

Permeation of Ethane-Butane Mixtures through Polyethylene

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Synopsis

Permeation of ethane-butane mixtures at atmospheric pressure through polyethylene was investigated in the temperature interval of 30-60°C. The integral permeation constant \bar{P} and the integral diffusion coefficient \bar{D} of both ethane and butane were satisfactorily correlated by using an exponential and also a linear function of butane concentration. This was attributed to the plasticizing of the film by butane, whose solubility constant is approximately ten times that of ethane in the temperature interval investigated. The separation factor G_{ij} , defined as the ratio of the permeation constant of butane to the permeation constant of ethane over the range of mixture compositions and temperatures investigated, remained nearly constant at values in the range of 2.8-3.2. The insignificant change in G_{ij} is due to the proximity of the activation energies of permeation of ethane and butane (10.95 and 10.75 kcal/mol, respectively) and the similar magnitude of change in the permeation constants with increasing butane concentration. Experiments were run in which the film was initially in equilibrium with the same partial pressure of butane as in the mixture to be studied. It can be shown that the diffusion coefficient of ethane in this case is related to the following function of film position: $D = D(o)(\beta_0 + \beta_1 x)^{\delta}$. The time lag of diffusion of ethane in these experiments decreased with increasing butane concentration.

INTRODUCTION

Studies of gaseous mixtures permeating polymeric membranes have generally been limited to cases of ideal behavior, such that the effect of one component on the permeation of another component is negligible.^{1,2} Pilar³ observed that the permeation rates of oxygen and nitrogen through polyethylene increased with relative partial pressure of *n*-hexane. It was also observed that the permeability of oxygen through regenerated cellulose increased with increasing relative humidity, owing to plasticization of the film by sorbed water.

Desorption studies of the ethane-butane-polyethylene system have been described previously,⁴ and the work described here is a study of the selective permeation characteristics of the system. Experimental data have been obtained to determine the effect of temperature, mixture composition, and initial boundary conditions on the permeation characteristics. Desorption studies of this system had shown that the diffusion coefficient of each com-

ponent for the range of 20–60°C is dependent upon mixture composition. The solubility constant was found to be concentration-dependent at 20 and 30°C for the range of partial pressures investigated (0–760 mm Hg) for both ethane and butane. Since the permeability constant is defined as the product of the diffusion coefficient and the solubility constant $P \equiv DS$, then the permeability constant would likewise be concentration-dependent: $\bar{P} \equiv \bar{D}\bar{S}$, where \bar{P} is the integral permeation constant, \bar{D} is the integral diffusion coefficient, and \bar{S} is the mean solubility constant as defined by Rogers.¹

EXPERIMENTAL

Materials

The ethane and *n*-butane gases used in this study had purity levels of 99.0 and 99.5%, respectively. The polyethylene film used was supplied by the Dow Chemical Company with a density ρ of 0.9238 and a nominal thickness of 10 mils. The exact film thickness was determined by a measuring microscope.

Apparatus

The experimental apparatus shown in Figure 1 consists of a permeation cell placed in a constant-temperature bath ($\pm 0.2^\circ\text{C}$) connected to the gas feed system and the penetrant trapping system.

The cell consists of two compartments separated by the test film. The test film is placed on top of filter paper, which is in turn supported by a sintered-metal disk. The trapping system for trapping penetrated butane and ethane consists of alternate glass U-tubes filled with glass spheres, to ensure adequate surface area for trapping. The glass U-tubes are maintained at liquid-nitrogen temperature. An air leak regulated by a micrometer flow valve was introduced on the downstream side of the permeation cell, to ensure adequate flushing without loss of penetrated butane or ethane in the trapping system.

