

Permeation of Organic Vapors Through Polymer in the Condensation Region

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Synopsis

Permeability coefficients have been measured for normal butane, isobutane, isobutylene, and butene-1 in Zendel Copolymer-I at temperatures between 30° and 70°C and at penetrant pressures p_1 up to 5.5 atm. The permeability coefficients of these organic vapors show behavior analogous to that observed for C_3 and C_2 hydrocarbons as detailed in our earlier work; i.e., near the condensation point of the penetrant, P increases as the temperature is decreased. Isothermal plots of $\log P$ versus p_1 in that region are generally linear and can be represented by empirical relations of the form

$$P = P_0 \exp (ap_1)$$

where P_0 is a constant. The slope a is a function of temperature:

$$a = a_0 \exp (bt)$$

where a_0 is a constant and b has the same value for the four hydrocarbons investigated.

INTRODUCTION

The anomalous permeation behavior of ethane, ethylene, propane, propylene, isobutylene, isobutane, butene-1, and butane through low-density polyethylene in the vicinity of condensation point of the penetrant has been studied by us and our associates.¹⁻¹⁵ Mixtures of these hydrocarbons show the same anomalous permeation near the dew point of the mixture.^{6,10-13} Other investigations were concerned with the solubility and diffusion of these hydrocarbons through polyethylene.¹⁶⁻¹⁹ Polymer-solvent interaction¹⁶⁻¹⁹ as well as solvent clustering¹⁸⁻²⁰ were also studied.

The present work was developed to verify the behavior of some hydrocarbons with four carbons atoms (isobutane, isobutylene, butene-1, and normal butane) through films of Zendel Copolymer-I (trademark) from Union Carbide.

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EXPERIMENTAL

Apparatus and Procedure

The permeability apparatus and the experimental procedure used in the present work have been described in detail elsewhere.⁷⁻⁹ The downstream pressure p_2 was kept constant during all permeability measurements at a value slightly higher than the prevailing atmospheric pressure. The upstream pressure p_1 could be varied as desired in the range from about 3.9 atm to 5.5 atm. During any single permeability measurement, p_1 was maintained constant.

The permeation cell was maintained at a constant temperature with an accuracy of $\pm 0.5^\circ\text{C}$, inside a controlled-temperature chamber. The permeability measurements were developed in a temperature range from 30° to 70°C . The permeability coefficient P was calculated from the relation:

$$P = qL/At\Delta p \quad (1)$$

where q is the steady-state volume of vapor passing through a membrane sample of area A and thickness L in time t ; $\Delta p = p_1 - p_2$ is the pressure difference across the membrane; and p_1 and p_2 are the gas pressures on the downstream and upstream sides of the membrane, respectively. The units of the permeability coefficient used in this study are $\text{cm}^3(\text{S.T.P.}) \cdot \text{cm}/(\text{sec} \cdot \text{cm}^2 \cdot \text{cm Hg})$. Each value of P presented in this work was obtained by averaging at least 12 determinations as detailed elsewhere.^{7,8} The values reported for P are believed to be accurate to within $\pm 5\%$.

Materials

Vapors. Isobutane, isobutylene, 1-butene, and normal butane were obtained from the Phillips Petroleum Company and had minimum purities of 99.9 mole-%.

Membrane. The polymer membrane used (Zedel Copolymer-I) was furnished by Union Carbide, Chemical and Plastics Division. The polymer had a specific gravity of 0.916 as measured by the ASTM-D 792-50 method. The effective permeation area of the film sample was 20.25 cm^2 , and its thickness, 0.0046 cm .

RESULTS AND DISCUSSION

Temperature Dependence of Permeability

The effect of temperature on the permeability coefficient can be visualized through plots of $\log P$ versus $10^3/T$, as shown in Figures 1, 2, 3, and 4 for isobutane, isobutylene, 1-butene, and normal butane, respectively. Each isobaric curve shows similar behavior when the temperature is decreased near the condensation point of the penetrant; i.e., the permeability coefficient increases as the temperature approaches the point at which the diffusing agent liquifies.

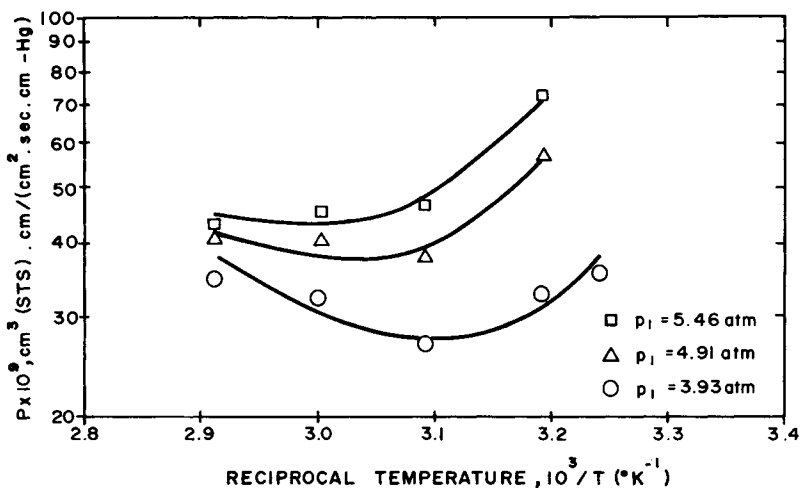


Fig. 1. Permeability coefficient for isobutane a function of temperature.

