

## The Desorption of Ethane-Butane Mixtures from Polyethylene

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### Synopsis

The desorption of mixtures of ethane and butane at atmospheric pressure from low-density polyethylene was investigated over the temperature range from 20 to 60°C. Desorbed penetrants were continuously trapped in glass tubes immersed in liquid nitrogen, and composition was determined as a function of time by means of gas chromatography. The ratio of the quantity of desorbed gas at any time  $t$ ,  $q_t$ , to the quantity at complete desorption,  $q_\infty$ , was used to determine diffusion coefficients and solubility constants. The diffusion coefficients for both ethane and butane increase with increasing butane concentration in the temperature interval investigated. The solubility of both penetrants can be correlated by Henry's law at 40, 50, and 60°C. However, at 20 and 30°C. the solubility constant for both penetrants increases with increasing butane concentration. This trend is consistent with experimental observations for single-component diffusion and solubility of several hydrocarbons in polyethylene, where increasing concentration of penetrant plasticizes the polymer, resulting in increasing diffusion coefficients and solubility constants.

### INTRODUCTION

Considerable interest has arisen recently in the diffusion of gaseous mixtures in polymeric membranes. Various reports<sup>1-3</sup> have discussed the feasibility of utilizing the phenomena of selective permeation in commercial separation processes such as helium recovery from natural gas and oxygen enrichment of air. Several binary mixtures including C<sub>2</sub>H<sub>6</sub>-C<sub>3</sub>H<sub>8</sub>,<sup>4</sup> H<sub>2</sub>-C<sub>2</sub>H<sub>6</sub>,<sup>5</sup> H<sub>2</sub>-O<sub>2</sub>,<sup>6</sup> CO<sub>2</sub>-N<sub>2</sub>,<sup>7</sup> and He-O<sub>2</sub>,<sup>8</sup> have been experimentally studied. Experimental studies have generally been limited to the determination of permeation constants through analysis of the penetrated mixture at steady state.

The work described here is an attempt to characterize the effect of mixture composition on the diffusion coefficient, the solubility constant, and the activation energy of diffusion for the individual components of a gas mixture. Mixtures of ethane and butane were studied because of the significant difference in the solubility of each gas in polyethylene, and because preliminary studies indicated that the diffusion coefficient of butane is concentration-dependent over the temperature and partial

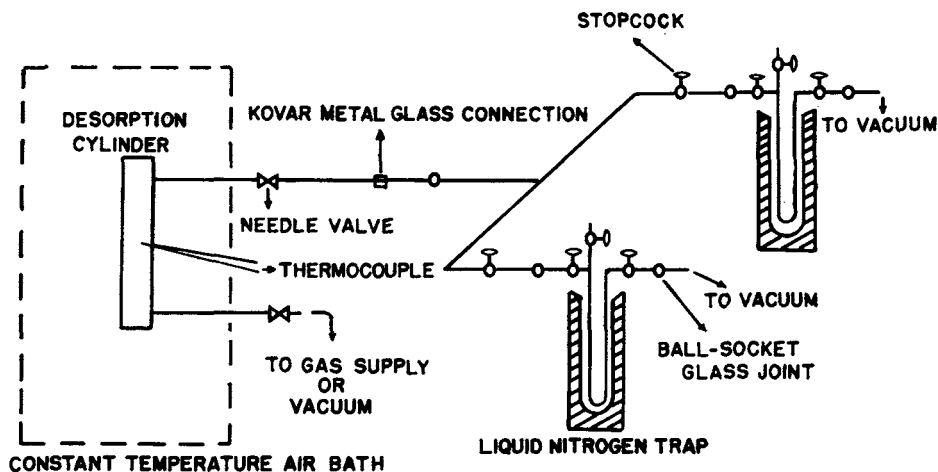


Fig. 1. Schematic diagram of experimental desorption apparatus.

pressure range experimentally studied. The standard desorption experiment was used throughout the work, since data from this type of experiment allows one to determine the diffusion coefficient as well as the solubility constant of each component.

## EXPERIMENTAL

### Materials

Ethane and butane were obtained from the Matheson Company with minimum purity of 99.0 and 99.5%, respectively. Low-density polyethylene film of density 0.9238 g./cm.<sup>3</sup> was supplied by the Dow Chemical Company and used directly without modification. The film was fractured in liquid nitrogen, and the film thickness was determined with a measuring microscope. Two films, of thickness 9.30 and 9.17 mils, were used for all experimental data.

### Apparatus

The desorption apparatus is shown in Figure 1. The apparatus consists of a cylindrical copper chamber with two copper tubing outlets. One outlet is connected to the gas-mixture cylinder and the other outlet is connected to a system for trapping the desorbed gases. The trapping system is constructed of glass and consists of U-shaped tubes immersed in liquid nitrogen. Each glass tube is sealed at both ends with stopcocks and is partially filled with small glass spheres, to ensure adequate surface area for trapping the desorbed gases. The trapping system is divided into two sections, and traps may be changed during the course of a de-

sorption experiment without interrupting the experiment. This arrangement provides a means of trapping desorbed gases in steps and permits the determination of the quantity of each gas desorbed as a function of time. The desorption chamber is located in a constant-temperature air bath regulated to  $\pm 0.2^\circ\text{C}$ . The temperature inside the chamber is measured by a copper-constantan thermocouple connected to a recording potentiometer.

