

The Solubility of Gases and Volatile Liquids in Polyethylene and Polyisobutylene at Elevated Temperatures

LEONARD I. STIEL, DAH-KANG CHANG, HOU-HSEIN CHU, and CHANG DAE HAN, *Department of Chemical Engineering, Polytechnic Institute of New York, Brooklyn, New York 11201*

Synopsis

The solubility of gases and volatile liquids in low-density polyethylene (LDPE) and polyisobutylene (PIB) at elevated temperatures has been correlated, using the experimental data available in the literature. In the present study, a Henry's constant K_p at a total pressure of approximately 1 atm defined as $P_1 = K_p V_1^0$, where P_1 is the partial pressure of the solute in the vapor phase and V_1^0 is the solubility (cm^3 solute/g polymer at 273.2 K and 1 atm), is correlated for nonpolar solutes with the following expressions: (1) For LDPE, $\ln(1/K_p) = -1.561 + (2.057 + 1.438\omega)(T_c/T)^2$; (2) For PIB, $\ln(1/K_p) = -1.347 + (1.790 + 1.568\omega)(T_c/T)^2$, in which ω is the acentric factor and T_c the critical temperature of the solute. In obtaining the above correlations we have used 27 solutes covering 115 data points for LDPE, and 18 solutes covering 148 data points for PIB. We have calculated values of $1/K_p$ from the literature data reported in terms of the retention volume (V_R^0), weight-fraction Henry's constant (H_1), activity coefficient at infinite dilution (Ω_1^0), Flory-Huggins interaction parameter (χ), or V_1^0/P obtained from high pressure sorption experiments. The correlations obtained in this study permit one to estimate with reasonable accuracy the solubility of gases and volatile liquids in either LDPE or PIB, with information on the acentric factor (ω) and critical temperature (T_c) only. The relationship for LDPE is also applicable for solubilities in high-density polyethylene. Relationships for the heat of vaporization of solutes from infinitely dilute LDPE or PIB solutions are also derived from the temperature variation of $1/K_p$.

INTRODUCTION

Values of the solubility of gases and volatile liquids in molten polymers are required in important applications, including foam extrusion and polymer devolatilization processes. In recent years, a number of experimental studies have been conducted to determine solubilities of fluids in polymers for wide ranges of temperatures, particularly by gas chromatographic procedures. It is desirable to utilize this information to develop generalized equations for the prediction of solubilities for conditions or components for which data are not available.

In this study, accurate relationships have been developed for the prediction of Henry's constants in polyethylene and polyisobutylene at elevated temperatures. The analysis of data for solubilities at infinite dilution in molten polymers also provides insight into the interactions between the solutes and the polymer molecules.^{1,2} In addition, values of the Henry's constants at low pressures can be utilized to determine interaction constants of an equation of state for the solute-polymer mixture in order to estimate solubilities at elevated pressures and finite concentrations.^{3,4}

PREVIOUS INVESTIGATIONS

Several previous studies have been concerned with the estimation of Henry's constants in molten polymer systems. Durrill and Griskey⁵ related the Henry's constants for gases in polystyrene at 461 K to the Lennard-Jones force constants or critical temperatures of the solutes. For polyethylene, Stern et al.⁶ showed that the available solubility data for a wide range of temperatures could be represented as a linear relationship between the logarithm of the Henry's constant and $(T_c/T)^2$, where T_c is the critical temperature. Stiel and Harnish⁷ found that a similar approach was applicable for the solubility of gases and volatile liquids in polystyrene for temperatures greater than 393 K. A Henry's constant K_p , at a pressure P which is approximately atmospheric, was defined as

$$Py_1 = K_p V_1^0 \quad (1)$$

where y_1 is the mole fraction of solute in the vapor phase and V_1^0 is the solubility (cm^3 solute/g polymer at 273.2 K and 1 atm). Solubility data for polystyrene obtained from high pressure sorption experiments and gas chromatographic studies were utilized to obtain the following relationship which is applicable for $(T_c/T)^2 > 0.6$:

$$\ln(1/K_p) = -2.338 + 2.706(T_c/T)^2 \quad (2)$$

Stiel and Harnish⁷ found that for 109 data points the average error between the experimental values and values calculated with eq. (2) was 7.53%.

Maloney and Prausnitz⁸ developed an improved relationship for Henry's constants of nonpolar gases and liquids in low-density polyethylene at low pressures. Based on the Flory-Huggins relationship for solubility in polymers, available data were utilized to develop the following relationship:

$$\log(H_1 M_1 / T_c) = g^{(0)} + \omega g^{(1)} \quad (3)$$

in which $g^{(0)}$ and $g^{(1)}$ are defined by

$$g^{(0)} = 2.401 - \frac{1.383}{(T/T_c)} - \frac{0.4913}{(T/T_c)^2} + 2.006 \exp(-0.0148T_c) + \frac{371.4}{T} \quad (4)$$

and

$$g^{(1)} = 0.690 + \frac{0.4813}{(T/T_c)} - \frac{1.1328}{(T/T_c)^2} \quad (5)$$

respectively. In eq. (3), ω is the acentric factor of the solute and H_1 is the weight-fraction Henry's constant defined as

$$H_1 = 22,414K_p/M_1 \quad (6)$$

and M_1 is the molecular weight of the solute. According to Maloney and Prausnitz,⁸ for 84 data points for 24 solutes the average error between the experimental and calculated Henry's constants was 12%.

Liu and Prausnitz⁹ utilized an equation of state resulting from hard-chain theory applicable for both solutes and polymers to develop a relationship for Henry's constants in polymer solutions. Experimental solubility data are required to obtain a binary interaction parameter for the solute-polymer system. Values of Henry's constants were calculated by this approach for gases and liquids in polyethylene, polyisobutylene, and poly(dimethyl siloxane) for temperatures greater than 25°C.

Won¹⁰ proposed a relationship for Henry's constants in polyethylene at elevated temperatures in terms of the reduced temperature and critical constants of the solute. Different constants are required in the relationship for different types of solutes. Iwai and co-workers^{11,12} utilized the UNIFAC group contribution model combined with a free-volume term developed by Oishi and Prausnitz¹³ to calculate Henry's constants for *n*-alkanes and aromatic hydrocarbons in polystyrene and polyethylene at elevated temperatures. For polyethylene, different parameters were required for the free volume term for the *n*-alkanes than for benzene and toluene.

REDUCTION OF EXPERIMENTAL DATA

In order to develop the generalized relationships of this study, experimental data from various sources were analyzed to obtain values of the Henry's constant K_p , expressed on a consistent basis. For gas chromatographic experiments at approximately atmospheric pressure, K_p is equivalent to the retention volume V_g^0 (cc of solute at 273.2 K and average column pressure \bar{P} /g polymer), which is measured as⁷

$$V_g^0 = \frac{Q\Delta t 273.15}{\bar{P}WT_F} \quad (7)$$

where Q is the flow rate of the carrier gas at atmospheric pressure and temperature T_F , Δt is the difference in retention times for the solute and a reference gas, and W is the weight of polymer. Values of the weight-fraction Henry's constant H_1 from these experiments are related to K_p through eq. (6).