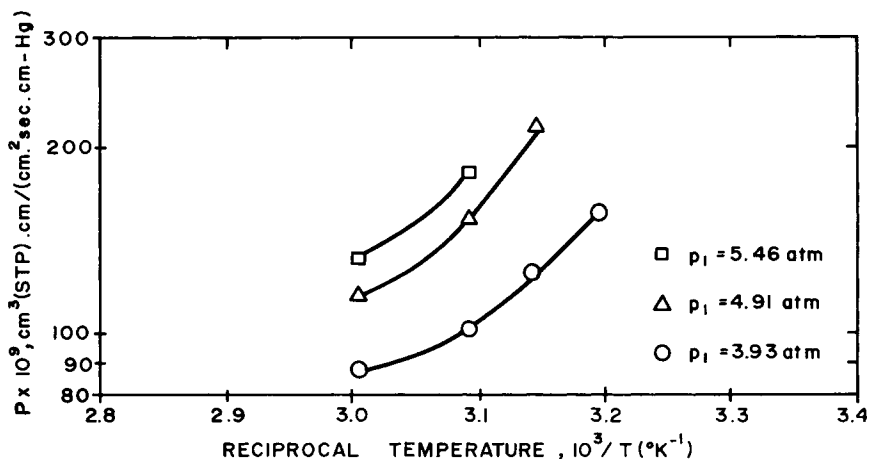


Fig. 2. Permeability coefficient for isobutylene as a function of temperature.

Such behavior has already been observed¹⁻¹⁵ for other hydrocarbons close to the condensation point. These previous results were obtained mainly with polyethylene at low temperature (from $+30^{\circ}$ to -40°C) for hydrocarbons with two and three carbon atoms and also at high temperatures (from $+30^{\circ}$ to 70°C) for hydrocarbons with four carbon atoms. It was deduced that such behavior depends on the proximity of the penetrant condensation point, and not on the proximity of the glass transition temperature.

Within the temperature range investigated, the plots of P for isobutane and butene-1 (Figs. 1 and 3) show a minimum. For the other hydrocarbons (isobutylene and normal butane), such a minimum would probably have been found at a temperature above 70°C had these plastic films been resistant to high temperature.

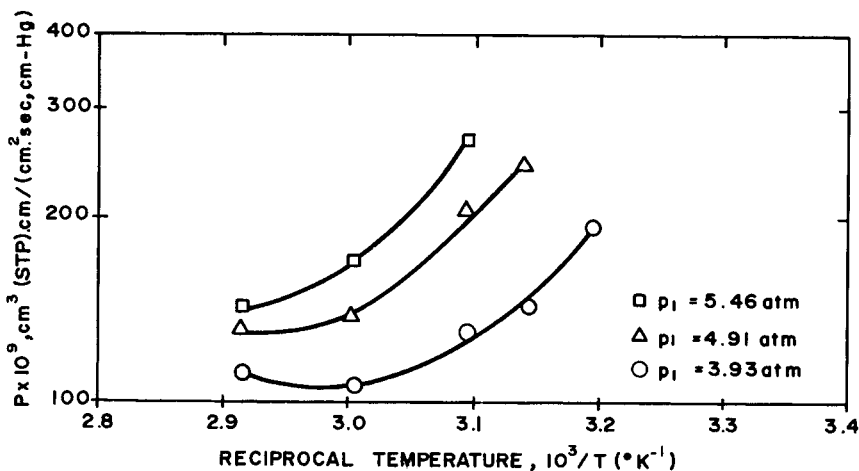


Fig. 3. Permeability coefficient for butene-1 as a function of temperature.

