

Permeability of Polyethylene Film to Organic Vapors

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Synopsis

The permeabilities of polyethylene film to vapors of 19 organic compounds at temperatures of 21°C, 38°C, and 49°C were measured by a sorption method. The film was formed into a pouch, which was filled with silica gel, sealed, and suspended in a saturated atmosphere. The permeability was calculated from the steady-state rate of the gain in weight. The permeability data were correlated with the Hildebrand solubility parameters of the organic substances.

INTRODUCTION

The use of polymer films for packaging chemicals and drugs has created an interest in the vapor and gas permeability characteristics of these films. Previous studies have concentrated on water vapor and gas permeation, with somewhat limited attention to the permeation of organic vapors.

Simril and Hershberger¹ observed that vapors generally behave quite differently from gases and that permeation rates of vapors through polymer films are about 10,000 times greater than gas permeation rates. The situation of sorption of organic vapors in plastic films becomes quite complex, and deviation from ideality becomes more critical as the penetrant-polymer interaction increases. The sorbed vapor swells and plasticizes the polymer, resulting in increased mobilities of both polymer segments and penetrant molecules.

This permeability study is concerned with saturated organic vapors in polyethylene.

Previous work directly related to obtaining permeability constants of polyethylene-organic vapor systems over a range of temperature is somewhat limited. Martinovich and Boeke,² Waack and co-workers,³ and Rogers, Stannett, and Szwarc⁴ obtained permeability constants at one or two temperatures utilizing the standardized permeation cell at various levels of sophistication. Bent and Pinsky⁵ observed the weight loss with time of 4-oz polyethylene bottles filled with various organic liquids and then calculated the permeability. Coughlin and Pollak⁶ used radioactive tracers in various organic liquids to measure transport across previously swollen polyethylene which divided equal volumes in a stirred bath. Michaels and co-workers⁷ used a permeation cell to investigate permeation characteristics of organic liquids to films that were cold drawn and annealed.

In this study, the permeabilities of 19 organic vapors through polyethylene are reported at temperatures of 70°, 100°, and 120°F. By correlating the Hildebrand solubility parameter with the activation energy of permeation, a method of predicting the permeability is developed.

THEORY

For the mass transport through a membrane at steady state, Fick's law can be written

$$J = D \frac{dc}{dx} \quad (1)$$

where J = diffusion flux; D = diffusion coefficient; c = concentration; and x = distance. If Henry's law is obeyed, there is a linear relationship between concentration and pressure, and the solubility coefficient is constant. Therefore, the steady-state flux can be expressed as

$$J = DS \frac{(p_1 - p_2)}{L} \quad (2)$$

or

$$P = DS = \frac{JL}{(p_1 - p_2)} \quad (3)$$

where S = solubility coefficient (c/p); L = thickness; p = partial pressure or vapor activity; and P = permeability coefficient.

Organic vapors adsorbed on polyethylene may deviate significantly from Henry's law. Rogers, Stannett, and Szwarc³ obtained isotherms for which S was an exponential function of c :

$$S = S(0) \exp(\sigma_c) \quad (4)$$

where $S(0)$ is the intercept at $c = 0$, $S(0)$ being a measure of the initial sorption of the unassociated penetrant in a polymer; and σ_c is a constant characterizing the concentration dependence of the solubility coefficient.

When the diffusion process is concentration dependent, an average diffusion coefficient can be defined:

$$\bar{D} = \left[\frac{1}{c_1 - c_2} \right] \int_{c_2}^{c_1} D dc \quad (5)$$

Estimates of the integral diffusion coefficient for organic vapors in polyethylene were made by Rogers, Stannett, and Szwarc³ by three different methods, who found that their data could be represented by

$$D = D(0) \exp\left(\frac{\gamma_c}{1 + \sigma_c}\right) \quad (6)$$

with

$$\gamma = \frac{\alpha}{p^0 S(0)} \quad (7)$$

where $D(0)$ is the diffusion coefficient at zero activity, pressure, and concentration, while α is a constant for the penetrant-polymer system at a given temperature. When the vapor obeys Henry's law, $\sigma = 0$ and S then becomes a constant.