Gas chromatographic results are also reported as activity coefficients at infinite dilution, Ω_1^∞ , which are related to K_p as follows⁷:

$$K_p = \frac{\Omega_1^\infty P_1^\dagger M_1}{22,414} \exp \left[\frac{P_1^\dagger}{RT} (B_{11} - V_1) - \frac{\bar{P}}{RT} (2B_{13} - B_{33} - \bar{V}_1^\infty) \right] \quad (8)$$

where P_1^\dagger , V_1 , and \bar{V}_1^∞ are the vapor pressure, molar liquid volume, and partial molar volume at infinite dilution of the solute at the temperature of the solution, and B_{13} , B_{11} , and B_{33} are the interaction and pure component second virial coefficients for the solute and carrier gas. At infinite dilution of solute, the Flory-Huggins relationship for solubility can be expressed as¹⁴

$$\ln \Omega_1^\infty = \ln \left(\frac{v_1}{v_2} \right) + \left(1 - \frac{V_1}{M_2 v_2} \right) + \chi \quad (9)$$

where v_1 and v_2 are the specific volumes of the solute and polymer, and \bar{M}_2 is the number-average molecular weight of the polymer. Values of K_p can be obtained from Flory-Huggins interaction parameters χ derived from chromatographic experiments through eqs. (8) and (9).

The results of sorption experiments at elevated pressures are usually presented as values of V_1^0/P at the system pressure P . Assuming the applicability of Henry's law and the second virial equation of state, the pressure-effect on the solubility is given as⁷

$$P \exp(B_{11}P/RT) = K_p^{(0)} V_1^0 \exp(\bar{V}_1^\infty P/RT) \quad (10)$$

in which $K_p^{(0)}$ is the Henry's constant corrected to zero pressure. Since $1/K_p$ represents V_1^0/P at atmospheric pressure, it follows from eq. (10) that

$$1/K_p = (1/K_p^{(0)}) \exp[(B_{11} - \bar{V}_1^\infty)/RT] \quad (11)$$

Substitution of eq. (10) into eq. (11) gives

$$\frac{1}{K_p} = \left(\frac{V_1^0}{P}\right) \exp[(\bar{V}_1^\infty - B_{11})(P - 1)/RT] \quad (12)$$

The partial molar volume \bar{V}_1^∞ can be determined through eq. (12) by plotting values of $\ln(V_1^0/P)$ at constant temperature against $(P - 1)/RT$.

The solubility of a pure solute for this case can also be represented in terms of the weight-fraction activity coefficient, Ω_1^∞ , as

$$P \exp(B_{11}P/RT) = \Omega_1^\infty \exp(\bar{V}_1^\infty P/RT) \left(\frac{V_1^0 M_1}{22,474}\right) P_1^\ddagger \exp[(B_{11} - V_1)P_1^\ddagger/RT] \quad (13)$$

Therefore, from eqs. (9) and (13), $1/K_p$ is related to values of χ obtained by extrapolation of sorption measurements to infinite dilution of solute, as follows:

$$\ln\left(\frac{1}{K_p}\right) = \frac{(B_{11} - \bar{V}_1^\infty)}{RT} + \frac{(V_1 - B_{11})P_1^\ddagger}{RT} + \ln\left(\frac{22,414}{P_1^\ddagger V_1}\right) + \ln v_2 + \left(\frac{V_1}{\bar{M}_2 v_2} - 1\right) - \chi \quad (14)$$

where $V_1 = M_1 v_1$.

In the present investigation, values of $1/K_p$ were calculated with these equations from reported data for V_2^0 , Ω_1^∞ , χ , or V_1^0/P . In the application of these relationships, assumptions consistent with those made by the investigators were utilized.

DEVELOPMENT OF GENERALIZED RELATIONSHIPS FOR SOLUBILITIES IN MOLTEN POLYMERS

Henry's Constants for Low-Density Polyethylene

Gas chromatographic studies of solubility in low-density polyethylene (LDPE) were made by Maloney and Prausnitz⁸ for ethylene, *n*-butane, *n*-hexane, benzene, toluene, *n*-octane, and vinyl acetate for temperatures from 124°C to 300°C, by Schreiber et al.¹⁵ for 20 hydrocarbons at 120°C and 145°C, by Newman and Prausnitz¹⁶ for eight organic liquids for 110–200°C, by Liu and Prausnitz¹⁷ for eight solutes for 125–250°C, and by DiPaola-Baranyi et al.¹ for 13 nonpolar and polar solutes at 135°C. High pressure sorption experiments were also conducted for LDPE by Durrill and Griskey⁵ for nitrogen, carbon dioxide, helium, argon, and chlorodifluoromethane at 189°C and pressures to 20 atm, by Lundberg et al.¹⁸ for nitrogen and methane for 125–230°C and pressures to 140 atm, by Cheng and Bonner¹⁹ for nitrogen at 125.8°C and 188.4°C and pressures to 140 atm, and by Atkinson²⁰ for nitrogen for 130–190°C and pressures to 1000 atm.

An analysis of eq. (14) indicates that $1/K_p$ for nonpolar solutes depends on properties of the solute including critical constants and acentric factor, and properties of the polymer such as molecular weight and density. For each solute, values of $\ln(1/K_p)$ from the literature data for LDPE were plotted against $(T_c/T)^2$. As shown in Figures 1–4 for *n*-butane, *n*-hexane, *n*-octane, and benzene, linear relationships resulted for all the substances, similar to the behavior exhibited by the solubility data of polystyrene.⁷ The slopes of these relationships varied for all the substances, but a common intercept, $1/K_p = 0.21$, resulted at $(T_c/T)^2 = 0$, as shown in Figure 5. Therefore, the solubility behavior in LDPE can be represented as

$$\ln(1/K_p) = -1.561 + B(T_c/T)^2 \quad (15)$$

This analysis indicates that $1/K_p$ should not be reduced with other parameters of the solute. For example, if $\ln(P_c/K_p)$ is related to $(T_c/T)^2$ as suggested in a preliminary investigation,²¹ the intercepts in Figure 5 should vary with the critical pressures of the solutes.

It was also found that the slope B of each nonpolar solute is related to the acentric factor ω , which characterizes the size and shape of the molecule. The acentric factor is defined as

$$\omega = -\log P_{Rs}|_{T_R=0.7} - 1.00 \quad (16)$$

The critical constants and acentric factors utilized in this study were obtained from Reid, Prausnitz, and Sherwood.²²

As shown in Figure 6, a linear relationship was obtained between the slope B of eq. (15) and ω for 27 nonpolar solutes considered with $\omega > 0.08$. This relationship can be represented as

$$B = 2.057 + 1.438\omega \quad (17)$$

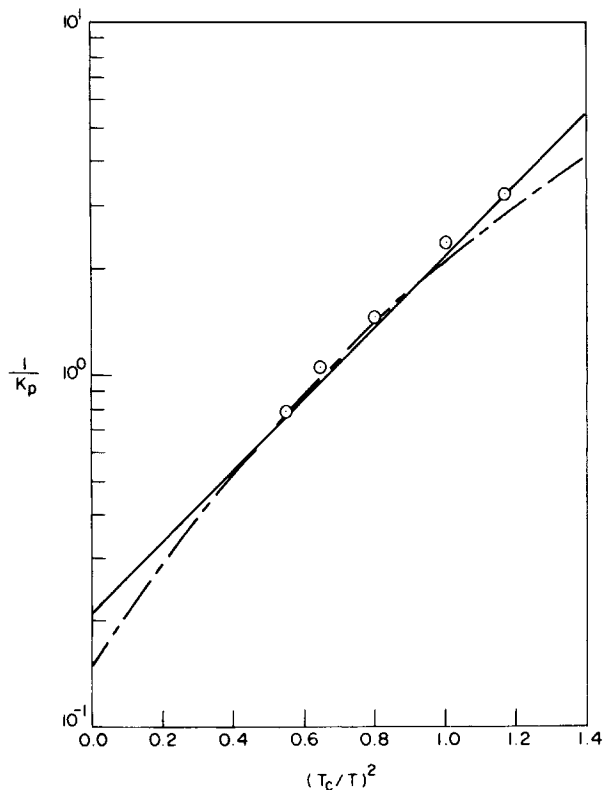


Fig. 1. $1/K_p$ vs. $(T_c/T)^2$ for *n*-butane in LDPE: (O) Maloney and Prausnitz⁸; (—) eq. (3); (---) eq. (18).