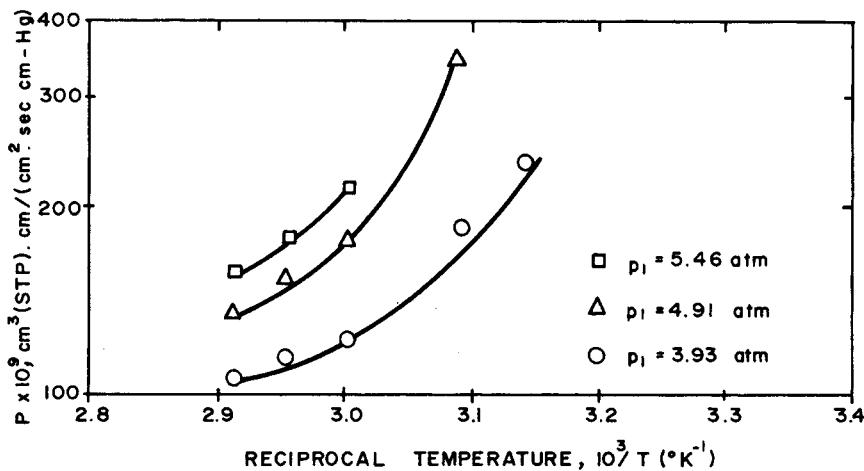


Fig. 4. Permeability coefficient for *n*-butane as a function of temperature.

Another interesting feature is exhibited by both isobutane and 1-butene; i.e., the temperature of the minimum P increases as the upstream pressure is increased. The same behavior was observed for other hydrocarbons in polyethylene.⁶⁻¹¹

Average energies of activation for the permeation of hydrocarbons vapors, obtained from the slopes of the isobars (Figs. 1 to 4), are strong functions of temperature in the region of the condensation point of the penetrant.

Pressure Dependence of Permeability

Tables I to IV present the experimental results for Zendel Copolymer-I with isobutane, isobutylene, butene-1, and normal butane, respectively. Figure 5 is a plot of $\log P$ versus p_1 for the system isobutane—Zendel

Copolymer-I. This is a typical graph, and the behavior of the other hydrocarbons investigated are analogous. The isotherms are all straight lines. This result confirms the tendency previously observed by us and other investigators^{6-13,21} when working with other gases. For some of these

TABLE I
Permeability Coefficients and Isothermal Slopes for Isobutane

Temp., °C	$P \times 10^9, \text{cm}^3(\text{S.T.P.}) \cdot \text{cm}/\text{cm}^2 \cdot \text{sec} \cdot \text{cm Hg}$			<i>a</i>
	3.93 atm	4.91 atm	5.46 atm	
35	35	—	—	—
40	33	57	72	0.553
50	26	38	46	0.350
60	32	40	45	0.229
70	35	50	43	0.132

TABLE II
Permeability Coefficients and Isothermal Slopes for Isobutylene

Temp., °C	$P \times 10^9, \text{cm}^3(\text{S.T.P.}) \cdot \text{cm}/\text{cm}^2 \cdot \text{sec} \cdot \text{cm Hg}$			<i>a</i>
	3.93 atm	4.91 atm	5.46 atm	
40	15	—	—	—
45	126	213	—	0.510
50	101	154	185	0.392
60	88	114	131	0.260

TABLE III
Permeability Coefficients and Isothermal Slopes for Butene-1

Temp., °C	$P \times 10^9, \text{cm}^3(\text{S.T.P.}) \cdot \text{cm}/\text{cm}^2 \cdot \text{sec} \cdot \text{cm Hg}$			<i>a</i>
	3.93 atm	4.91 atm	5.46 atm	
40	194	—	—	—
45	144	246	—	0.560
50	132	208	267	0.442
60	105	138	170	0.286
70	110	131	143	0.163

TABLE IV
Permeability Coefficients and Isothermal Slopes for Butane

Temp., °C	$P \times 10^9, \text{cm}^3(\text{S.T.P.}) \cdot \text{cm}/\text{cm}^2 \cdot \text{sec} \cdot \text{cm Hg}$			<i>a</i>
	3.93 atm	4.91 atm	5.46 atm	
45	236	—	—	—
50	189	338	—	0.603
60	119	174	216	0.381
65	115	152	178	0.284
70	107	135	153	0.240