The permeability constant follows from eqs. (4) and (6):

$$P = P(0) \exp\left(\frac{\gamma_c}{1 + \sigma_c} + \sigma_c\right) \quad (8)$$

with

$$P(0) = D(0) S(0) \quad (9)$$

Thus, rewriting eqs. (2) and (3) for the situation where the permeability coefficient is concentration dependent, we obtain

$$J = \left[\frac{1}{c_1 - c_2} \int_{c_2}^{c_1} D dc \right] \left[\frac{c_1 - c_2}{p_1 - p_2} \right] \left[\frac{p_1 - p_2}{1} \right] \quad (10)$$

or

$$J = \overline{DS} \left[\frac{p_1 - p_2}{1} \right] \quad (11)$$

and

$$\bar{P} = \overline{DS} \quad (12)$$

The plot of weight gain versus time passes from an unsteady-state portion to a steady-state portion, which is a straight line. The slope of the straight line, w/t , is used to calculate the permeability coefficient, using this equation:

$$P = \frac{w}{t} \times \frac{22400}{MW} \times \frac{L}{A} \times \frac{1}{p^0} \times \frac{1}{60} \quad (13)$$

where P = permeability constant in (std cc)(cm)/(sec)(cm²)(cm Hg); MW = molecular weight; w/t = rate of weight gain g/min; L = thickness in cm; A = surface area in cm²; and p^0 = vapor pressure of liquid in cm Hg.

EXPERIMENTAL

In the dynamic sorption method, an adsorbent-filled polymer pouch is suspended in a chamber containing the permeant vapor, and the weight gain versus time is measured. From the surface area of the pouch and the vapor pressure of the vapor at that particular temperature, the permeability is calculated.

Apparatus

In all experiments, the film was du Pont polyethylene film, 1 mil thick. The polymer had a density of 0.915 and a 58% crystallinity. A pouch approximately 4.5×1.2 cm was constructed by taking a piece of film, folding

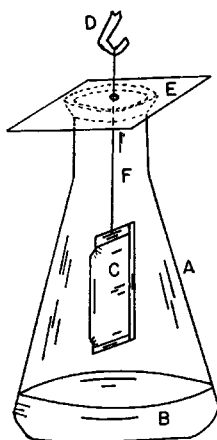


Fig. 1. Essential features of Dynamic Sorption Method: A, flask; B, organic liquid; C, pouch containing silica gel; D, balance arm; E, cover; F, suspension wire.

it over, and heat sealing the bottom and the side. After filling the pouch with adsorbent, the top was then heat sealed. The adsorbent used was silica gel activated at 200°C. The main reasons for using silica gel were its high affinity for organic vapors and the low organic vapor pressure when saturated. Other advantages are that it remained unchanged in physical condition and exerted no chemical or physical action.

TABLE I
Characteristics of Liquids Used

Compound	Molecular weight	Boiling point, °C	Density at 25°C, g/cc
Acetic acid	60	118.1	1.049
Acetone	58	56.7	0.791
Aniline	93	184.3	1.020
Benzene	78	80.1	0.878
<i>n</i> -Butyl alcohol	74	117.8	0.809
<i>s</i> -Butyl alcohol	74	99.7	0.808
<i>t</i> -Butyl alcohol	74	83	0.785
Camphor	152	mp 178.8	0.990
Carbon tetrachloride	154	76.7	1.594
Chlorobenzene	112.5	131.9	1.106
Cyclohexane	84	80.9	0.799
Ethyl acetate	88	77.3	0.900
Formic acid	46	100.7	1.220
<i>n</i> -Heptane	100	98.6	0.683
<i>n</i> -Hexane	86	68.9	0.659
Menthol	156	mp 42.5	0.904
Methyl acetate	74	57.3	0.972
Methyl alcohol	32	64.8	0.791
Nitrobenzene	123	210.8	1.200
Toluene	92	110.8	0.866
<i>o</i> -Xylene	106	144.6	0.896

The test chamber in which the pouch was suspended was a 125-ml flask which contained 30–40 ml of organic liquid or an equivalent amount of solid. An aluminum plate covered the flask to maintain a saturated vapor condition inside the chamber. A small hole in the center of the plate allowed passage of a wire to connect the pouch and the balance arm. Figure 1 illustrates the flask assembly.