Procedure and Analysis

The boundary and initial conditions used for this study were:

$$C_i = 0 \quad 0 < x < l \quad t = 0 \quad (1)$$

$$C_i = 0 \quad x = l \quad t \geq 0 \quad (2)$$

$$C_i = C_{i0} \quad x = 0 \quad t \geq 0 \quad (3)$$

The permeation cell was evacuated for a sufficient length of time such that any absorbed penetrants had been removed. At time zero the mixture was introduced into the upstream side of the cell at atmospheric pressure and allowed to flow through the upstream side of the cell at a slow rate for the course of each experimental run, to eliminate concentration gradients at the film surface. Permeated ethane and butane were trapped in the glass

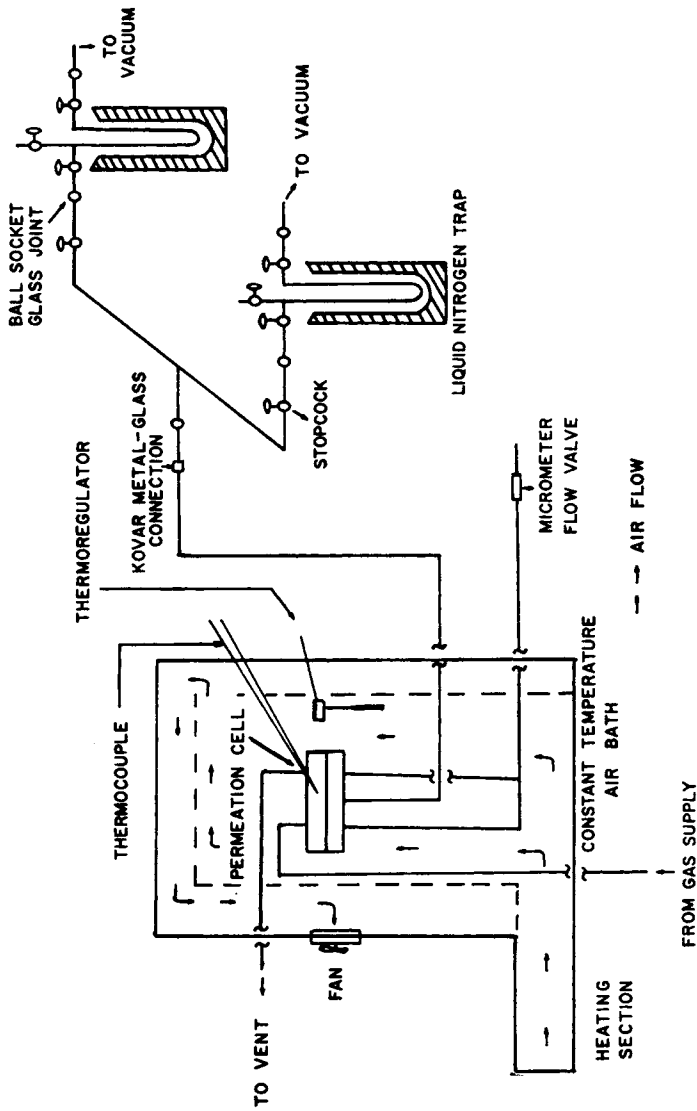


Fig. 1. Diagram of permeation apparatus.

U-tubes, each of which was used for a predetermined length of time. The total length of each run was determined such that a suitable number of data points were obtained to determine the steady-state slope of a plot of Q_t , quantity of a specific penetrant permeating the film at time t , versus time. The amount of each penetrated component was determined by a gas chromatography analysis technique similar to that described previously.⁴

The integral permeation constant \bar{P} is calculated from the experimental data, and the integral diffusion coefficient \bar{D} , given by

$$\bar{D} = 1/C_i \int_0^{C_i} D dC \quad (4)$$

is calculated from the relationship $\bar{P} = \bar{D}\bar{S}$; \bar{S} is determined from

$$\bar{S} = (C_i - C_0)/(P_i - P_0) \quad (5)$$

where C_i and P_i are the ingoing film concentration and partial pressure of the penetrant, and C_0 and P_0 are the outgoing concentration and partial pressure. $\bar{S} = C_i/P_i$ for the conditions of this study as $C_0, P_0 = 0$, and experimental values of \bar{S} have been previously reported.⁴

RESULTS

The permeation of pure butane and pure ethane at various partial pressures between 0 and 760 mm Hg was investigated. The valve outlet of the permeation cell was connected to a vacuum pump, and by proper valve positioning the desired partial pressure was maintained throughout the experiment. The results are given in Table I for both ethane and butane permeation at 30°C.