Combining eqs. (15) and (17) yields

$$\ln(1/K_p) = -1.561 + (2.057 + 1.438\omega)(T_c/T)^2 \quad (18)$$

The average deviation between the values of B resulting from the experimental data and those calculated from eq. (18) is 1.5% for the 27 substances. In Table I, values of $1/K_p$ obtained from each literature source for 31 nonpolar solutes are compared with the values calculated with eq. (18). For 121 data points, the average percent error is 6.0%. The largest errors result for cyclohexane, *cis*-decalin, and tetralin, which may be due to inaccuracies in the data or the critical constants or acentric factors of the substances. Values of $1/K_p$ calculated with eq. (18) for *n*-butane, *n*-hexane, *n*-octane, and benzene are included in Figures 1-4.

For the 121 data points the relationships of Maloney and Prausnitz⁸ for solubilities in LDPE result in an average error of 7.7%. The values of $1/K_p$ calculated by this method are included in Figures 1-4. The relationships of Maloney and Prausnitz do not always result in the correct temperature dependence of $1/K_p$, as shown in Figure 1 for *n*-butane, and large variations in the intercepts of $\ln(1/K_p)$ at $(T_c/T)^2 = 0$ are predicted.

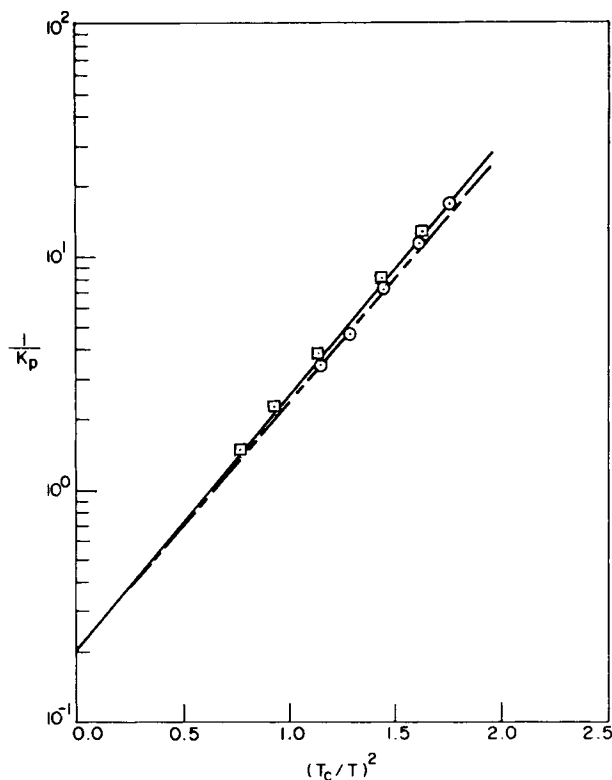


Fig. 2. $1/K_p$ vs. $(T_c/T)^2$ for *n*-hexane in LDPE: (O) Newman and Prausnitz¹⁶; (□) Maloney and Prausnitz⁸; (---) eq. (3); (—) eq. (18).

The available solubility data for methane and nitrogen which have low acentric factors indicate that the intercept of eq. (15) is the same for these substances as for nonpolar fluids with $\omega > 0.08$, as shown in Figure 7. However, the slopes for these molecules are considerably lower than those calculated from eq. (15). For nitrogen, which also has a quadrupole moment, the indicated slope is highly negative.

Large positive deviations in $1/K_p$ result from eq. (18) for polar fluids, including the values for vinyl acetate,^{8,17} for methyl ethyl ketone, isopropyl alcohol, acetone, and methyl chloride,¹⁷ for butyl alcohol, phenol, and 2-pentanone,¹ and for chlorodifluoromethane.⁵ The intercepts at $(T_c/T)^2 = 0$ are the same for the polar fluids as for nonpolar substances, as shown in Figure 7. However, the values of the slope B for these fluids are lower than those calculated from eq. (17), as shown in Figure 8. Therefore, the experimental values of $1/K_p$ become increasingly lower than the calculated values with increasing T_c/T . The relationships of Maloney and Prausnitz,⁸ eqs. (3)–(5), also result in large errors for polar fluids. The data for the slightly polar fluids, chloroform, butyl chloride, and chlorobenzene at 135°C,¹ conform to the behavior of the nonpolar substances and are included in the comparisons of Table I.

In order to accurately correlate the solubility behavior of polar substances, a fourth parameter characterizing polarity effects is required in

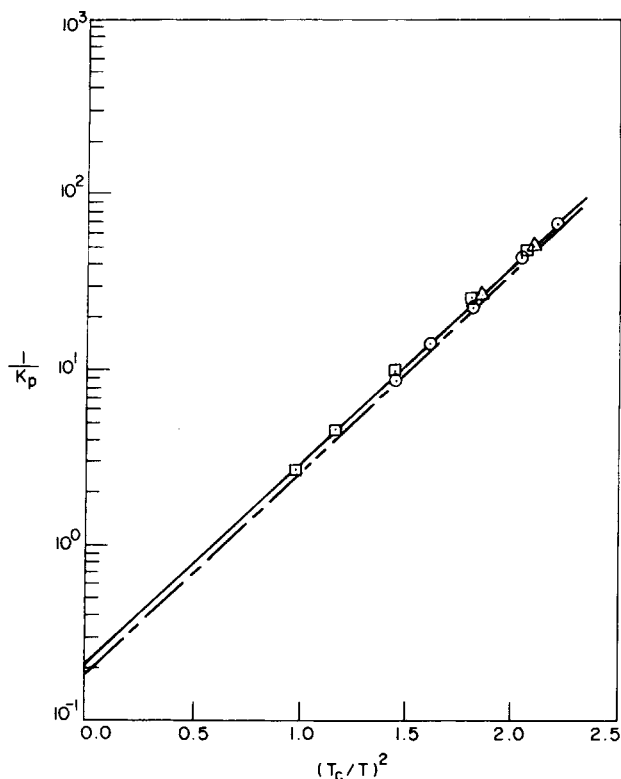


Fig. 3. $1/K_p$ vs. $(T_c/T)^2$ for *n*-octane in LDPE: (○) Newman and Prausnitz¹⁶; (△) Maloney and Prausnitz⁸; (□) Schreiber et al.¹⁵; (---) eq. (3); (—) eq. (18).

the relationship for the slope B of eq. (15). Because the values of B increase with the size and decrease with the polarity of the molecules, the slopes are approximately equal to 2.0 for all the polar substances considered.

