Separation of Gaseous Mixtures by Permeation Through Polyethylene Film

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The permeation of polyethylene film by carbon dioxide, ethane, and propane at elevated pressures was investigated. In addition, the separation of mixtures of ethane and propane by permeation was studied.

Both hydrocarbon vapors' permeation exhibited pressure dependence, with propane showing the greatest variation over the same range.

In the case of the mixture separation study, the achieved degree of separation was lower than would be predicted on the basis of the pure component permeation constants. Moreover, the total flow of vapor through the film was greater than would be expected on the basis of the individual gas flows. This was attributed to an anomalous diffusion phenomenon of ethane in the presence of dissolved propane due to a plasticization of the polymer network.

The permeation of a nonporous polymeric barrier by a penetrant vapor is generally considered to involve three consecutive steps: solution or absorption of the penetrant at one surface of the membrane, activated diffusion of the dissolved penetrant through the membrane from a region of high activity to one of lower activity, and desorption or evaporation of the penetrant from the other surface of the membrane.

Since the diffusion process through the membrane is generally slow, an equilibrium condition exists between the concentration of dissolved penetrant and the partial pressures at the respective membrane surfaces (*1*).

For the case of the so-called *permanent gases*, it has been demonstrated that their solubility obeys Henry's law, and the diffusion follows Fick's laws (*2* to *7*). This may be ascribed to the absence of any polymer-penetrant interactions for these systems.

Alternatively, the solubility and/or diffusivity of penetrants in highly interacting polymer-penetrant systems display a rather complicated concentration and pressure dependence. This has been illustrated previously by such investigators as Rogers, Stannett, and Szwarc (*8*); Li and Henley (*9*), and others (*10*, *11*).

The permeability of both ethane and propane as observed in this study follows an exponential relationship of the form

$$P = Pop \exp (Ap_2) \qquad (1)$$

The value of A is indicative of the degree of polymer-penetrant interaction, the higher values attributable to a more extensive swelling and/or plasticization of the polymer network.

The purpose of this study was to determine the feasibility of utilizing the difference in the permeation pressure dependencies of two vapors, namely, ethane and propane, to effect their separation from mixtures at elevated pressures.

EXPERIMENTAL APPARATUS

The equipment used is depicted schematically in Figure 1. The polymer membrane was sandwiched between two thin neoprene gaskets and was supported by perforated spring-bronze plates to prevent distortion. The entire assembly was then clamped between the permeation cell flanges by using a Teflon O ring to insure a leakproof seal around the film. A bypass line was supplied in the cell's high pressure chamber to effect good mixing at the upstream face of the film. The entire apparatus was enclosed in an insulated, thermostatically controlled air bath. Pressures on both sides of the membrane were controlled by back pressure regulators (BPR). Calibrated test gauges were used to monitor all pressures.

For the separation study, a continuously monitoring, online Beckman gas chromatograph (model 320-E) was employed. The membranes used for the entire experimental program were Visking Visqueen polyethylene of 4 mil thickness. The polymer density was determined by a pycnometer and found to be 0.920 g./cc. This corresponds to an amorphous volumetric fraction of 0.55. (Densities of the crystalline and amorphous phases were taken from reference *12*.) Thicknesses were determined by a micrometer and were found to be remarkably uniform across any film.

EXPERIMENTAL PROCEDURE

The back pressure regulators were set to the desired upstream operating pressure, and the system was filled with the pure gas or mixture to be tested. The valve connecting the high and low pressure sides of the cell was closed and a pressure differential established by bleeding off from the low pressure side regulator. The system was allowed to equilibrate with respect to temperature and pressures at continuous feed bypass conditions. Gas flow rates were measured by liquid displacement for both permeated and bypass streams. In the case of mixture separation studies, gas analyses were performed continuously during both transient and steady state periods of the run.