Mixtures of ethane and butane were studied over the entire range of ethane-butane compositions (760 mm) at 30, 40, 50, and 60°C. The

TABLE I
Pure-Component Permeation Results for Butane and Ethane*

Butane partial pressure, mm Hg	$\bar{P} \times 10^9$ ml(STP)/cm-sec-cmHg	Time lag L , sec
Butane permeation results:		
154	2.98	2430
306	3.28	2300
468	4.25	2150
616	5.20	2060
768	5.82	1930
Ethane permeation results:		
156	.96	1000
296	1.00	940
463	.95	1010
616	.975	900
764	1.01	930

* Film, Dow polyethylene film (sample No. 5); temperature, 30°C.

TABLE II
Permeation Data for Butane-Ethane Mixtures at 30°C^a

C ₄ H ₁₀ , %	C ₂ H ₆ , %	\bar{P} , C ₄ H ₁₀	\bar{D} , C ₄ H ₁₀	L, C ₄ H ₁₀	\bar{P} , C ₂ H ₆	\bar{D} , C ₂ H ₆	L, C ₂ H ₆	G_{ij}	No. ^b
100.0	0.0	5.82	0.568	1930					5
88.5	11.5	5.47	0.541	1860	1.66	1.55	1000	3.28	5
78.8	21.2	4.98	0.500	2100	1.58	1.48	900	3.16	5
58.1	41.9	4.11	0.425	2230	1.33	1.29	1050	3.09	5
50.8	49.2	4.15	0.431	2270	1.27	1.22	980	3.26	5
44.4	55.6	3.78	0.397	2270	1.16	1.13	1060	3.25	5
41.8	58.2	3.69	0.390	2330	1.20	1.17	1020	3.08	5
22.2	77.8	3.22	0.352	2440	1.075	1.075	950	3.00	5
0.0	100.0				1.01	1.03	930		5
100.0	0.0	6.64	0.654	2150					1
79.0	21.0	5.40	0.542	2450	1.81	1.69	1100	2.99	1
57.3	42.7	4.63	0.480	2250	1.38	1.32	1050	3.35	1
42.6	57.4	3.87	0.409	2450	1.32	1.28	1150	2.94	1
21.9	78.1	3.12	0.338	2400	1.09	1.09	900	2.89	1
0.0	100.0				0.99	1.01	1000		1

^a Film, Dow polyethylene film. Film thickness, No. 1, 0.02365 cm; No. 5, 0.0226 cm. P = ml(STP)/cm-sec-cmHg $\times 10^3$. D = cm²/sec $\times 10^7$.

L = sec. Mixture pressure: atmospheric pressure.

^b Film sample number.

TABLE III
 Permeation Data for Butane-Ethane Mixtures^a

Temp., °C	C ₄ H ₁₀ , %	C ₃ H ₆ , %	\bar{P} , C ₄ H ₁₀	\bar{D} , C ₄ H ₁₀	L, C ₄ H ₁₀	\bar{P} , C ₂ H ₆	\bar{D} , C ₂ H ₆	L, C ₂ H ₆	G_{ij}	No. ^b
40	100.0	0.0	9.50	1.14	1180	2.71	2.98	440	3.26	1
40	94.7	5.3	8.87	1.06	1080	2.61	2.86	620	3.08	1
40	86.9	13.1	8.05	0.964	1200	2.22	2.43	590	3.34	1
40	73.4	26.6	7.42	0.888	1100	2.38	2.60	500	2.86	1
40	59.0	41.0	6.81	0.816	1070	2.06	2.25	530	3.22	1
40	38.2	61.8	6.65	0.795	1180	2.05	2.24	540	2.68	1
40	21.4	78.6	5.48	0.656	1400	1.54	1.69	600		4
40	0.0	100.0								2
50	100.0	0.0	13.8	2.09	540	4.81	5.80	260	2.86	2
50	83.0	17.0	13.8	2.09	560	4.09	4.95	275	3.30	2
50	67.7	32.4	13.5	2.04	570	3.87	4.66	280	2.95	2
50	51.9	48.1	11.4	1.73	605	3.91	4.72	270	2.90	2
50	38.5	61.5	11.3	1.72	630	3.66	4.43	340	2.88	2
50	22.6	77.3	10.5	1.59	645	3.29	3.98	290		2
50	0.0	100.0								2
60	100.0	0.0	20.4	3.51	285	7.76	9.92	125	2.64	3
60	83.9	16.1	20.5	3.54	260	6.61	8.47	140	2.92	2
60	61.7	38.3	19.3	3.30	250	6.05	7.72	150	3.02	2
60	48.0	52.0	18.2	3.11	340	6.06	7.74	140	2.82	2
60	22.9	77.1	17.7	2.98	355	5.51	7.01	140		2
60	0.0	100.0								2