The flask assembly was in a Mettler balance case, and a wire hooked to the pouch was connected to the balance arm. A platform was placed over the balance pan to support the flask so that only the weight of the pouch was measured.

A constant-temperature chamber was used to obtain the data at various temperatures. The Mettler balance was placed inside a glove box approximately $2 \times 3 \times 2$ feet, with two large windows in front to view the experiment, a door at the side, and two arm holes in front. A fan was used to circulate air at the desired temperature in the glove box. For elevated temperatures, a heating element was added.

The properties of the liquids used in the experiments are listed in Table I.

Procedure

A test pouch was constructed as described above. The pouch, flask, and organic liquid were now held separately inside the constant-temperature chamber for approximately 1 hr in order to bring all components to the desired temperature, to avoid condensation on the outside of the pouch.

The liquid was poured into the flask, the wire was hooked to one end of the pouch, and the flask assembly with the pouch hanging freely in flask and a metal plate covering the flask was placed in the Mettler balance case. The wire hooked to the pouch was also hooked to the balance arm, and weight-versus-time data were taken on each organic liquid at 21°C, 38°C and 49°C.

RESULTS AND DISCUSSION

A test run at a particular temperature consisted of measuring weight gain versus time and going through both the unsteady-state and steady-state portions until the amount adsorbed by the silica gel reached a limit. The slope of the linear portion, or steady-state part, was used in calculating the permeability, as previously described.

Figure 2 is a typical plot of the weight gain versus time for an adsorbent-filled pouch and for the pouch with no adsorbent. The tare plot first goes through an unsteady-state portion; then after a time the plastic becomes saturated, and the weight remains constant.

When the tare curve is subtracted from the curve of the silica gel-filled pouch, a straight line is obtained in the steady-state portion. This line has the same slope as the original curve, since the tare curve is horizontal. It is the slope of this steady-state portion which is used to calculate the permeability.

TABLE II
Comparison of Measured Permeabilities^a with Literature Values²

Compound	21°C		38°C		49°C	
	Experiment	Literature	Experiment	Literature	Experiment	Literature
Chlorobenzene	517 ± 27	446	430 ± 9	568	590 ± 21	659
Nitrobenzene	460 ± 15	155	780 ± 9	216	1100 ± 27	263
Toluene	326 ± 7	201	388 ± 8	382	501 ± 12	560
<i>o</i> -Xylene	284 ± 16	333	418 ± 13	575	440 ± 14	806
Aniline	250 ± 11	22	360 ± 22	46	450 ± 19	76
Benzene	211 ± 36	70	241 ± 40	114	259 ± 29	154
<i>n</i> -Heptane	188 ± 14	72	209 ± 10	106	220 ± 15	135
<i>n</i> -Hexane	139 ± 3	31	163 ± 13	81	175 ± 11	143
CCl ₄	132 ± 14	47	150 ± 21	85	206 ± 27	118
Cyclohexane	90 ± 5	40	149 ± 13	74	182 ± 10	108
Ethyl acetate	34 ± 7	2.5	44 ± 11	5.7	84 ± 10	9.6
Acetic acid	32 ± 6	3.4	35 ± 9	7.3	93 ± 11	11.8
<i>n</i> -Butyl alcohol	15 ± 4	0.88	20 ± 4	2.79	45 ± 6	4.8
Methyl acetate	13 ± 4	1.06	35 ± 7	2.58	63 ± 9	4.4
<i>s</i> -Butyl alcohol	13 ± 10	0.55	17 ± 4	1.76	45 ± 9	3.6
Camphor	11	4.84	130	85	440	320
Formic acid	9.4 ± 3	0.41	15 ± 5	0.82	18 ± 7	1.3
Acetone	5.9 ± 2	0.67	17 ± 2	2.20	34 ± 5	4.5
<i>t</i> -Butyl alcohol	3.5 ± 1	0.10	6.3 ± 2	0.43	8.3 ± 2	1.0
Methyl alcohol	2.5 ± 1	0.38	8.1 ± 3	0.85	11 ± 3	1.4

$$^a P = \frac{(\text{std cc})(\text{cm})}{(\text{sec})(\text{cm}^2)(\text{cm Hg})} \times 10^8.$$