Similarly, the experimental values of $1/K_p$ at low temperatures are lower than the calculated values for benzene, ethylene, and ethane which have quadrupole moments. The values of B for several quadrupolar substances are included in Figure 8. The slopes for carbon dioxide which has a quadrupole moment ($B = 1.05$) and for sulfur dioxide which has dipole and quadrupole moments ($B = 1.65$) appear to be too low compared to those for the other polar fluids. This behavior may be due to the inaccuracies in the gas chromatographic measurements for gaseous solutes as indicated by Liu and Prausnitz.⁹

Maloney and Prausnitz⁸ found little variation of Henry's constants in LDPE for samples with $\bar{M}_n > 10,000$. All of the solubility data utilized in this investigation were obtained with polyethylenes of high molecular weight. Comparisons were also made between the values of $1/K_p$ calculated with eq. (18) and the corresponding experimental values for high-density polyethylene (HDPE) from the sorption experiments of Meyer and Blanks²³ for propane and isobutane at 148.9°C, 204.4°C, and 260°C, and from the gas chromatographic measurements of Senich²⁴ for *n*-decane at 150°C and of

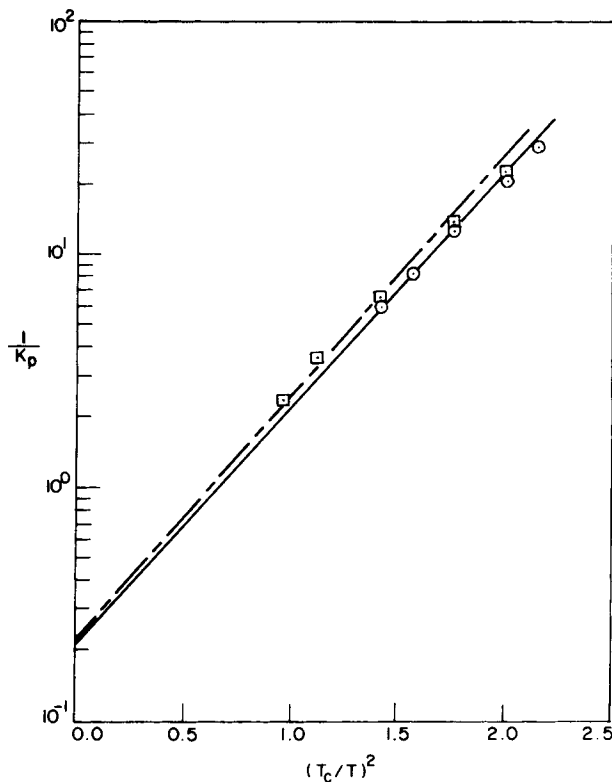


Fig. 4. $1/K_p$ vs. $(T_c/T)^2$ for benzene in LDPE: (○) Newman and Prausnitz¹⁶; (□) Maloney and Prausnitz⁸; (---) eq. (3); (—) eq. (18).

Schreiber et al.¹⁵ for 20 hydrocarbons at 120°C and 145°C. The results of these comparisons are presented in Table II. For 47 data points the average error is 7.0%. The experimental solubilities for HDPE appear to be slightly lower than the corresponding values for LDPE.

Henry's Constants for Polyisobutylene

For polyisobutylene (PIB), gas chromatographic solubility studies were conducted by Newman and Prausnitz²⁵ for benzene, cyclohexane, and *n*-pentane for 25–50°C²⁵ and for benzene, cyclohexane, toluene, and *n*-hexane for 50–150°C,¹⁶ by Leung and Eichinger^{26,27} for *n*-pentane, *n*-hexane, *n*-heptane, *n*-octane, *n*-nonane, cyclohexane, and benzene for 25–65°C, and by Hammers and deLigny for 12 nonpolar organic substances for 40–160°C.²⁸ Lichtenthaler, Liu, and Prausnitz²⁹ conducted studies for *n*-hexane, cyclohexane, and benzene for 50–125°C with both packed and capillary chromatographic columns.

High pressure sorption experiments with PIB were conducted by Durrill and Griskey⁵ for nitrogen, carbon dioxide, argon, helium, and krypton at 188.3°C and pressures to 20 atm, and by Lundberg, Mooney, and Rogers³⁰ for methane for 101.9–188.5°C and pressures to 341 atm. Low pressure

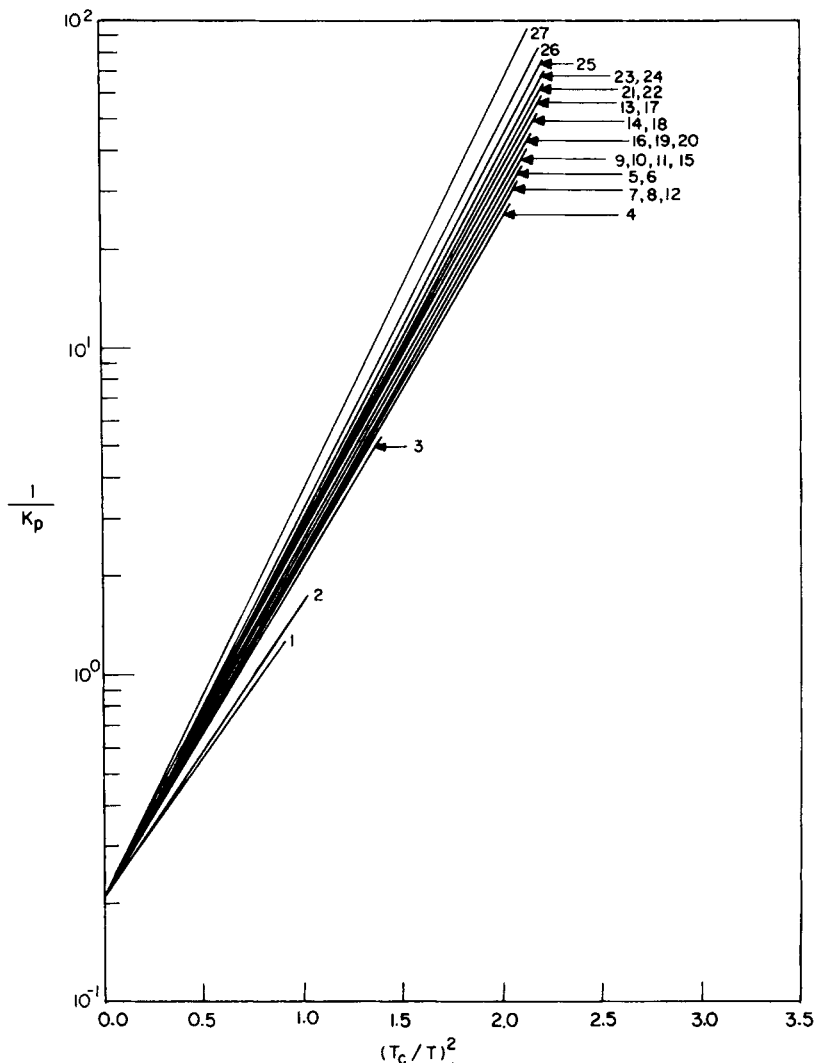


Fig. 5. $1/K_p$ vs. $(T_c/T)^2$ for 27 nonpolar substances in LDPE, represented by eq. (15): (1) ethane; (2) ethylene; (3) *n*-butane; (4) benzene; (5) cyclohexane; (6) *cis*-decalin; (7) toluene; (8) *trans*-decalin; (9) *n*-hexane; (10) ethylbenzene; (11) 2,2,4-trimethylpentane; (12) tetralin; (13) 2,2,4-trimethylhexane; (14) 3-methylhexane; (15) *p*-xylene; (16) *m*-xylene; (17) 3,4-dimethylhexane; (18) 2,4-dimethylhexane; (19) *n*-heptane; (20) 2,5-dimethylhexane; (21) 3-methylheptane; (22) 2-methylheptane; (23) *n*-octane; (24) mesitylene; (25) *n*-nonane; (26) *n*-decane; (27) *n*-dodecane.

sorption experiments at finite concentrations were also performed by Bonner and Prausnitz³¹ for benzene at 80°C and cyclohexane at 100°C, by Prager, Bagley, and Long³² for propane, *n*-butane, isobutane, *n*-pentane, isopentane, and neopentane for 25–46.5°C, by Baker et al.³³ for *n*-pentane for 25–45°C, and by Eichinger and Flory³⁴ for *n*-pentane at 25°C. The results from the finite concentration studies were extrapolated to infinite dilution of the solute to obtain the values of $1/K_p$ utilized in this study.