^a Film, Dow polyethylene film. Film thickness: No. 1, 0.02365 cm; No. 2, 0.0238 cm; No. 3, 0.0227 cm; No. 4, 0.0243 cm. \bar{P} = ml(STP)/cm-sec-cmHg $\times 10^6$. \bar{D} = cm²/sec $\times 10^7$. L = sec. Mixture pressure: atmospheric pressure.

^b Film sample number.

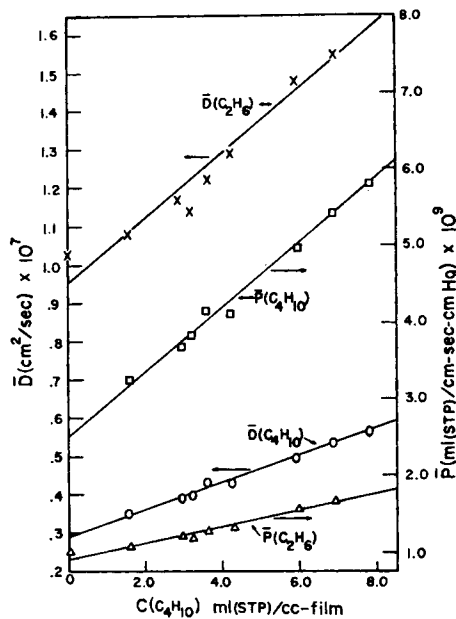


Fig. 2. \bar{D} and \bar{P} vs. butane concentration (30°C).

permeation data for ethane-butane mixtures at 30°C are listed in Table II; for 40, 50, and 60°C, in Table III. The separation factor G_{ij} , listed in Tables II and III, is defined as

$$G_{ij} = [q]_i [f]_j / [q]_j [f]_i \quad (6)$$

where $[f]_i$ and $[f]_j$ are the concentrations of components i and j in the feed stream, and $[q]_i$ and $[q]_j$ are the concentrations in the permeated stream. G_{ij} is the ratio of the observed permeation constants (P_i/P_j), where i and j represent butane and ethane, respectively.

The concentration dependence of the diffusion coefficient and the permeation constant are commonly correlated by the following relationships:

$$\bar{D} = D(0) (1 + bC) \quad (7)$$

$$\bar{P} = P(0) (1 + b'C) \quad (8)$$

$$\bar{D} = D(0) \exp \{ \alpha C \} \quad (9)$$

$$\bar{P} = P(0) \exp \{ \alpha' C \} \quad (10)$$

Figure 2 illustrates the linear model, and Figure 3 illustrates the exponential model, for the dependence of \bar{D} and \bar{P} on butane concentration in the film.

The dependence of \bar{P} on temperature was studied at concentration levels of 0-100%, 55.0-45%, and 100-0% ethane-butane for the same film sample. The results are shown in Figure 4 for an Arrhenius type of plot.

For a series of experiments at 30 and 40°C the boundary conditions were changed, to observe the effect of butane concentration on the time lag of diffusion for ethane. For each mixture investigated the film was brought to equilibrium permeation with butane at the same partial pressure as in

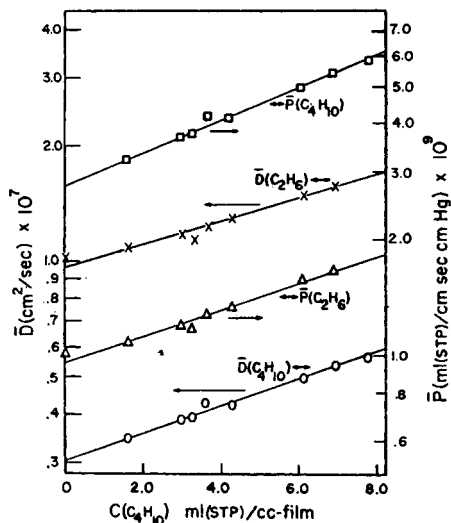


Fig. 3. $\log \bar{D}$ and $\log \bar{P}$ vs. butane concentration (30°C).