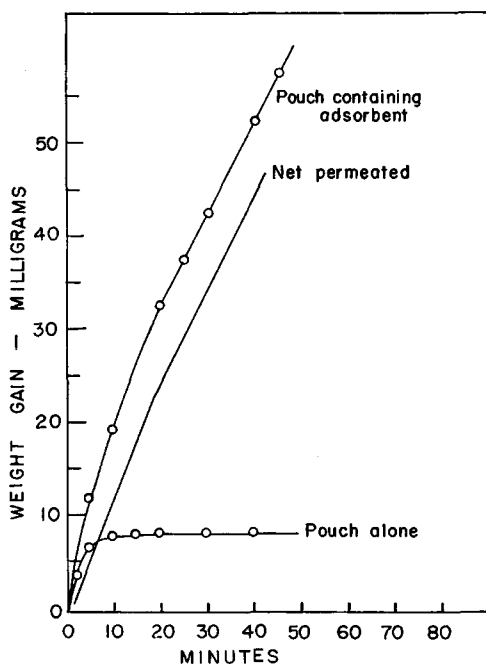


Fig. 2. Weight gain vs. time for toluene permeation through polyethylene film at 70°F.

Three measurements were made at each of the three temperatures, and the average and standard deviations were calculated. Table II gives the comparison of the experimental values obtained by the dynamic sorption method with those obtained by Bent and Pinsky,⁵ and Table III with those of other authors.

The permeability values obtained follow the order predicted in polyethylene based on structural similarity for the various chemical families. On a log P -versus- $1/T$ plot of the experimental values, a straight line is obtained, as would be expected. A strict comparison of the experimentally

TABLE III
Permeability Coefficients. Comparison of Data with Literature

	Temp.	This work ($\rho = 0.915$)	Martino- vich and Boeke ² ($\rho = 0.96$)	Bent & Pinsky ⁵ (58% Crystal- linity)	Rogers, Stannett, Szwarc ⁴
Acetic acid	27°C	37	0.8	4.4	
Aniline	27°C	280	15.1	29	
Ethyl acetate	27°C	35	1.63	3.3	
Heptane	27°C	194	13.1	81	
Benzene	0°C	180		33	90.9 ($P_1/P_1^\circ = 0.822$)
<i>n</i> -Hexane	0°C	112		7.2	116 ($P_1/P_1^\circ = 0.880$)
<i>n</i> -Hexane	30°C	150		60	155 ($P_1/P_1^\circ = 0.650$)

obtained values with the data of Bent and Pinsky is perhaps not justified since a number of conditions are different; nevertheless, these are the only data available for comparison. The film was of the same crystallinity as that used by Bent and Pinsky; their films were 30 to 40 mils thick, whereas ours were 1 mil. In general, our values are higher. It is notable that for the alcohols the values are about 15 times larger than the literature values, whereas for hydrocarbons the experimental values are only 2 to 3 times larger. Since the polyethylene bottles used by Bent and Pinsky were stored for periods as long as a year, it was possible that water vapor permeated through the bottle to dissolve in the liquid, reducing the net loss and thereby the permeability. This is plausible, since alcohols are considerably more hydrophilic than are hydrocarbons. The transport of water vapor into the bottles would not necessarily interfere with the rate of organic vapor permeation outward, but would give an error in calculating the weight loss. This source of error is minimized in the dynamic sorption method.