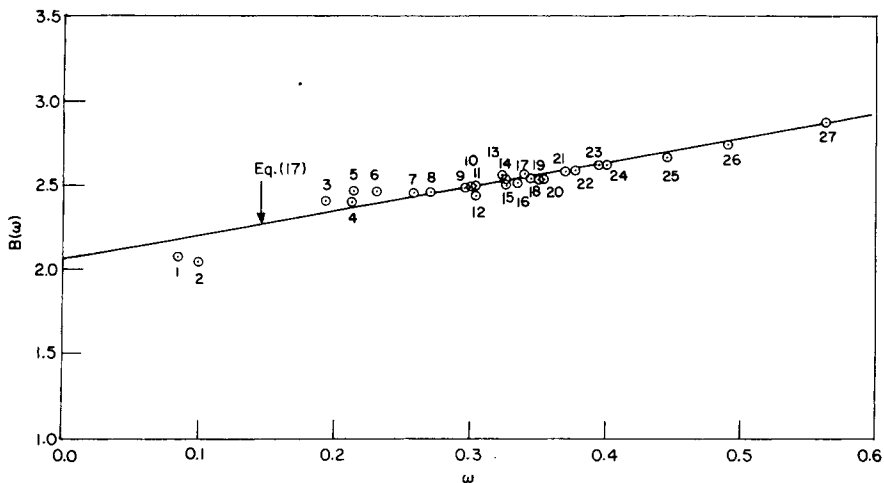


Fig. 6. Slope B of eq. (15) vs. ω for 27 nonpolar substances in LDPE.

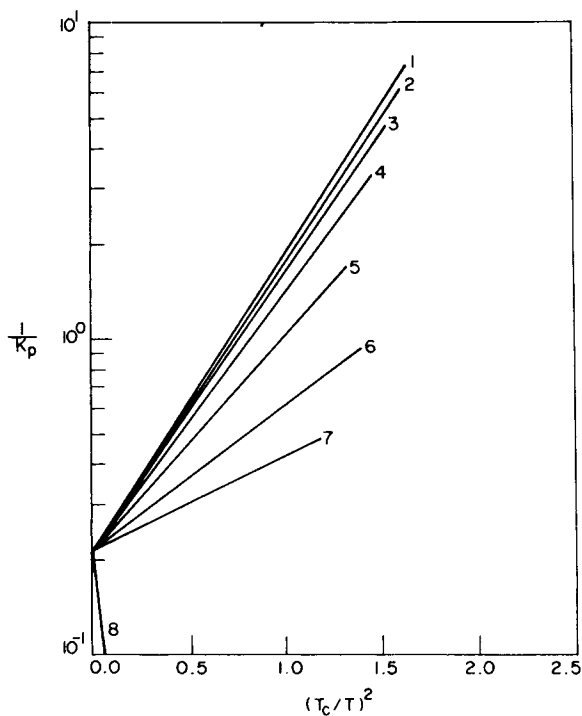


Fig. 7. $1/K_p$ vs. $(T_c/T)^2$ for polar and low molecular weight substances in LDPE: (1) methyl ethyl ketone; (2) methyl chloride; (3) vinyl acetate; (4) acetone, isopropyl alcohol; (5) sulfur dioxide; (6) carbon dioxide; (7) methane; (8) nitrogen.

TABLE I
Average Errors between Experimental and Calculated Values of $1/K_p$ for Low-Density Polyethylene

Solute	References	Temperature range (°C)	No. of points	Average absolute % error
Ethylene	17	125-250	6	4.2
Ethylene	8	124-300	5	4.9
Ethane	17	125-250	6	9.2
<i>n</i> -Butane	8	124-300	5	4.9
Benzene	8	110-200	5	5.4
Benzene	16	124-300	5	9.0
Benzene	1	135	1	1.2
<i>n</i> -Octane	8	110-200	5	2.7
<i>n</i> -Octane	16	124-300	5	2.9
<i>n</i> -Octane	15	120-145	2	0.6
3-Methylhexane	15	120-145	2	1.9
2-Methylheptane	15	120-145	2	6.2
3-Methylheptane	15	120-145	2	1.9
2,4-Dimethylhexane	15	120-145	2	1.3
2,5-Dimethylhexane	15	120-145	2	2.3
2,2,4-Trimethylpentane	15	120-145	2	0.9
3,4-Dimethylhexane	15	120-145	2	4.8
2,2,4-Trimethylhexane	15	120-145	2	9.9
Ethylbenzene	15	120-145	2	6.1
<i>p</i> -Xylene	15	120-145	2	1.0
<i>m</i> -Xylene	15	120-145	2	4.0
Mesitylene	15	120-145	2	2.5
<i>Cis</i> -Decalin	15	120-145	2	3.6
<i>Trans</i> -Decalin	15	120-145	2	8.1
Tetralin	15	120-145	2	18.7
<i>n</i> -Nonane	15	120-145	2	2.8
<i>n</i> -Nonane	1	135	1	3.9
<i>n</i> -Decane	1	135	1	6.4
<i>n</i> -Decane	15	120-145	2	1.4
<i>n</i> -Dodecane	15	120-145	2	7.7
Cyclohexane	16	110-200	5	16.5
Cyclohexane	1	135	1	15.6
Toluene	8	110-200	5	2.5
Toluene	16	124-300	5	9.7
Toluene	15	120-145	2	1.1
<i>n</i> -Hexane	8	110-200	5	3.6
<i>n</i> -Hexane	15	124-300	5	4.0
<i>n</i> -Heptane	15	110-200	5	7.4
Carbon tetrachloride	1	135	1	10.1
Chloroform	1	135	1	0.1
Butyl chloride	1	135	1	0.9
Chlorobenzene	1	135	1	12.9
1-Octene	1	135	1	3.1

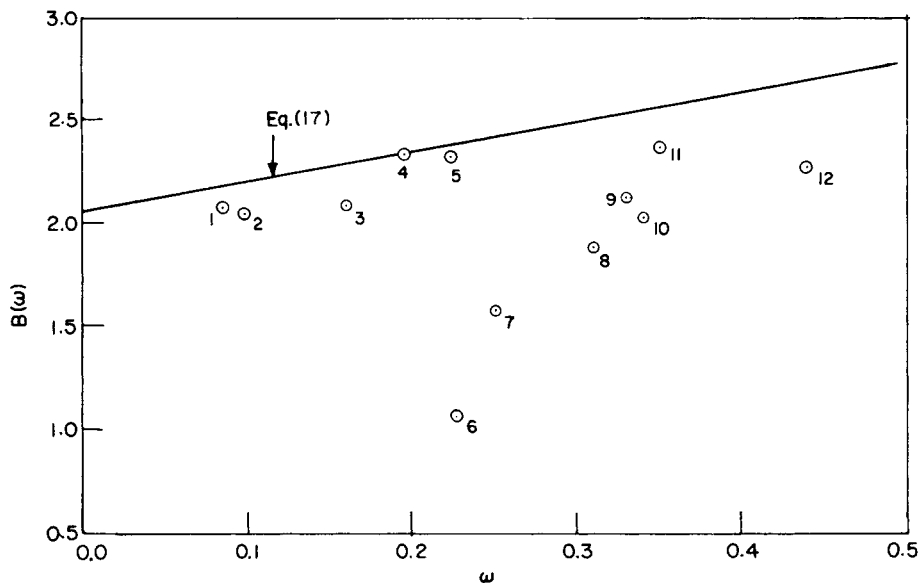


Fig. 8. Slope B of eq. (15) vs. ω for polar and quadrupolar substances in LDPE: (1) ethylene; (2) ethane; (3) methyl chloride; (4) butyl chloride; (5) chlorobenzene; (6) carbon dioxide; (7) sulfur dioxide; (8) acetone; (9) methyl ethyl ketone; (10) vinyl acetate; (11) 2-pentanone; (12) phenol.