### Procedure

All desorption experiments were performed at atmospheric pressure at temperatures of 20, 30, 40, 50, and  $60^\circ\text{C}$ . The percentage compositions studied were approximately 0:100, 20:80, 38:62, 50:50, 70:30, 80:20, and 100:0 ethane-butane mixtures.

A film sample was sealed in the desorption chamber, the system evacuated, and sufficient time allowed for the desorption chamber to reach the desired temperature. The gas mixture was then introduced into the evacuated cylinder, and the pressure in the cylinder was allowed to return to atmospheric pressure. To ensure constant concentration of the gas mixture within the cylinder during sorption of the mixture by the film, the mixture flowed through the cylinder until sufficient time had elapsed such that the film had reached the equilibrium concentration. At time 0 the cylinder was quickly evacuated with a vacuum pump and flushed with a small controlled air leak for 15 sec., to remove all traces of butane and ethane except that dissolved in the film. After 15 sec. the cylinder was connected to the trapping system, which was in turn connected to a vacuum pump, and a controlled air leak was set to maintain the cylinder pressure at 1-2 mm. Hg. The air leak aided in immediately sweeping desorbed gas out of the cylinder into the traps. Each glass trap was used for a predetermined time interval during desorption, so that desorbed gas composition data as a function of time could be obtained. After the desorption had been completed, the glass tubes were allowed to reach room temperature and then brought to atmospheric pressure by slowly introducing air. After a sufficient time had elapsed for the concentration in the tubes to reach equilibrium, a 1 ml. sample from each tube was injected into a gas chromatograph for analysis. From the volume calculation for each trap and the gas chromatograph analysis the amount of both butane and ethane trapped during each time interval was calculated.

During the initial 15 sec. evacuation a significant amount of desorption of ethane and butane occurs, especially at higher temperatures, and must be accounted for. To calculate the quantity desorbed from 0 to 15 sec., the diffusion equation was solved by a trial-and-error procedure on a digital computer with the use of the diffusion coefficient experimentally determined from the first trapping interval as the diffusion coefficient for the first 15 sec.

### MATHEMATICAL ANALYSIS

If we consider the case of desorption from a film bounded by planes  $x = 0$  and  $x = l$ , then the initial and boundary conditions for penetrant  $i$  are:

$$\begin{aligned} C_i &= C_{i_0} && \text{for } t = 0 && \text{at } 0 < x < l \\ C_i &= 0 && \text{for } t \geq 0 && \text{at } x = 0 \\ C_i &= 0 && \text{for } t \geq 0 && \text{at } x = l \end{aligned}$$

The solution<sup>9</sup> to Fick's law for unsteady-state diffusion

$$\partial C / \partial t = D(\partial^2 C / \partial x^2) \quad (1)$$

for these conditions is

$$C_i(x, t) = (2C_{i_0}/l) \sum_{n=1}^{\infty} \sin(n\pi x/l) \exp\{-D\pi^2 n^2 t/l^2\} \int_0^l \sin(n\pi x/l) dx \quad (2)$$

which by trigonometric manipulation reduces to

$$\begin{aligned} C_i(x, t) &= (4C_{i_0}/\pi) \sum_{m=0}^{\infty} [1/(2m+1)] \sin[(2m+1)\pi x/l] \\ &\quad \times \exp\{-D(2m+1)^2 \pi^2 t/l^2\} \quad (3) \end{aligned}$$

Since the data obtained from the desorption experiments are expressed as the ratio of the amount desorbed at time  $t$  to the amount desorbed at time  $\infty$ , the mathematical solution for  $q_t/q_\infty$  is desired and is given as follows:

$$\begin{aligned} q_t &= q_0 - \int_0^l C_i(x, t) dx \\ &= lC_{i_0} \left( 1 - (8/\pi^2) \sum_{m=0}^{\infty} [1/(2m+1)^2] \exp\{-D(2m+1)^2 \pi^2 t/l^2\} \right) \quad (4) \end{aligned}$$

$$q_\infty = q_0 = lC_{i_0}, \quad \text{since} \quad \int_0^l C_i(x, t) dx = 0 \quad \text{at } t = \infty \quad (5)$$

$$q_t/q_\infty = 1.0 - (8/\pi^2) \sum_{m=0}^{\infty} [1/(2m+1)^2] \exp\{-D(2m+1)^2 \pi^2 t/l^2\} \quad (6)$$

Equation (6) is only exact for a diffusion coefficient which is not concentration-dependent or time-dependent. For a system such as ethane-butane in polyethylene, in which the diffusion coefficients are concentration-dependent, the diffusion coefficient calculated from this equation represents a mean diffusion coefficient.