Correlation of Permeability

Salame⁹ developed a method for predicting permeability of plastic membranes to organic vapors, based on a correlation of permeability with number of carbon atoms. The activation energy of permeation, E_p , was assumed to be independent of temperature and permeating vapor, which is actually not the case. In the following derivation, Salame's method is modified to include the variation in E_p .

The mechanism of permeation of a vapor through a polymer involves a number of steps.¹⁰ First, a diffusing molecule condenses on the high-pressure side of the polymer. Then, this is followed by solution of the condensed vapor by the polymer. Next, the solution process is followed by diffusion through the polymer, which takes place by the movement of a penetrant molecule through a tangled mass of polymer chains and holes which are constantly disappearing and reforming as the result of thermal vibrations. Usually the holes are smaller than the penetrant molecule; hence, several jumps in the same direction must be made before the molecule is displaced by a distance equal to its length. Following the diffusion process, there is desorption of the permeate on the low-pressure side of the film by evaporation.

For most systems, the diffusivity and permeability are generally higher when the polymer and penetrant are similar. In polyethylene, which is nonpolar, the permeability is lowest for polar materials and highest for nonpolar materials such as hydrocarbons.¹¹

The diffusion coefficient at zero concentration $D(0)$, generally decreases as the volume of the penetrant molecule increases, but branching has a greater effect than does molecular size. Addition of a methyl group on a given paraffin reduces the value of $D(0)$ more than does increasing the chain length by one carbon atom. This suggests that diffusion occurs preferentially along the direction of greatest length of the penetrant molecule.

The solubility coefficient, $S(0)$, on the other hand, increases exponentially with the increase in molecular volume and cross-sectional area of the penetrant molecule. As a result of this compensating dependence of $D(0)$ and $S(0)$ on penetrant size and shape, the zero concentration permeability coefficient, $P(0)$, which equals the product of $D(0)$ and $S(0)$, is much less dependent on the size and shape of the penetrant than either term separately.

Temperature Dependence

In general, the temperature dependence of the permeability coefficient, diffusion coefficient, and solubility coefficient can be represented by exponential relationships:¹⁰

$$D = D_0 \exp(-E_d/RT) \quad (14)$$

$$S = S_0 \exp(-\Delta H_s/RT) \quad (15)$$

$$P = P_0 \exp(-E_p/RT) \quad (16)$$

where E_p is the overall energy of permeation, E_d is the energy of diffusion, and ΔH_s is the heat of solution. The terms D_0 , S_0 , and P_0 are the pre-exponential factors at "infinite" temperature for diffusion, solubility, and permeation, respectively.

From the definition of P as the product of D and S , it follows that

$$E_p = E_d + \Delta H_s. \quad (17)$$

As would be predicted from eq. (16), the graph of $\log P$ versus $1/T$ is a straight line with slope $-E_p/2.303R$ and intercept at $1/T = 0$ of $\log P_0$. The activation energy of diffusion, E_d , is associated with the energy required for hole formation against the cohesive forces of the polymer plus the energy necessary to force the molecule through the surrounding structure. For organic liquids in polymers, this value is generally between 10 and 40 kcal/mole.

The heat of solution ΔH_s is the sum of two terms:

$$\Delta H_s = \Delta H_{\text{cond}} + \Delta H_1 \quad (18)$$

where ΔH_{cond} = heat of condensation and ΔH_1 = partial molar heat of mixing. The value of the heat of mixing can be estimated from the cohesive energy densities of the penetrant and the polymer by means of the Hildebrand solubility parameter¹⁴

$$\Delta \bar{H}_1 = \frac{(\delta_L - \delta_0)^2}{\rho \cdot \text{MW}} \quad (19)$$

where δ_L = Hildebrand solubility parameter of penetrant; δ_0 = Hildebrand solubility parameter of polymer; ρ = density of liquid; and MW = molecular weight of liquid; δ is the square root of the internal pressure or cohesive energy density of the pure substances; a working definition is

