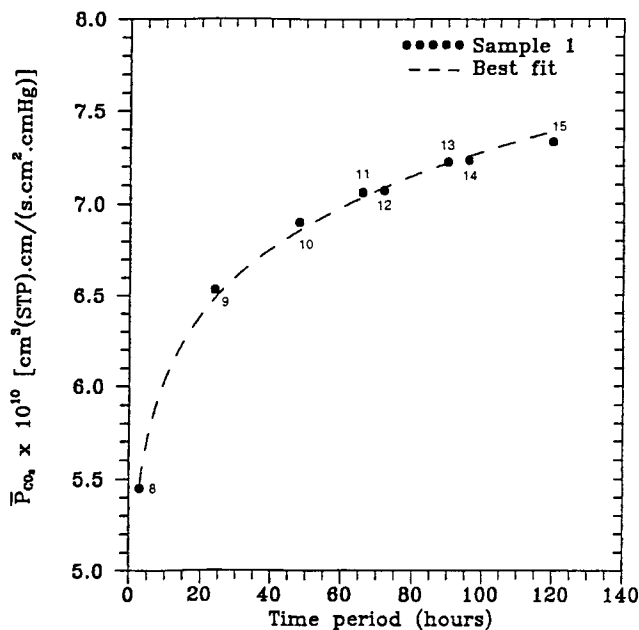

Figure 7 Time dependence of permeability of cellulose acetate (DS = 2.45) to CO_2 at 35°C and 27.2 atm (400 psia). The solid line is the best fit. The measurements were made with membrane sample 1. Numbers 8–15 indicate the sequence of measurements.

pressure in a stepwise manner. Figure 8 shows that the permeability of this membrane to pure CH_4 was much higher, particularly at low pressures, than the value obtained for the membrane that was not previously exposed to high-pressure CO_2.

Figure 8 also shows that the value of $\bar{P}_{CH_4}$ for the "conditioned" CA membrane decreased much more rapidly with increasing pressure than that for the membrane that was not conditioned. Since these measurements were made sequentially over a period of time, the sharp decrease in the permeability of the former membrane to CH_4 may indicate that the CA was regaining its not-conditioned state. Stern and Kulkarni[32] have suggested that the rate of depressurization after conditioning may also have an effect on the magnitude of the conditioning effect observed in CA (DS = 2.4). Puleo and coworkers[17] have stated that "the response of the films to plasticization by CO_2 is not only time- and pressure-dependent but also reversible."

CONCLUSIONS

The permeability and selectivity of dense (homogeneous) CA (DS = 2.45) membranes to CO_2 and CH_4 have been determined with the pure gases and with CH_4/CO_2 mixtures containing 9.7, 24.0, and 46.1 mol % CO_2. The measurements were made at 35°C (95°F) and at pressures up to 54.4 atm (800 psia). The following results were obtained:

1. The permeability coefficient for CH_4, $\bar{P}_{CH_4}$, determined with pure CH_4, decreases with increasing CH_4 pressure, as expected from the "dual-mode" sorption model of gas transport in and through glassy polymers.
2. The permeability coefficient for CO_2, $\bar{P}_{CO_2}$, determined with pure CO_2, passes through a shallow minimum and then increases with increasing CO_2 pressure. The initial decrease in $\bar{P}_{CO_2}$ as the pressure is raised is expected from the "dual-mode" sorption model, whereas the subsequent increase in $\bar{P}_{CO_2}$ is probably due to the plasticization (swelling) of CA by CO_2. Plasticization of the polymer may cause an increase in its free volume and chain mobility.
3. The values of $\bar{P}_{CH_4}$ and $\bar{P}_{CO_2}$ determined with the CH_4/CO_2 mixtures containing 9.7 and 24.0 mol % CO_2 decrease with increasing total pressure. However, $\bar{P}_{CH_4}$ and $\bar{P}_{CO_2}$ obtained with the mixture with the highest CO_2 concentration (46.1 mol %) pass through a min-
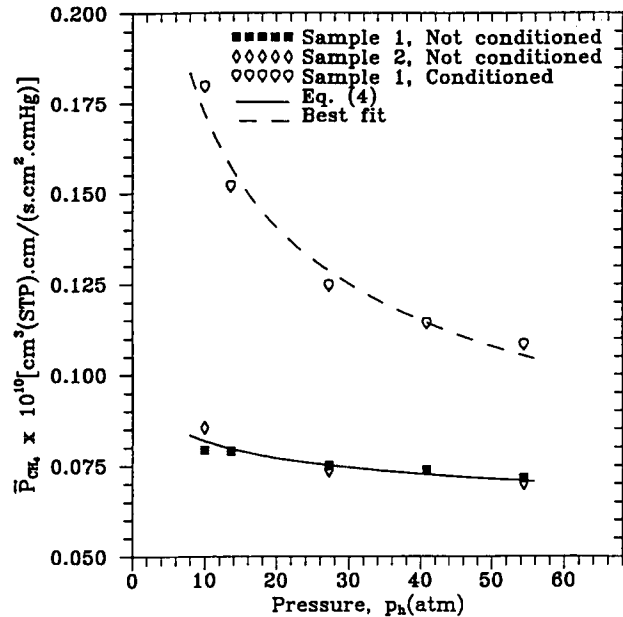

Figure 8 Mean permeability coefficient for CH_4 in cellulose acetate (DS = 2.45) measured with pure CH_4 as a function of pressure at 35°C. The measurements were made with a "conditioned" membrane (i.e., exposed to CO_2 at 30 atm for 5 days) (Sample 1) and not-conditioned membranes (Samples 1 and 2). The solid line was calculated from eq. (4) and the parameters in Tables I and II. The values of $\bar{P}_{CH_4}$ for a not-conditioned CA membrane are reproduced from Figure 2.

imum and then increase as the pressure is raised, probably due to the plasticization of CA by CO_2 at higher pressures.

4. The value of $\bar{P}_{CH_4}$ determined with the CH_4/CO_2 mixtures increases at constant total pressure with increasing CO_2 concentration, probably also due to the plasticization of CA by CO_2. The values of $\bar{P}_{CO_2}$ at constant total pressure are essentially unchanged when the CO_2 concentration of the mixture is increased from 9.7 to 24 mol %, but increase when the CO_2 concentration is further raised to 46.1 mol %.
5. The CO_2/CH_4 selectivity ($\equiv \bar{P}_{CO_2}/\bar{P}_{CH_4}$) decreases with increasing total pressure and, at constant pressure, decreases with increasing CO_2 concentration in the CO_2/CH_4 mixtures.

The effect of "conditioning" of CA by exposure to CO_2 on the permeability of the CA membranes to CH_4 and CO_2 is also dependent on the exposure time to CO_2 and on the past "history" of the membranes. Therefore it is not unexpected that different investigators have observed significant differences in the

permeability of CA membranes to CH_4, CO_2, and their mixtures, even under comparable experimental conditions (pressure, temperature, gas composition).

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