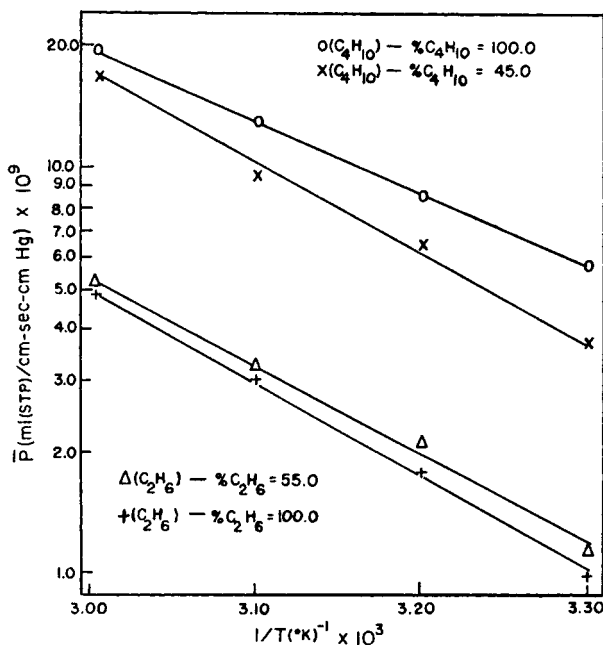


Fig. 4. Variation of \bar{P} with temperature.

TABLE IV
Permeation Results for Initial Butane Equilibrium in the Film^a

Temp., °C.	C ₄ H ₁₀ , %	C ₂ H ₆ , %	\bar{P} , C ₄ H ₁₀	\bar{D} , C ₄ H ₁₀	\bar{P} , C ₂ H ₆	\bar{D} , C ₂ H ₆	<i>L</i> , C ₂ H ₆
30	100.0	0.0	5.34	0.525			
30	78.7	21.3	5.09	0.511	1.43	1.34	660
30	63.2	36.8	4.22	0.431	1.26	1.19	700
30	45.3	54.7	3.78	0.398	1.14	1.07	770
30	22.5	77.5	3.21	0.348	1.04	1.03	900
30	0.0	100.0			0.951	0.978	1080
40	100.0	0.0	7.88	0.940			
40	75.8	24.2	7.31	0.876	2.02	2.21	380
40	62.8	37.2	6.52	0.780	1.91	2.09	400
40	45.6	54.4	6.14	0.734	1.83	2.00	440
40	22.9	77.1	5.47	0.654	1.81	1.98	500
40	0.0	100.0			1.54	1.69	600

^a Film, Dow polyethylene film (sample No. 4); thickness = 0.0243 cm. \bar{P} = ml(STP)/cm-sec-cm Hg × 10³. \bar{D} = cm²/sec × 10⁷. *L* = sec.

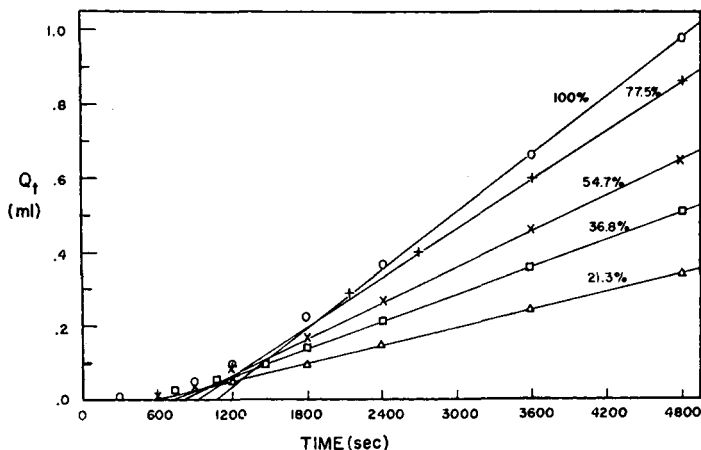


Fig. 5. Ethane permeation with the film initially in equilibrium with butane.

the mixture. As Figure 5 for 30°C shows, the time lag of diffusion decreases as butane concentration increases, which would be predicted from the time lag relationship $L = l^2/6D$. The data for these experiments are given in Table IV.