$$\delta_L = (-E/V')^{1/2} \quad (20)$$

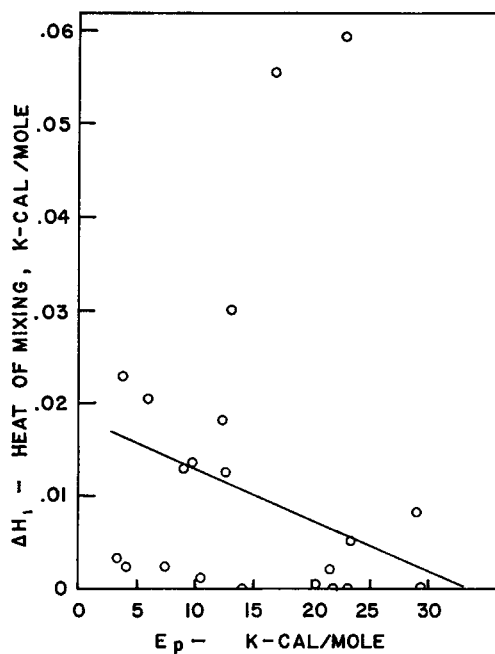


Fig. 3. Correlation of activation energy of permeation with Hildebrand solubility parameter, for organic vapor permeation through polyethylene.

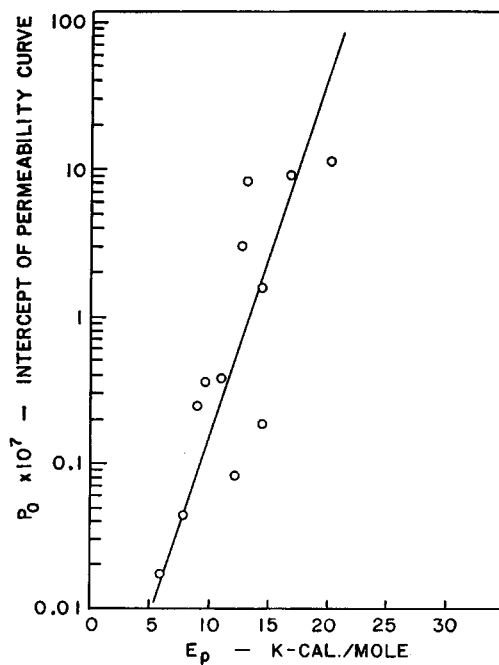


Fig. 4. Correlation of permeability coefficient at $1/T = 0$ with activation energy of permeation, for organic vapor permeation through polyethylene.

where $-E$ = energy of vaporization to the gas at zero pressure (infinite separation of the molecules); and V' = molal volume of liquid. Both $-E$ and V' change with temperature; therefore, δ must be calculated for each temperature.

The solubility parameter δ can be calculated by a number of different approaches: heats of vaporization, internal pressure, equations of state and critical constants, surface tension, optical data, and solubility data. For example, from the heat of vaporization, it is

$$\delta_L = \left[\frac{\Delta H^v - RT}{V'} \right]^{1/2} \quad (21)$$

where ΔH^v = heat of vaporization.

Since the Hildebrand solubility parameter is a measure of the internal pressure of the molecule, it should be related to the energy of permeation. In Figure 3, $(\delta_L - \delta_0)^2/(\rho \cdot MW)$ is plotted against E_p , which was calculated from the slope of the plot of $\log P$ versus $1/T$. The correlation coefficient from a least-squares analysis is 0.64, and some of the points deviate quite a bit from the correlation curve. However, a general trend is evident.

TABLE IV
Correlations to Predict Permeability Derived and Experimental Values

<i>Experimental Correlation</i>	
$E_p = 33.20 - 1810 \frac{(\delta_L - \delta_0)^2}{\rho \cdot MW}$	
$\log P_0 = 2.7379 + 0.2460E_p$	
$P = \lambda P_0 \exp(-E_p/RT)$	
<i>Correlation Factor λ</i>	
Hydrocarbons	... 20
Halogenated hydrocarbons	... 25
Esters	... 1
Alcohols	... 2.5
Acids	... 15
Amines	... 1
Nitrates	... 20
Ketones	... 1

Figure 4 shows the correlation of $\log P_0$ with E_p . The values of P_0 were obtained from the intercepts of the plot of $\log P$ versus $1/T$. The correlation coefficient for this line is 0.95.