A corresponding solution,<sup>9</sup> which can be used for graphical solution at small values of  $(Dt/l^2)^{1/2}$ , is:

$$q_t/q_\infty = 4(Dt/l^2)^{1/2} \left\{ \pi^{-1/2} + 2 \sum_{n=1}^{\infty} (-1)^n \operatorname{ierfc} [nl/2(Dt)^{1/2}] \right\} \quad (7)$$

For small  $q_i/q_\infty$ :

$$2 \sum_{n=1}^{\infty} (-1)^n \operatorname{ierfc} [nl/2(Dt)^{1/2}] \ll \pi^{-1/2} \quad \text{and}$$

$$q_i/q_\infty = (4/\pi^{1/2})(Dt/l^2)^{1/2} \quad (8)$$

The diffusion coefficient for each component can then be calculated from the slope of a plot of  $q_i/q_\infty$  versus  $(t/l^2)^{1/2}$ , since the plot is linear for  $q_i/q_\infty < 0.5$ , even when  $D = f(C)$ , as shown by Crank.<sup>9</sup> For the case of  $D = f(C)$ ,  $D$  calculated by the above procedure again represents a mean diffusion coefficient.

## RESULTS AND DISCUSSION

Plots of  $q_i/q_\infty$  are shown at various concentration levels of butane and ethane in Figures 2 and 3 for 20 and 40°C. and in Figures 4 and 5 for 30 and 50°C. As is clearly shown in these figures, the diffusion coefficient calculated from the desorption data for this system is concentration-dependent. Solution of eq. (6) for  $D$  from  $q_i/q_\infty$  data was accomplished by a trial-and-error computation on a digital computer and yields a mean diffusion coefficient, since  $D = f(C)$ . For comparison purposes the value of  $D$  for  $q_i/q_\infty = 0.5$ , calculated from eq. (6), is listed in Table I for the various concentrations and temperatures investigated. Also listed in Table I are diffusion coefficients for butane at 20, 30, 40°C. and for ethane

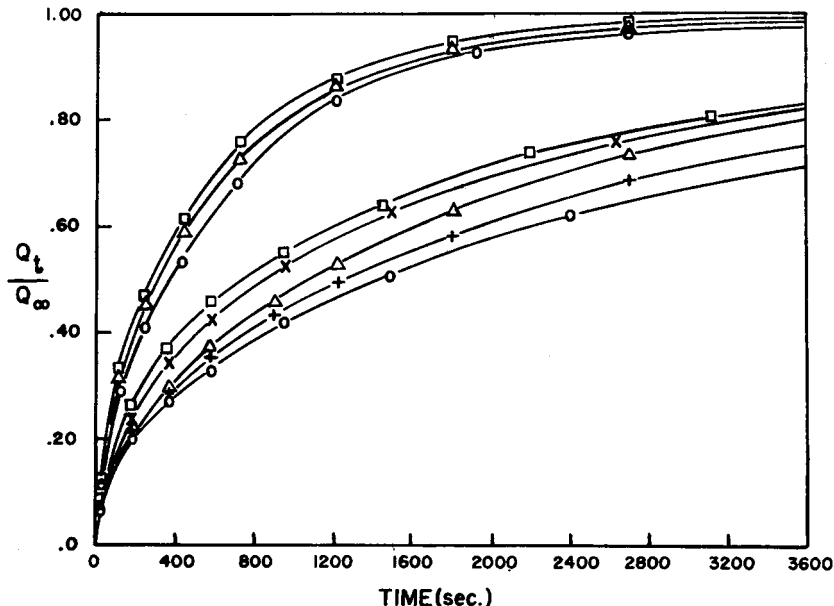


Fig. 2. Desorption curves for butane at different concentration levels (%). Lower set of curves (20°C.): (□) 100, (×) 82.2, (Δ) 52.1, (+) 38.9, (O) 19.3. Upper set of curves (40°C.): (□) 100, (Δ) 52.1 (O) 20.1.