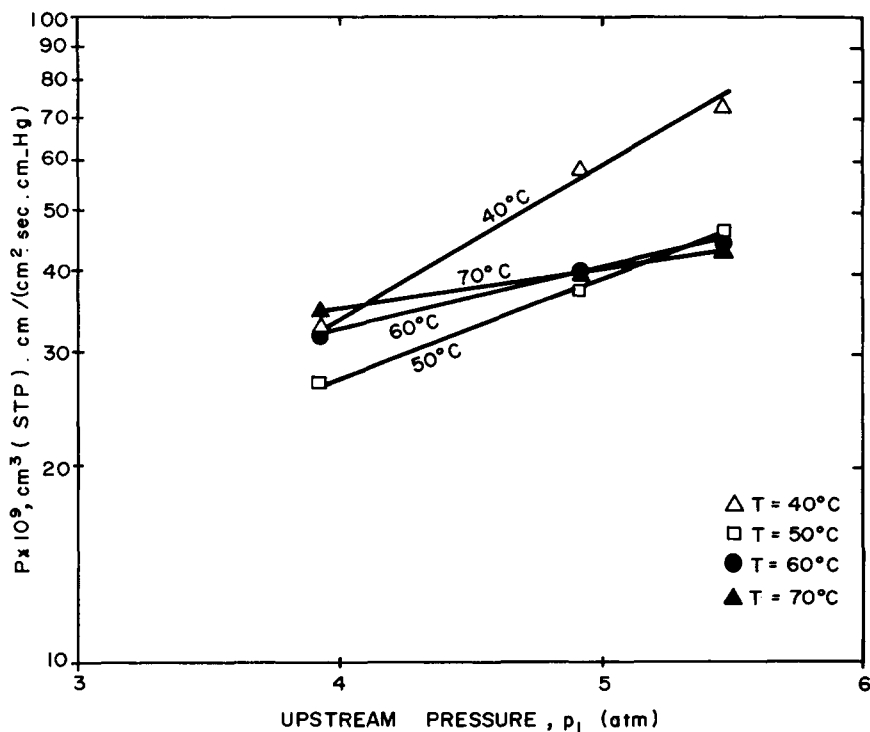


Fig. 5. Permeability coefficient for isobutane as a function of upstream pressure p .

vapors, at the lowest temperature of the investigation (such as 40°C for isobutylene and butene-1 and 45°C for *n*-butane), the data were insufficient to establish a straight line.

The isothermal plots of $\log P$ versus p_1 can be represented by empirical relations of the form

$$P = P_0 \exp (ap_1) \quad (2)$$

where P and a are parameters that depend on temperature. Values of a were obtained by a linear least-squares analysis and are tabulated also in Tables I to IV. It is important to note that the slope a of the linear isotherms, as shown in Figure 5, decreases with increasing temperature. As has been shown in other work,^{18,19} this result may be due in part to the fact that the solubility of isobutane, isobutylene, butene-1, and *n*-butane in polyethylene decreases with increasing temperature.

Figure 6 shows the dependence of the isothermal slope a upon the temperature in the case of the four hydrocarbons. These plots of $\log a$ versus temperature fall on parallel straight lines, which can be represented by an expression of the form

$$a = a_0 \exp (bT) \quad (3)$$

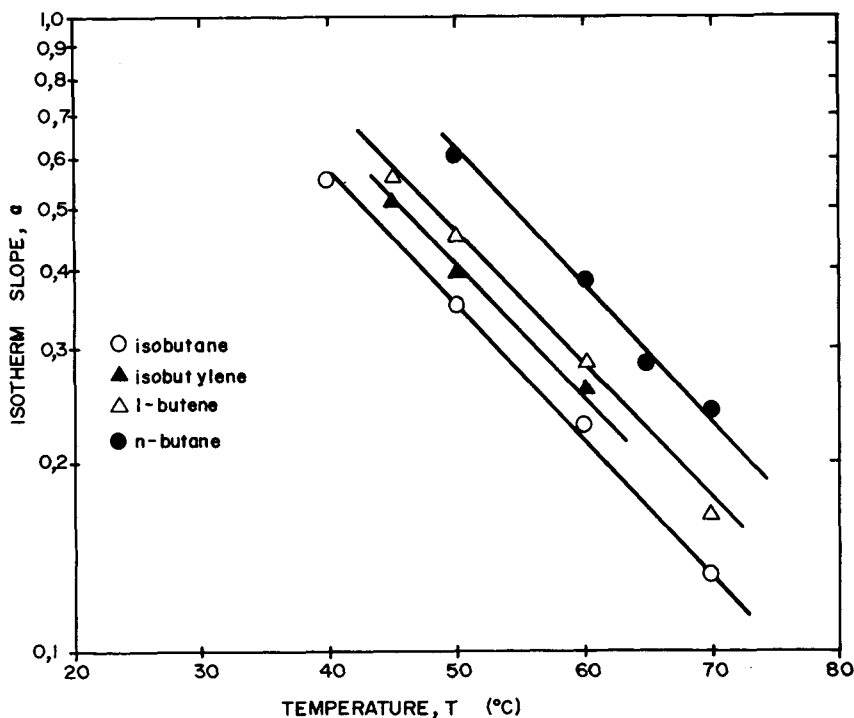


Fig. 6. Isothermal slopes of $\log P$ vs. p_1 as a function of temperature.

where a_0 is a parameter that depends only on the nature of the vapor, and $b \approx -0.05$ is a constant for all the hydrocarbons investigated. Thus, Eq. (2) can also be written in the form

$$P = P_0 \exp \{ a_0 p_1 \exp (bT) \}. \quad (4)$$

This equation can be applied successfully for correlating the permeability coefficient with the parameters investigated in this work.

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