TABLE II
Average Errors between Experimental and Calculated Values of $1/K_p$ for
High-Density Polyethylene

Solute	References	Temperature range (°C)	No. of points	Average absolute % error
Propane	23	149-260	3	4.0
Isobutane	23	149-260	3	5.8
3-Methylhexane	15	145-153	2	10.0
<i>p</i> -Xylene	15	145-153	2	3.7
<i>m</i> -Xylene	15	145-153	2	5.7
2-Methylheptane	15	145-153	2	9.0
3-Methylheptane	15	145-153	2	6.9
2,4-Dimethylhexane	15	145-153	2	6.7
2,5-Dimethylhexane	15	145-153	2	8.1
3,4-Dimethylhexane	15	145-153	2	1.0
2,2,4-Trimethylpentane	15	145-153	2	5.3
2,2,4-Trimethylhexane	15	145-153	2	3.4
Ethylbenzene	15	145-153	2	7.8
Mesitylene	15	145-153	2	4.0
Toluene	15	145-153	2	3.2
<i>n</i> -Octane	15	145-153	2	6.6
<i>n</i> -Nonane	15	145-153	2	4.4
<i>n</i> -Decane	15	145-153	2	9.5
<i>n</i> -Decane	24	151	1	4.3
<i>n</i> -Dodecane	15	145-153	2	4.3
<i>Cis</i> -Decalin	15	145-153	2	23.2
<i>Trans</i> -Decalin	15	145-153	2	8.6
Tetralin	15	145-153	2	14.9

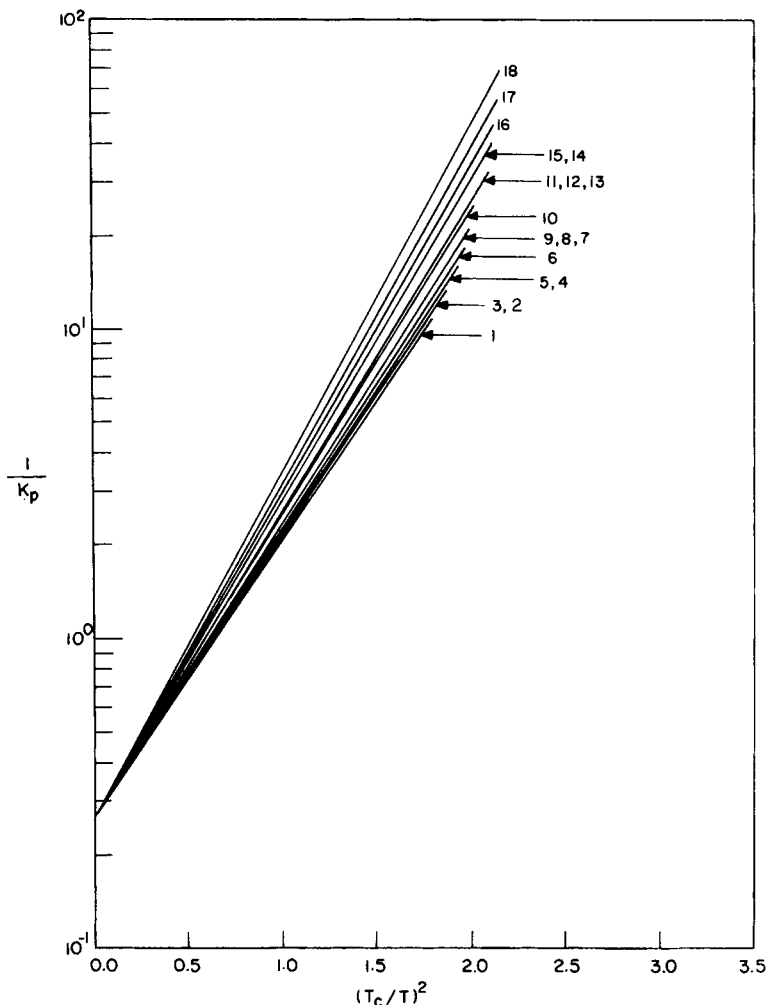


Fig. 9. $1/K_p$ vs. $(T_c/T)^2$ for 18 nonpolar substances in PIB, represented by eq. (19): (1) isobutane; (2) *n*-butane; (3) tetrachloromethane; (4) neopentane; (5) benzene; (6) cyclohexane; (7) isopentane; (8) 2,3-dimethylbutane; (9) *n*-pentane; (10) toluene; (11) 2,2-dimethylpentane; (12) *n*-hexane (13) 2,2,4-trimethylpentane; (14) *n*-heptane; (15) 2,5-dimethylhexane; (16) *n*-octane; (17) *n*-nonane; (18) *n*-decane.

Plots of $\ln(1/K_p)$ against $(T_c/T)^2$ resulting from these sources were prepared for all the substances for which sufficient data were available. As shown in Figure 9, the intercepts at $(T_c/T)^2 = 0$ were constant at $1/K_p = 0.26$. Therefore, for PIB the Henry's constant can be expressed as

$$\ln(1/K_p) = -1.347 + C(T_c/T)^2 \quad (19)$$

For 18 nonpolar solutes with $\omega > 0.15$, the slopes C of eq. (19) are related linearly to ω , as shown in Figure 10. For these substances, the following

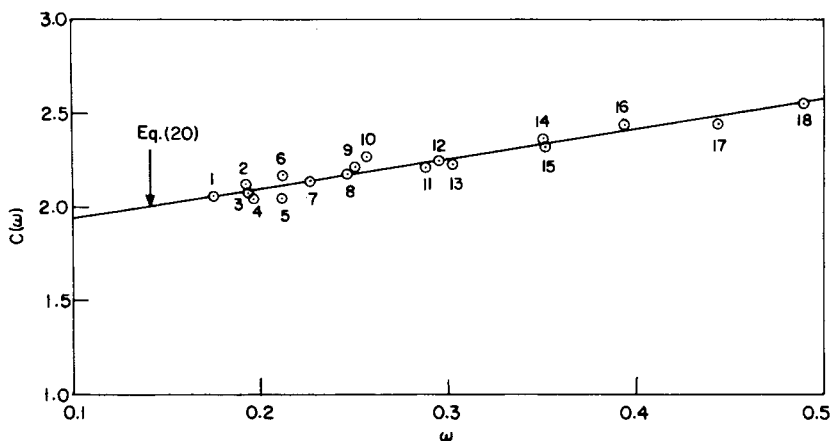


Fig. 10. Slope C of eq. (19) vs. ω for 18 nonpolar substances in PIB.

relationship represents the experimental values of C with an average deviation of 1.1%:

$$C = 1.790 + 1.568\omega \quad (20)$$

Combining eqs. (19) and (20) yields

$$\ln(1/K_p) = -1.347 + (1.790 + 1.568\omega)(T_c/T)^2 \quad (21)$$

In Figures 11–13, values of $1/K_p$ calculated from eq. (21) for *n*-pentane, *n*-hexane, and benzene are compared with the experimental values for these solutes. In Table III results of comparisons between the calculated and experimental values are presented for each data source. For 149 experimental points the average error is 8.9%. Hammers and deLigny²⁸ presented calculated results for 40–160°C in 20°C intervals derived from their chromatographic data. The values of $1/K_p$ resulting from this source at 140°C and 160°C are consistently lower than those calculated from eq. (21) and were not included in these comparisons. A similar trend is detected for the data at 120°C.