TABLE I  
 Ethane and Butane Diffusion Coefficients

| Temp.,<br>°C. | C <sub>2</sub> H <sub>6</sub> ,<br>% | C <sub>4</sub> H <sub>10</sub> ,<br>% | Ethane                                     |  | Butane                                     |  |
|---------------|--------------------------------------|---------------------------------------|--|--|--|--|
|               |                                      |                                       | <i>D</i><br>× 10 <sup>7</sup> ,<br>eq. (6) | <i>D</i><br>× 10 <sup>7</sup> ,<br>eq. (8) | <i>D</i><br>× 10 <sup>7</sup> ,<br>eq. (6) | <i>D</i><br>× 10 <sup>7</sup> ,<br>eq. (8) |
| 20            | 0.0                                  | 100.0                                 |  |  | 0.371                                      | 0.408                                      |
|               | 17.8                                 | 82.2                                  | 1.12                                       | 1.13                                       | 0.327                                      | 0.335                                      |
|               | 30.9                                 | 69.1                                  | 0.894                                      | 0.899                                      | 0.262                                      | 0.278                                      |
|               | 47.9                                 | 52.1                                  | 0.860                                      | 0.865                                      | 0.252                                      | 0.250                                      |
|               | 61.1                                 | 38.9                                  | 0.768                                      | 0.775                                      | 0.244                                      | 0.256                                      |
|               | 80.7                                 | 19.3                                  | 0.614                                      | 0.625                                      | 0.191                                      | 0.207                                      |
|               | 100.0                                | 0.0                                   | 0.432                                      | 0.438                                      |  |  |
| 30            | 0.0                                  | 100.0                                 |  |  | 0.654                                      | 0.657                                      |
|               | 17.6                                 | 82.4                                  | 1.59                                       | 1.59                                       | 0.604                                      | 0.604                                      |
|               | 30.2                                 | 69.8                                  | 1.44                                       | 1.45                                       | 0.504                                      | 0.513                                      |
|               | 47.9                                 | 52.1                                  | 1.39                                       | 1.39                                       | 0.463                                      | 0.440                                      |
|               | 63.0                                 | 37.0                                  | 1.30                                       | 1.32                                       | 0.373                                      | 0.368                                      |
|               | 80.1                                 | 19.9                                  | 1.00                                       | 1.01                                       | 0.352                                      | 0.353                                      |
|               | 100.0                                | 0.0                                   | 0.890                                      | 0.875                                      |  |  |
| 40            | 0.0                                  | 100.0                                 |  |  | 1.00                                       | 0.998                                      |
|               | 18.3                                 | 81.7                                  | 2.79                                       |  | 0.997                                      | 0.997                                      |
|               | 29.7                                 | 70.3                                  | 2.79                                       |  | 0.990                                      | 0.987                                      |
|               | 47.9                                 | 52.1                                  | 2.58                                       |  | 0.920                                      | 0.901                                      |
|               | 61.2                                 | 38.8                                  | 2.14                                       |  | 0.859                                      | 0.871                                      |
|               | 79.9                                 | 20.1                                  | 2.12                                       |  | 0.754                                      | 0.777                                      |
|               | 100.0                                | 0.0                                   | 1.79                                       |  |  |  |
| 50            | 0.0                                  | 100.0                                 |  |  | 1.75                                       |  |
|               | 18.3                                 | 81.7                                  | 4.21                                       |  | 1.78                                       |  |
|               | 29.7                                 | 70.3                                  | 4.09                                       |  | 1.70                                       |  |
|               | 49.9                                 | 50.1                                  | 4.32                                       |  | 1.61                                       |  |
|               | 61.2                                 | 38.8                                  | 3.94                                       |  | 1.46                                       |  |
|               | 80.9                                 | 19.1                                  | 3.43                                       |  | 1.43                                       |  |
|               | 100.0                                | 0.0                                   | 2.96                                       |  |  |  |
| 60            | 0.0                                  | 100.0                                 |  |  | 3.09                                       |  |
|               | 18.3                                 | 81.7                                  | 6.40                                       |  | 3.19                                       |  |
|               | 29.7                                 | 70.3                                  | 6.93                                       |  | 3.21                                       |  |
|               | 49.4                                 | 50.6                                  | 6.27                                       |  | 2.64                                       |  |
|               | 61.2                                 | 38.8                                  | 5.66                                       |  | 2.80                                       |  |
|               | 80.9                                 | 19.1                                  | 5.95                                       |  | 2.67                                       |  |
|               | 100.0                                | 0.0                                   | 5.90                                       |  |  |  |

at 20 and 30°C. calculated from a plot of  $q_t/q_\infty$  versus  $(t/l^2)^{1/2}$ . At higher temperatures, where desorption was rapid, sufficient data points for  $q_t/q_\infty < 0.5$  did not exist for an adequate analysis by this method.

The diffusion coefficient for ethane and for butane both increase with increasing butane concentration. The effect of increasing butane concentration on the diffusion coefficients decreases with increasing temperature. A plot of  $\log D$  versus  $1/T$  for ethane and butane in Figure 6 shows this phenomenon clearly. The activation energy of diffusion,  $E_d$ , and  $D_0$ , calculated from  $D = D_0 \exp \{-E_d/RT\}$  are listed for ethane and