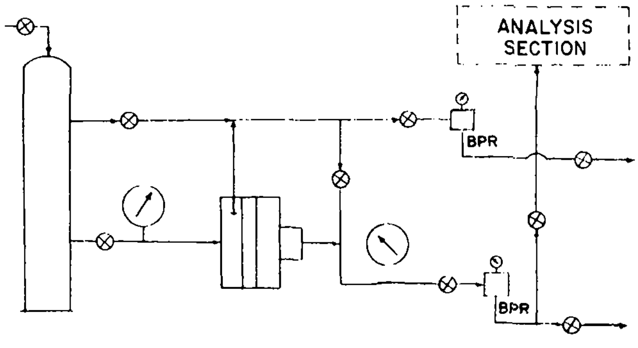

Fig. 1. Schematic diagram of apparatus.

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TABLE 1. PERMEATION CONSTANTS OF ETHANE

Temperature: 306°K.
z: 0.004 in.

Run No.	p_2, lb./sq. in. abs.	Δp, lb./sq. in.	$P \times 10^{9}$* $\left(\frac{\text{cc. STP} \equiv (0^\circ\text{C., 1 atm.})}{\text{sec. sq. cm.} \cdot \text{cm. Hg}}\right)$
1	14.7	26.1	2.001
2	81.1	31.4	2.654
3	85.2	23.6	2.868
4	123.4	23.6	3.501
5	140.8	31.1	3.712
6	143.2	11.4	4.119
7	144.3	20.5	3.849
8	145.5	26.9	3.919
9	168.3	19.0	4.472
10	176.2	29.3	5.289
11	176.2	27.0	5.145
12	186.7	30.0	5.625
13	207.2	31.3	6.147
14	217.4	25.0	6.501

* Fugacity coefficient applied in Δp to correct for nonideality.

TABLE 2. PERMEATION CONSTANTS OF PROPANE

Temperature: 306°K.
z: 0.004 in.

Run No.	p^2, lb./sq. in. abs.	Δp, lb./sq. in.	$P \times 10^{9}$* $\frac{\text{cc. (STP) cm.}}{\text{sec. sq. cm. cm. Hg}}$
1	43.5	17.2	10.219
2	56.7	31.3	10.845
3	57.2	32.5	13.386
4	68.0	27.2	22.677
5	69.0	21.6	18.523
6	82.1	30.2	33.177
7	82.1	25.1	30.993
8	83.8	21.1	27.406
9	88.2	29.0	32.179
10	100.6	15.0	52.727
11	109.0	21.5	58.685
12	115.8	23.4	81.978

* Fugacity coefficient applied in Δp to correct for nonideality.

RESULTS

Carbon Dioxide

It has previously been demonstrated by Li and Henley (9) that the permeability of carbon dioxide through polyethylene film is independent of pressure over the range of 1 to 11 atm. Furthermore, no discernible effect of pressure differential was observed for Δp values up to 8 lb./sq.in.

The present investigation extends the pressure range to 14 atm. with pressure differentials of from 16.4 to 41.5 lb./sq.in. Again, the permeation of carbon dioxide showed no dependence on either pressure or Δp. The data are plotted in Figure 2.

Ethane and Propane

Examination of the data in Tables 1 and 2 and Figure 2 indicate that the permeation of both ethane and propane through polyethylene exhibits pressure dependence. However, as is evident from the data of runs 6, 7, and 8 of Table 1, there is no correlatible variation of the permeation constant of ethane at a constant downstream pressure as the pressure differential across the membrane was varied from 11.4 to 27.0 lb./sq.in.

SEPARATION OF ETHANE AND PROPANE FROM A MIXTURE

The separation of a gas mixture of ethane and propane by permeation through polyethylene film was investigated over a range of pressures. The data for these runs are compiled in Table 3.

It was discovered that in every run the expected separation of the two components as predicted by the pure component's permeation constant taken at the respective downstream partial pressure was not obtained. In each case, the permeated gas contained a higher mole percent ethane than was expected. In addition, the total flux rate predicted for the mixture based on the pure gas permeation rates was exceeded in every run.