The PIB samples utilized in the experimental studies have viscosity average molecular weights greater than 10,000. It has been found that $1/K_p$ is virtually independent of molecular weight in this range, as shown in Figure 14 for benzene at 50°C, 75°C, and 100°C.

No solubility data are available for PIB for solutes with acentric factors in the range $0.01 < \omega < 0.15$ or for polar substances. The values of C of eq. (19) for argon, krypton, nitrogen, and methane are negative and substantially lower than those resulting from eq. (20). For the quadrupolar substance benzene, it can be seen from Figure 13 that the deviations between the calculated and experimental values of $1/K_p$ increase with decreasing temperature. The experimental value of $1/K_p$ for carbon dioxide⁵ is also lower than that calculated from eq. (21).

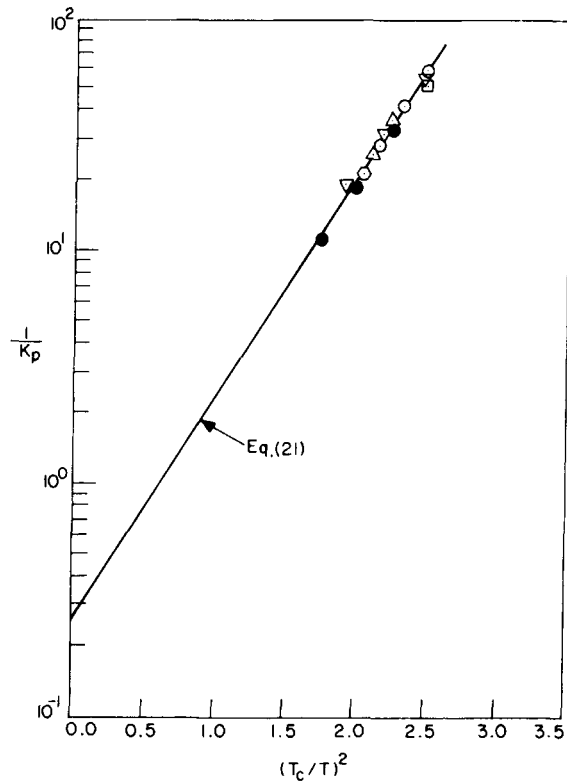


Fig. 11. $1/K_p$ vs. $(T_c/T)^2$ for *n*-pentane in PIB: (○) Prager et al.³²; (△) Newman and Prausnitz²⁵; (□) Eichinger and Flory³⁴; (▽) Leung and Eichinger²⁶; (◇) Baker et al.³³; (●) Hammers and deLigny.²⁸

DISCUSSION

A relationship for L , the heat absorbed in the vaporization of 1 mol of solute from an infinitely dilute polymer solution at constant temperature and atmospheric pressure, can be derived from the temperature variation of K_p as follows:

$$\frac{d \ln K_p}{dT} = \frac{L}{RT^2} \quad (22)$$

where R is the gas constant. For nonpolar solutes with $\omega > 0.08$ in LDPE, the following relationship is obtained from eq. (18):

$$L = (4.114 + 2.876\omega)(T_c^2/T)R \quad (23)$$

Similarly, for nonpolar solutes with $\omega > 0.15$ in PIB, the heat of vaporization is obtained from eq. (21) as

$$L = (3.580 + 3.136\omega)(T_c^2/T)R \quad (24)$$

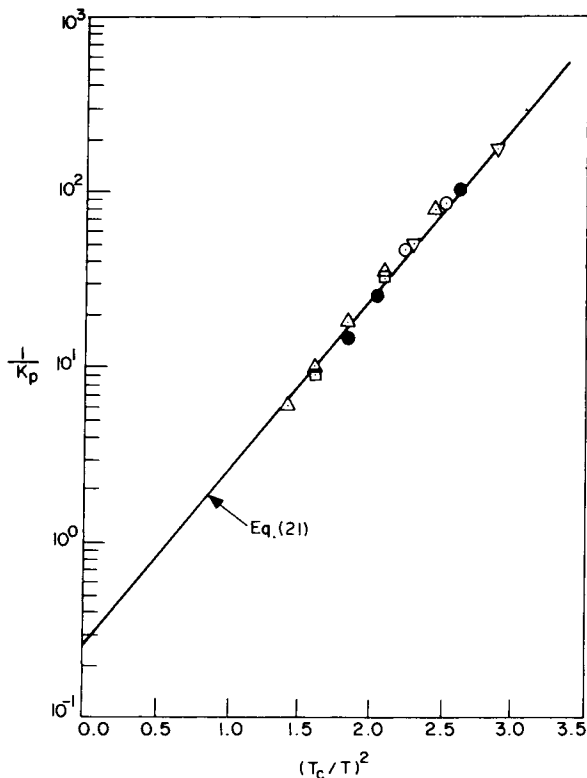


Fig. 12. $1/K_p$ vs. $(T_c/T)^2$ for *n*-hexane in PIB: (○) Leung and Eichinger²⁷; (△) Newman and Prausnitz¹⁶; (□) Lichtenthaler et al.²⁹; (▽) Leung and Eichinger²⁶; (●) Hammers and deLigny.²⁸

These relationships indicate that the temperature dependences of the Henry's constants in LDPE and PIB solutions for the appropriate temperature ranges are strongly influenced by the molecular interactions of the solute and polymer.

In Table IV, heats of vaporization calculated from eq. (23) for LDPE solutions at 135°C are compared with the values obtained by DiPaola-Baranyi et al.¹ from the temperature variations of experimental retention volumes. It can be seen that, in general, good agreement is obtained for nonpolar solutes. For polar solutes the calculated values of L are higher than those resulting from the experimental data.