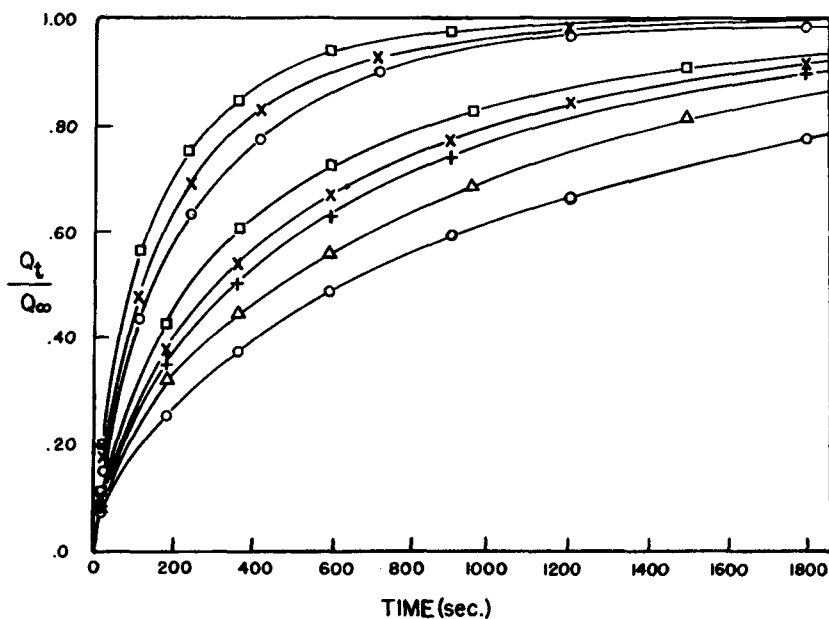


Fig. 3. Desorption curves for ethane at different concentration levels (%). Lower set of curves (20°C.): (□) 17.8, (×) 30.9, (+) 47.9, (Δ) 82.2, (O) 100. Upper set of curves (40°C.): (□) 18.3, (×) 62.1, (O) 100.

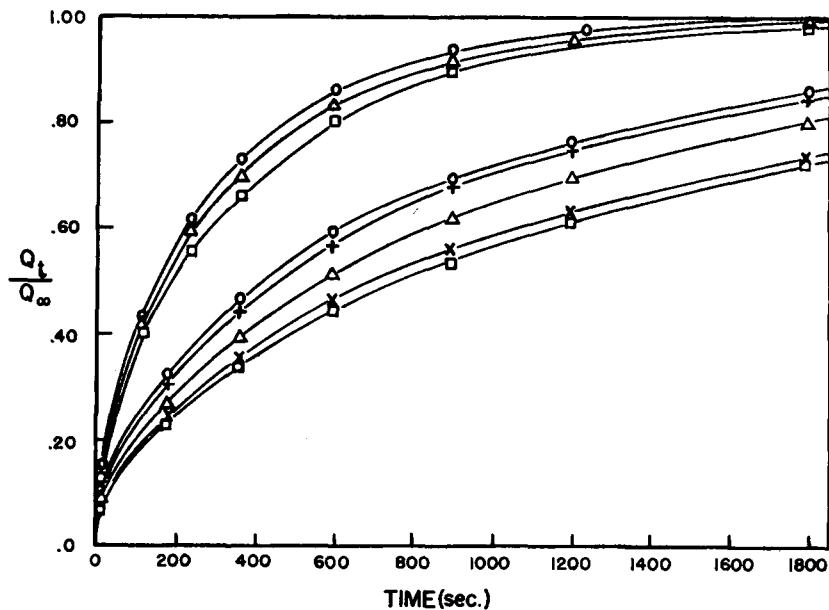


Fig. 4. Desorption curves for butane at different concentration levels (%). Lower set of curves (30°C.): (O) 100, (+) 82.4, (Δ) 52.0, (×) 37.0, (□) 19.9. Upper set of curves (50°C.): (O) 100, (Δ) 38.8, (□) 19.1.

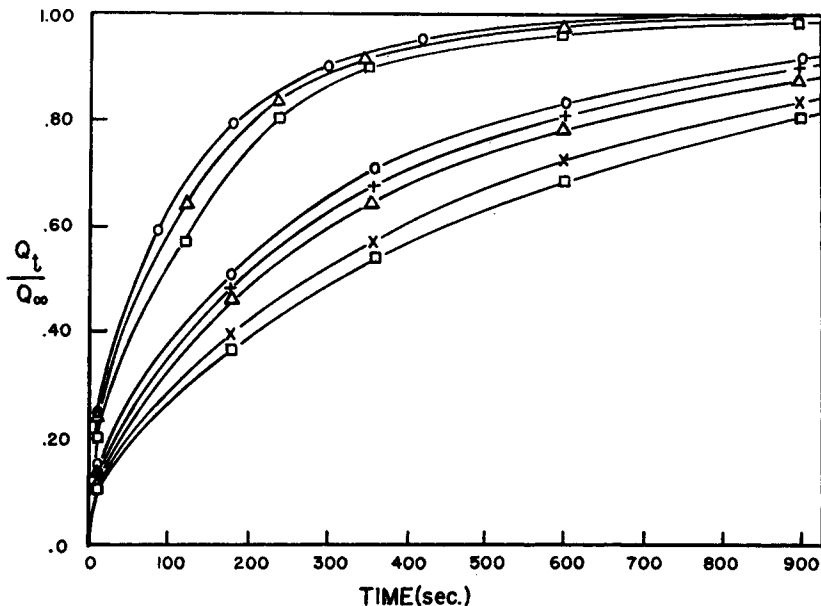


Fig. 5. Desorption curves for ethane at different concentration levels (%). Lower set of curves (30°C.): (O) 17.6, (+) 47.9, ( $\Delta$ ) 63.0, ( $\times$ ) 80.1, ( $\square$ ) 100. Upper set of curves (50°C.): (O) 18.3, ( $\Delta$ ) 61.2, ( $\square$ ) 100.

butane at various concentration levels in Table II. The activation energy of diffusion for both ethane and butane decreases with increasing butane concentration.