In order to determine whether the steady-state value obtained from the steady-state slope of the plot of Q_t versus time was the actual steady-state value and not a "pseudo" steady-state value, as observed by Casper and Henley⁵ and Stern et al.⁶ for two different polymer-penetrant systems, an extended run of 110 hr was made. The initial steady-state permeation constants for butane and ethane were found to be 4.15×10^{-9} and 1.27×10^{-9} ml(STP)/cm-sec-cm Hg, respectively, and the average steady-state values taken at various time intervals were $4.41 \pm 0.09 \times 10^{-9}$ and $1.34 \pm 0.013 \times 10^{-9}$ ml(STP)/cm-sec-cm Hg (90% confidence limits).

DISCUSSION OF RESULTS

The results obtained from the permeation data help substantiate the observations and conclusions drawn in the study⁴ of the desorption of butane-ethane mixtures from polyethylene. The permeation constants of both ethane and butane increase with increasing butane concentration in the feed stream, owing to the plasticizing effect of sorbed butane, whose equilibrium concentration in the film is an order of magnitude larger than that of ethane.

Correlation of the diffusion coefficients and permeation constants as a function of butane concentration only, for both ethane and butane, is valid for the range of partial pressures investigated. At higher ethane partial pressures the effect of sorbed ethane will have to be taken into account. Butane permeation data⁷ at different partial pressures in the presence of ethane mixtures at 760 mm Hg, compared with permeation data

for the same film for pure butane, indicated a small increase (5%) in the permeation constant of butane in the limit of 760 mm Hg of ethane, as shown in Figure 6.

Variation in permeation data was observed in a comparison of different film samples. This type of variation has been discussed in detail by Alter⁸ and others.^{9,10} As extruded film was used for this study; variation in diffusion properties with film position as observed by Alter⁸ may be a possible cause of data scatter. Since the course of this study covered 6 mo., any process which may be slowly time-dependent, such as crystallization, crystal reorientation, and oxidation, would alter permeation properties.

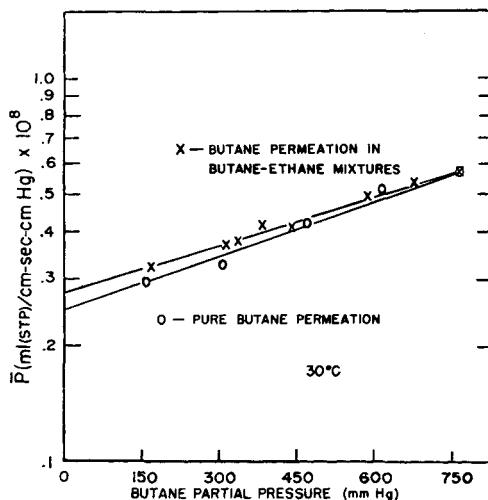


Fig. 6. Comparison of pure butane permeation with butane permeation in ethane-butane mixtures.

For determination of the effect of a specific variable, such as mixture concentration or temperature, the same film sample was used for the series of experiments involved, to eliminate the effect of film variation.

The separation factor for all compositions, temperatures, and film samples was in the approximate range of 2.8–3.2, expressed as the ratio of the butane permeation constant to the ethane permeation constant.

$$G_{ij} = P_i/P_j, \quad i = \text{butane}, j = \text{ethane} \quad (11)$$

$$P_i = P_{i0} \exp \{ -E_{P_i}/RT \} \quad \text{for } C_i = 0 \quad (12)$$

$$P_j = P_{j0} \exp \{ -E_{P_j}/RT \} \quad (13)$$

Since

$$P = P(0) \exp \{ \alpha' C_i \} \quad (14)$$

then for $C_i > 0$:

$$P_i(C_i) = P_{i0} \exp \{-E_{P_i}/RT\} \exp \{\alpha_i' C_i\} \quad (15)$$

$$P_j(C_i) = P_{j0} \exp \{-E_{P_j}/RT\} \exp \{\alpha_j' C_i\} \quad (16)$$

$$G_{ij} = (P_{i0} \exp \{-E_{P_i}/RT\} \exp \{\alpha_j' C_i\}) / (P_{j0} \exp \{-E_{P_j}/RT\} \exp \{\alpha_j' C_i\}) \quad (17)$$