The relationships developed in this study for solubilities are valid for low pressures and infinite dilution of the solutes. However, if Henry's law is applicable, eq. (18) for LDPE solutions and eq. (21) for PIB solutions can be utilized with eq. (12) to calculate solubilities in the polymers at elevated pressures. For a liquid solute, the partial molar volume can be approximated as the liquid molar volume. The relationships of this study can also be utilized to determine χ values of liquid solutes through eq. (14). Solubilities at elevated pressure and finite concentrations can also be estimated with the relationships for Henry's constants in conjunction with an equation of state for the polymer-solute mixture.^{3,4}

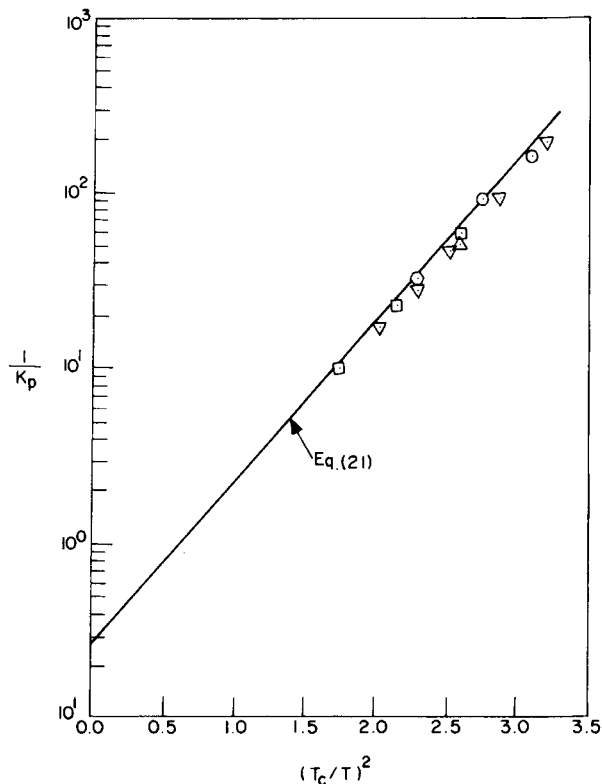


Fig. 13. $1/K_p$ vs. $(T_c/T)^2$ for benzene in PIB: (○) Leung and Eichinger²⁷; (△) Newman and Prausnitz²⁵; (□) Newman and Prausnitz¹⁶; (▽) Hammers and deLigny²⁸; (⊙) Lichtenthaler et al.²⁹

The results of this study indicate that the solubilities of nonpolar solutes with appreciable size ($\omega > 0.1$) exhibit similar behavior in LDPE for temperatures greater than 110°C and in PIB for temperatures greater than 25°C. The solubility of a nonpolar solute with $\omega = 0.3$ is virtually the same in these polymers at $(T_c/T)^2 = 1$ and is about 13% higher in LDPE at $(T_c/T)^2 = 1.5$. Similar behavior is expected for Henry's constants of nonpolar solutes in other nonpolar polymers. For these systems, the variation of $\ln(1/K_p)$ with $(T_c/T)^2$ is strongly dependent on the acentric factors of the solutes. The solubilities of polar solutes in nonpolar polymers are lower, and additional solute parameters are required to characterize the behavior of these systems. Additional solubility data for polar solutes and for nonpolar substances with small molecular size are required to extend the results of this study.

For polystyrene, no variation of the slope of eq. (2) with acentric factor could be detected for nonpolar or slightly polar solutes.⁷ For polar polymers, the solubilities of nonpolar solutes are lower than for polar substances.¹

TABLE III
Average Errors between Experimental and Calculated Values of $1/K_p$ for Polyisobutylene

Solute	References	Temperature range (°C)	No of points	Average absolute % error
Propane	32	35	1	12.3
Isobutane	32	25-47	3	0.5
<i>n</i> -Butane	32	25-47	3	4.2
Carbon tetrachloride	28	40-120	5	1.8
Neopentane	32	25-47	3	9.9
Benzene	27	25-65	3	19.9
Benzene	16	50-150	5	9.3
Benzene	25	25-50	3	33.9
Benzene	29 (capillary)	50-100	3	27.1
Benzene	29 (packed)	75-125	3	10.8
Benzene	28	40-120	5	22.0
Cyclohexane	26	25	1	2.7
Cyclohexane	16	50-150	5	18.4
Cyclohexane	25	25-50	3	11.5
Cyclohexane	29 (capillary)	50-100	3	7.9
Cyclohexane	29 (packed)	75-125	3	15.6
Cyclohexane	28	40-120	5	8.6
Isopentane	32	25-47	3	4.9
2,3-Dimethylbutane	28	40-120	5	6.2
<i>n</i> -Pentane	28	40-80	3	5.6
<i>n</i> -Pentane	34	25	1	9.1
<i>n</i> -Pentane	33	25-55	4	2.5
<i>n</i> -Pentane	27	25-65	3	5.7
<i>n</i> -Pentane	32	25-47	3	1.7
<i>n</i> -Pentane	25	25-50	3	3.2
Toluene	16	50-150	5	3.7
2,2-Dimethylpentane	28	40-120	5	8.8
<i>n</i> -Hexane	27	25-65	3	9.1
<i>n</i> -Hexane	16	50-150	5	9.5
<i>n</i> -Hexane	29 (capillary)	50-100	3	6.5
<i>n</i> -Hexane	29 (packed)	75-125	3	6.4
<i>n</i> -Hexane	28	40-120	5	9.5
2,2,4-Trimethylpentane	28	40-120	5	9.0
<i>n</i> -Heptane	28	40-120	5	7.4
<i>n</i> -Heptane	27	25-65	3	7.3
2,5-Dimethylhexane	28	40-120	5	7.4
<i>n</i> -Octane	28	40-120	5	5.7
<i>n</i> -Octane	27	25-65	3	8.1
<i>n</i> -Nonane	26	25	1	0.7
<i>n</i> -Nonane	28	60-120	4	4.8
<i>n</i> -Decane	28	60-120	4	4.6

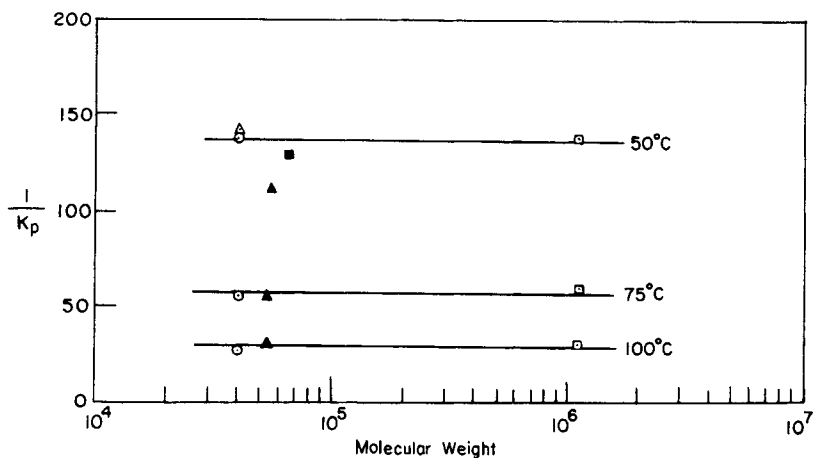


Fig. 14. $1/K_p$ vs. molecular weight for benzene in PIB: (○) Hammers and deLigny²⁸; (△) Leung and Eichinger²⁷; (□) Newman and Prausnitz¹⁶; (▲) Lichtenthaler et al.²⁹; (■) Newman and Prausnitz.²⁵

Additional studies with different types of polymers are required to establish the general behavior of solubilities in molten polymer systems.

TABLE IV
Comparisons of Calculated Heats of Vaporization for Low-Density Polyethylene with Reported Values at 135°C

Solute	Heat of vaporization, eq. (23) (kcal/mol)	Heat of vaporization ¹ , (kcal/mol)
Carbon tetrachloride	7.04	6.22
<i>n</i> -Nonane	9.28	9.07
<i>n</i> -Decane	10.26	10.17
Chloroform	6.63	6.05
Cyclohexane	7.04	6.30
1-Octene	8.16	8.09
Butyl chloride	6.78	6.32
Chlorobenzene	9.40	8.16
Benzene	7.27	6.46

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