The solubility of butane as a function of butane concentration in ethane-butane mixtures at atmospheric pressure is presented in Figure 7, and the solubility of ethane as a function of ethane concentration is shown in Figure 8. The data show that at 40, 50, and 60°C. ethane and butane appear essentially to obey Henry's law; that is,  $C = Sp$ , where  $C$  is the equilibrium solubility (milliliters at standard temperature and pressure

TABLE II  
Experimental Values for Arrhenius Equation  $D = D_0 \exp \{-E_a/RT\}$

| C <sub>2</sub> H <sub>6</sub> ,<br>% | C <sub>4</sub> H <sub>10</sub> ,<br>% | Ethane                                     |                                | Butane                                     |                                |
|--------------------------------------|---------------------------------------|--|--------------------------------|--|--------------------------------|
|                                      |                                       | D <sub>0</sub> ,<br>cm. <sup>2</sup> /sec. | E <sub>a</sub> ,<br>kcal./mole | D <sub>0</sub> ,<br>cm. <sup>2</sup> /sec. | E <sub>a</sub> ,<br>kcal./mole |
| 0.0                                  | 100.0                                 |  |                                | 0.360                                      | 9.38                           |
| 18.0                                 | 82.0                                  | 0.365                                      | 8.75                           | 3.90                                       | 10.8                           |
| 30.0                                 | 70.0                                  | 1.18                                       | 9.52                           | 7.90                                       | 11.3                           |
| 50.0                                 | 50.0                                  | 1.69                                       | 9.81                           | 11.0                                       | 11.6                           |
| 61.0                                 | 39.0                                  | 2.51                                       | 10.1                           | 17.5                                       | 11.9                           |
| 80.0                                 | 20.0                                  | 7.90                                       | 10.9                           | 53.6                                       | 12.7                           |
| 100.0                                | 0.0                                   | 77.3                                       | 12.4                           |  |                                |



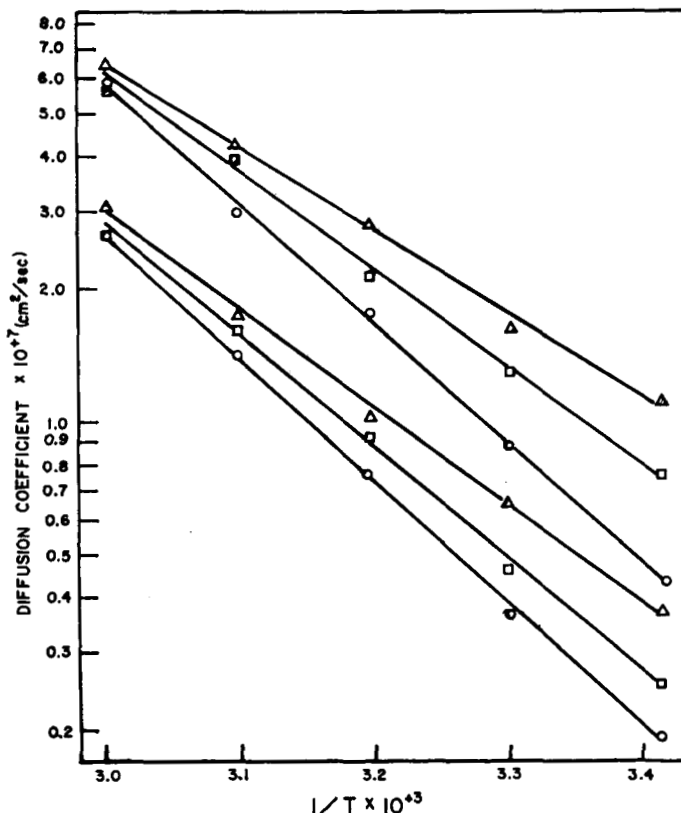


Fig. 6. Variation of  $D$  with temperature at different concentration levels (%). Lower set of curves (butane): ( $\Delta$ ) 100, ( $\square$ ) 52, (O) 20. Upper set of curves (ethane): ( $\Delta$ ) 18, ( $\square$ ) 62, (O) 100.

per cubic centimeters of film),  $S$  is the solubility constant [ml. at STP per ( $\text{cm}^3 \text{ film} \times \text{cm. Hg}$ )] and  $p$  is the partial pressure (cm. Hg). Values of  $S$  for ethane and butane for 40, 50, and 60°C. are listed in Table III. For 20 and 30°C. the solubility data for butane can be represented by  $C = S(0) p \exp \{ \alpha p \}$ , which has been shown<sup>10</sup> to describe adequately the sorption isotherm for nonpolar organic vapors in polyethylene. For butane at 20°C.  $S(0) = 0.102$  [ml. (STP)/( $\text{cm}^3 \times \text{cm. Hg}$ )] and  $\alpha = 0.0024$  ( $\text{cm. Hg}$ )<sup>-1</sup>, and at 30°C.  $S(0) = 0.089$  [ml. (STP)/( $\text{cm}^3 \times \text{cm. Hg}$ )] and  $\alpha = 0.0018$  ( $\text{cm. Hg}$ )<sup>-1</sup>. The solubility of ethane in polyethylene in the presence of butane also deviates from Henry's law at 20 and 30°C. and can best be represented by  $C = S(p_0) p \exp \{ \alpha(p_0 - p) \}$ , where  $S(p_0)$ , is the solubility constant of pure ethane at  $p = p_0$ , the pressure of the mixtures investigated (atmospheric pressure for this investigation). At 20°C.  $S(p_0) = 0.0105$  [ml. (STP)/( $\text{cm}^3 \times \text{cm. Hg}$ )] and  $\alpha = 0.0022$  ( $\text{cm. Hg}$ )<sup>-1</sup>, and at 30°C.  $S(p_0) = 0.0097$  [ml. (STP)/( $\text{cm}^3 \times \text{cm. Hg}$ )] and  $\alpha = 0.0016$  ( $\text{cm. Hg}$ )<sup>-1</sup>.