These two correlations permit the estimation of the permeability of a polymer-permeant system. It is first necessary to calculate $(\delta_L - \delta_0)^2/(\rho \cdot MW)$ from data in the literature. From Figure 3, the activation energy, E_p , can be read, and this value is used to obtain P_0 from Figure 4. The permeability is then calculated from eq. (16), as follows:

$$P = P_0 \exp(-E_p/RT)$$

TABLE V
Comparison of Observed Permeabilities with Those
Calculated by the Experimental Correlation (25°C)

Compound	Observed P	Calculated P
Chlorobenzene	430	688
Nitrobenzene	530	300
Toluene	270	1810
<i>o</i> -Xylene	305	1950
Aniline	270	120
Benzene	218	2800
<i>n</i> -Heptane	192	118
<i>n</i> -Hexane	146	89
Carbon tetrachloride	148	99
Cyclohexane	103	58
Ethyl acetate	34	2.3
Acetic acid	36	16
<i>n</i> -Butyl alcohol	15	9.0
Methyl acetate	18	8.9
<i>s</i> -Butyl alcohol	13	5.0
Formic acid	10	7810
Acetone	8.0	23
<i>t</i> -Butyl alcohol	4.2	5.0
Methyl alcohol	3.8	44

Following the procedure of Salame, a correction factor λ is used to bring calculated and observed values of each chemical family into agreement. The correlation equations and values of λ are listed in Table IV.

Table V shows the agreement between observed and calculated values at 25°C.

CONCLUSION

The permeabilities of polyethylene film to 19 organic vapors was measured by a new method. This method, called the "dynamic sorption" method, is a simple and inexpensive method of obtaining permeability data. It is convenient and uses general-purpose equipment. The method is generally recommended for measurements of permeability where the expense of the more sophisticated equipment is not justified.

Correlations are derived for the permeability of vapors through polyethylene, by which the value can be estimated at various temperatures from solubility parameters available in the literature.

Nomenclature

- A = area, cm²
 c = concentration
 D = diffusion coefficient, cm²/sec
 $D(0)$ = diffusion coefficient at zero concentration
 D_0 = diffusion coefficient at $1/T = 0$
 $-E$ = energy of vaporization to the gas at zero pressure, kcal/mole

E_d	= activation energy of diffusion, kcal/mole
E_p	= activation energy of permeation, kcal/mole
$\Delta\bar{H}_1$	= partial molar heat of mixing, kcal/mole
ΔH_s	= heat of solution, kcal/mole
ΔH_{cond}	= molar heat of condensation, kcal/mole
ΔH^v	= heat of vaporization, kcal/mole
J	= diffusion flux, g/(cm ² sec)
L	= thickness, cm
MW	= molecular weight of permeate
P	= permeability coefficient, $\frac{(\text{std cc})(\text{cm})}{(\text{sec})(\text{cm}^2)(\text{cm Hg})}$
$P(0)$	= permeability at zero concentration
P_0	= permeability coefficient at $1/T = 0$
p^0	= saturated vapor pressure, cm Hg
p	= partial pressure, cm Hg
R	= gas constant, kcal/(g-mole °K)
S	= solubility constant
$S(0)$	= solubility coefficient at zero concentration
S_0	= solubility coefficient at $1/T = 0$
T	= temperature, °K
t	= time, sec
VP	= vapor pressure, cm Hg
V'	= molal volume of liquid, cc/mole
w	= weight gain, g
x	= distance, cm
σ	= constant characterizing the concentration dependence of the solubility coefficient
γ	= $\alpha/p^0S(0)$
α	= constant for penetrant-polymer system at a given temperature
ρ	= density of organic liquid or solid, g/cc
δ	= Hildebrand solubility parameter, (kcal/cc) ^{1/2}
λ	= correlation factor for chemical families

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