No consistent trend in results was observed that would allow the temperature dependence of the experimental separation factor to be determined. From eq. (17), it would be expected that $E_{P_i} \approx E_{P_j}$. The calculated values of E_{P_i} and E_{P_j} in the limit of zero butane concentration were calculated to be 10.75 and 10.95 kcal/mole, respectively, substantiating the previously mentioned assumption. For the change in separation with increasing butane concentration the ratio of $(\exp \{\alpha_i' C_i\}) / (\exp \{\alpha_j' C_i\})$ will indicate the change of G_{ij} with concentration of butane. With values of $\alpha_i' > \alpha_j'$ the separation factor will increase with butane concentration. A least-squares fit of the relationship $G_{ij} = k_\theta \exp \{\alpha_\theta C_i\}$ for film no. 1 at 40°C and film no. 5 at 30°C yields positive values of α_θ , valid at the 80% confidence level, which illustrates the nearly insignificant change in G_{ij} with butane concentration.

Several investigators have shown that time-dependent permeation exists in certain polymer-penetrant systems.^{5,6,11} Variations in polymer film thickness have also been shown to influence permeation properties.^{12,13} It has been shown that the system reported here is not time-dependent, and also film thickness has been shown⁷ not to influence the permeation constants of ethane and butane. Anomalous permeation usually occurs in the region of the glass transition temperature. In this study measurements were made at temperatures well above the glass transition temperature, and thus one would not expect the system to exhibit time/or thickness-dependent permeation.

When the film is initially in equilibrium with the same butane partial pressure as in the mixture investigated, the time lag of diffusion for ethane decreased with increasing butane concentration, as expected from $L = l^2/6D$ and from the experimental observation that the ethane diffusion coefficient increases with increasing butane concentration. It must be noted here that this experiment represents diffusion of ethane into a medium in which the ethane diffusion coefficient is a function of position: $D_j = D_j(o)(\beta_o + \beta_1 x)^{\delta}$. It has been shown that eq. (9) correlates \bar{D} for both ethane and butane concentration. For small values of αC , as in this investigation, it can be shown that $D = D(o) \exp \{\gamma C\}$ can also be used to correlate the experimental data, as has been successfully done with other hydrocarbon-polymer systems.¹⁴

Substitution of $D_i = D_i(o) \exp \{\gamma_i C_i\}$ into the following relationship,¹⁵ which relates steady-state butane concentration with film position x will lead to the following results:

$$[C_{i0} + \mathfrak{F}(C_{i0}) - C_i - \mathfrak{F}(C_i)] / [C_{i0} + \mathfrak{F}(C_{i0})] = x/l \quad (18)$$

where $D = D_i(o)[1 + F(C_i)]$ and $\mathfrak{F}(C_i) = \int_0^{C_i} F(C_i) dC_i$.

$$F(C_i) = -1 + \exp \{ \gamma_i C_i \} \quad (19)$$

$$\mathfrak{F}(C_i) = (\exp \{ \gamma_i C_i \} / \gamma_i) - C_i - 1/\gamma_i \quad (20)$$

Substitution of eq. (20) into (18) yields

$$\exp \{ \gamma_i C_i \} = \beta_o + \beta_i x$$

where $\beta_o = \exp \{ \gamma_i C_{i0} \}$ and $\beta_i = -(\exp \{ \gamma_i C_{i0} \} - 1)/l$.

Solving for C_i and resubstituting into $D_j = D_j(o) \exp \{ \gamma_j C_i \}$ yields $D_j = D_j(o)(\beta_o + \beta_i x)^\delta$, where $\delta = \gamma_j/\gamma_i$. For $\gamma_j \approx \gamma_i$ the quantity D_j is a linear function of film position.

The permeation and desorption results for temperatures and partial pressures investigated in this study show that the permeation constants, the diffusion coefficients, and the solubility constants for both ethane and butane can be correlated as a function of butane alone, because the butane solubility is much greater than the ethane solubility. At lower temperatures or higher pressures the correlation of \bar{P} , \bar{D} , and \bar{S} will have to be related to both butane and ethane film concentrations.

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