TABLE III  
Ethane and Butane Solubility Constants

| Temp.,<br>°C. | Solubility constant, ml. (STP)/(cm. <sup>3</sup> film × cm. Hg) |        |
|---------------|---|--------|
|               | Ethane  | Butane |
| 40            | 0.00913   | 0.0843 |
| 50            | 0.00830   | 0.0662 |
| 60            | 0.00785   | 0.0585 |

The increase in the diffusion coefficients of ethane and butane with increasing butane concentration may be attributed to the high solubility of butane which "plasticizes" the film. The physical phenomenon that occurs on the molecular scale is not clearly understood. Reilly<sup>4</sup> found that the permeation constants of ethane and propane were pressure-dependent, and in mixtures of ethane and propane at high pressures the ethane permeation constant was higher than that for pure ethane. This was attributed to the high concentration of propane; relative to ethane, which produced "gaps" and "holes" in the polymer matrix. Further, Pilar<sup>11</sup> found that the constants of oxygen and nitrogen permeability through polyethylene increased with increasing concentration of *n*-hexane and carbon tetrachloride in equilibrium with polyethylene. Many ex-

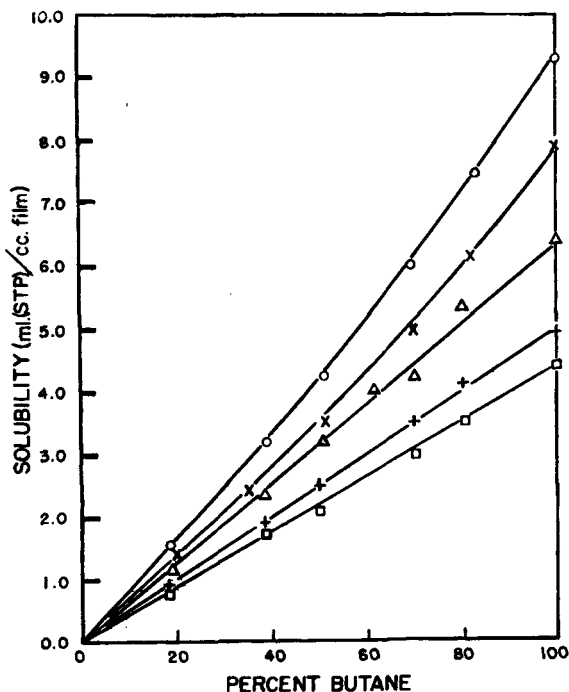


Fig. 7. Solubility of butane as a function of butane concentration (%) at various temperatures (°C.): (O) 20, (X) 30, (Δ) 40, (+) 50, (□) 60.

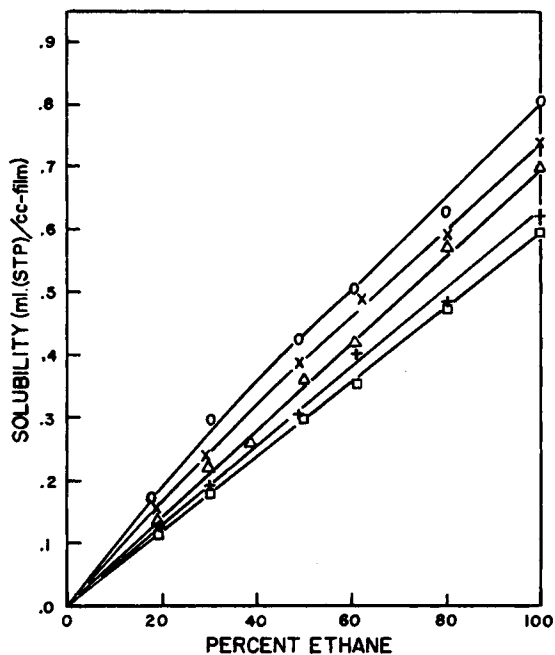


Fig. 8. Solubility of ethane as a function of ethane concentration (%) at various temperatures ( $^{\circ}\text{C}$ ): (O) 20, (X) 30, ( $\Delta$ ) 40, (+) 50, ( $\square$ ) 60.

amples of a diffusion coefficient's increase with concentration exist for a single-penetrant-polymer system.<sup>12</sup> Such behavior has been explained by Prager and Long<sup>13</sup> in hydrocarbon-polyisobutylene systems as the result of breaking of van der Waals bonds between polymer chains, forming holes between polymer chains. If polymer-polymer bonds are broken by the penetrant, the number of holes produced during the diffusion process will increase with penetrant concentration. Michaels and Bixler<sup>14</sup> have shown that in semicrystalline polyethylene diffusion and solubility of gases is negligible in the crystalline regions compared to that in the amorphous regions. For the system butane-ethane-polyethylene the increases in both ethane and butane diffusion coefficients with increasing butane concentration can be explained by the reasoning mentioned above. The amorphous regions of polyethylene are visualized as possessing a certain amount of order caused by van der Waals bonding, which is partially disrupted by the sorbed butane and so causes the polymer chain mobility to increase, which in turn decreases the resistance to penetrant diffusion. The possibility of butane disrupting portions of imperfect crystalline regions has not been completely ruled out and may contribute to the overall phenomena.