Pseudo permeation constants (Ᵽ) were calculated for each component according to the following equation:

$$L \cdot y_{i2} = \not{P}_i \left[p_1 y_{i_1} \nu_{i_1} - p_2 y_{i_2} \nu_{i_2}\right] \cdot \left(\frac{a}{z}\right) \qquad (2)$$

These pseudo permeation constants were then divided by the pure component permeation constants (P) taken at a downstream pressure equal to the partial pressure of the pure component. These ratios are included in Table 3.

Since the ratio (Ᵽ/P) for propane was essentially 1.0 in all cases, the increase in total flux experienced can be attributed to an anomalous permeation phenomenon of ethane. This is further supported by the analytical results obtained on the permeated stream compositions.

A value of the solubility constant for propane in polyethylene was taken from the paper by Michaels and Bixler (12) and the concentrations of dissolved propane in the film calculated. These concentrations appear in Table 3. In addition, the (Ᵽ/P) ratios for ethane are plotted against the propane concentrations in Figure 3.

DISCUSSION OF RESULTS

The explanation for this unexpected permeation be-

TABLE 3. SEPARATION OF ETHANE (A) AND PROPANE (B) FROM GAS MIXTURES

Temperature: 306°K.

Run No.	p_1, lb./sq. in. abs.	p_2, lb./sq. in. abs.	y_{B_f}	y_{B_2}	Δp_A, cm. Hg	Δp_B, cm. Hg	Ᵽ$_A$ (1)	Ᵽ$_B$ (1)	P_A (1)	P_B (1)	$C_B \times 10^3$ (g./g. pol.) (2)	(Ᵽ/P)$_A$	(Ᵽ/P)$_B$
1	118.5	55.4	0.518	0.557	160.9	131.8	4.29	6.60	1.97	6.61	14.0	2.18	1.00
2	116.7	55.4	0.518	0.549	158.7	125.6	4.10	6.30	1.98	6.49	13.6	2.08	0.97
3	109.9	64.1	0.556	0.579	109.6	100.1	4.83	7.28	2.00	7.61	14.9	2.42	0.96
4	105.2	64.2	0.556	0.584	99.0	88.8	4.43	6.93	1.99	7.71	14.6	2.23	0.90
5	87.3	54.0	0.518	0.540	85.9	73.9	3.75	5.12	1.97	6.00	11.6	1.90	0.86
6	87.0	23.2	0.518	0.568	162.1	152.5	3.12	4.36	1.81	3.74	9.0	1.72	1.16
7	80.1	39.5	0.556	0.588	100.5	98.4	3.33	4.85	1.88	5.04	10.5	1.77	0.96
8	71.1	24.1	0.518	0.564	121.7	112.8	2.64	3.68	1.82	3.78	7.9	1.45	0.97
9	69.1	14.7	0.518	0.570	138.5	134.1	2.63	3.60	1.77	3.26	6.9	1.49	1.10

(1) Taken from pure gas data at downstream pressures (p_2) equal to the partial pressure of the i^{th} component.
(2) Average concentration based on average partial pressures at the film surfaces.

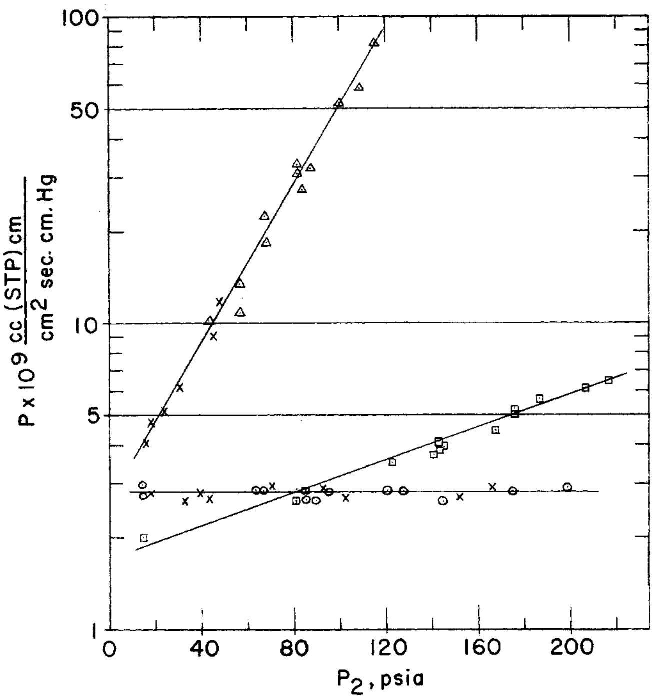

Fig. 2. ⊙ = carbon dioxide, □ = ethane, △ = propane, X = data of Li and Henley *(9)*. Temperature = 306°K.