The exponential increase in butane solubility with increasing butane concentration may be due partially to disruption of van der Waals bonding by the penetrant, which provides for more absorption sites at positions

previously taken by polymer-polymer interaction. This deviation from Henry's law is experimentally shown by an increase in the solubility constant of ethane with increasing butane concentration at 20 and 30°C. Multilayer absorption, in which an absorption site is a penetrant molecule sorbed on the polymer chain, also will contribute to an exponential increase in solubility with butane concentration. Any decrease in crystallinity caused by butane sorption would have a similar effect, since butane represents what may be considered an intermediate penetrant between hydrocarbon gases, which do not swell polyethylene film, and vapors, which can swell the polyethylene and cause partial dissolution of imperfect crystalline regions.

The decrease of activation energy of diffusion with increasing butane concentration may be partially attributed to the decrease in butane solubility with increasing temperature, causing a decrease in the plasticizing caused by sorbed butane. Another factor that may also be attributed to the decrease in activation energy is the decrease in concentration dependence on the diffusion coefficient at higher temperatures, as has been observed by Aitken and Barrer<sup>15</sup> for the system hydrocarbons-natural-rubber. It should be noted that the activation energy of diffusion is calculated from values of  $D$  at  $q_t/q_\infty = 0.5$ , which represents a mean value of  $D$  rather than a value of  $D = D(C=O)$ , for which  $E_d$  is commonly calculated for pure component diffusion.

The authors gratefully acknowledge a National Aeronautical and Space Administration grant supporting this work and express their thanks to the Dow Chemical Company for supplying film and to the Computer Science Center of the University of Maryland for the use of their facilities.

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### Résumé

La désorption de mélanges d'éthane et de butane, à pression atmosphérique, du polyéthylène à basse densité a été étudiée sur un domaine de température compris entre 20

et 60°C. Les produits désorbés sont retenus dans des tubes de verre immergés dans l'azote liquide et leur composition est déterminée en fonction du temps par chromatographie gazeuse. Le rapport de la quantité de gaz désorbé au temps  $t$ ,  $q_t$ , à la quantité après désorption complète,  $q_\infty$  a été utilisé pour déterminer les coefficients de diffusion et les constantes de solubilité. Les coefficients de diffusion aussi bien pour l'éthane que pour le butane augmentent avec la concentration en butane dans l'intervalle de température étudié. La solubilité des deux produits peut être reliée à la loi de Henry à 40, 50 et 60°C. Toutefois, à 20 et 30°C, la constante de solubilité de ces deux produits croît avec la concentration en butane. Cette tendance est en accord avec les observations expérimentales concernant la diffusion d'un seul composant et la solubilité de plusieurs hydrocarbures dans le polyéthylène; dans ce cas, l'accroissement de la concentration d'un produit plastifié le polymère ce qui accroît les coefficients de diffusion et les constantes de solubilité.

### Zusammenfassung

Die Desorption von Äthan-Butangemischen bei Atmosphärendruck von Polyäthylen niedriger Dichte wurde im Temperaturbereich von 20 bis 60°C untersucht. Die desorbierten Gemische wurden kontinuierlich in mit flüssigem Stickstoff gekühlten Glasrohren aufgefangen und die Zusammensetzung als Funktion der Zeit gaschromatographisch bestimmt. Aus dem Verhältnis der Menge von desorbiertem Gas zur Zeit  $t$ ,  $q_t$ , zur Menge bei vollständiger Desorption,  $q_\infty$ , wurden Diffusionskoeffizienten und Löslichkeitskonstanten bestimmt. Die Diffusionskoeffizienten für Äthan und Butan nehmen mit steigender Butankonzentration im untersuchten Temperaturbereich zu. Die Löslichkeit beider Stoffe gehorcht bei 40, 50 und 60°C dem Henry'schen Gesetz. Bei 20 und 30°C nimmt jedoch die Löslichkeit beider Stoffe mit steigender Butankonzentration zu. Dieses Verhalten stimmt mit den Beobachtungen bei Versuchen über die Diffusion und Löslichkeit einzelner Kohlenwasserstoffe in Polyäthylen überein, bei welchen steigende Kohlenwasserstoffkonzentrationen eine Weichmachung des Polymeren bewirkt und damit zu einem Anstieg der Diffusionskoeffizienten und Löslichkeitskonstanten führt.

Received February 28, 1967

Revised April 25, 1967

Prod. No. 1611