havior can be found by considering two possibilities: a preferential increase in the ethane solubility due to the presence of dissolved propane, and a preferential increase in the ethane diffusivity due to the presence of dissolved propane. Two recent works support these two explanations. Li and Long (*13*) measured the solubilities of mixtures of methane and ethylene as well as the pure component solubilities. The results indicated a higher solubility of the nonpreferentially permeating component in the presence of the more highly soluble component compared with pure component solubilities. In addition, Robeson (*14*) found a similar effect in solubility behavior for ethane-butane systems. Furthermore, the latter also determined an increasing diffusivity for the nonpreferentially permeating molecule (ethane) with increasing concentration of the more soluble butane in the polymer.

It is believed that the actual explanation for the behavior experienced in this work is a combination of the two effects, namely, the solubility and diffusional phenomena.

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NOTATION

A = characteristic constant reflecting the pressure dependence of permeation
a = membrane cross-sectional area
D = diffusion constant
L = permeated stream flow rate
P = pure component permeation constant
Pop = permeation constant a zero downstream pressure
$\mathcal{P}$ = pseudo permeation constant for component in a mixture
p = pressure
Δp = pressure differential across membrane
S = solubility constant
y = mole fraction (vapor)
z = film thickness

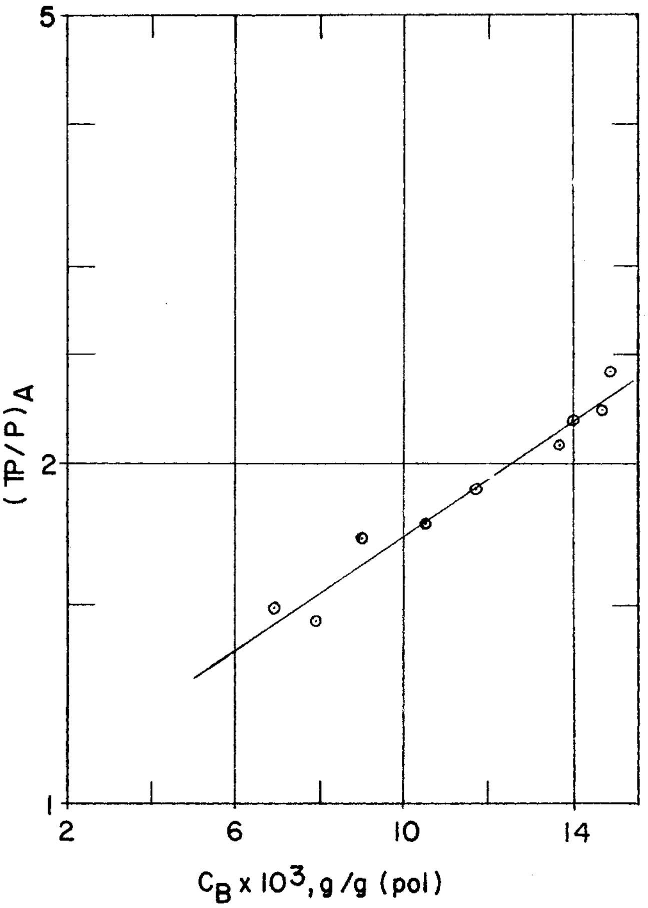

Fig. 3. Concentration dependence of ethane's permeation parameter.

Greek Letters

ν = fugacity coefficient

Subscripts

1 = high pressure side of permeation cell
2 = low pressure side of permeation cell
A = ethane
B = propane
f = feed

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