Solubility of Nonpolar and Slightly Polar Organic Compounds in Low-Density Polyethylene by Inverse Gas Chromatography with Open Tubular Column

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Synopsis

Inverse gas chromatography (IGC) with open tubular column was used to determine low pressure solubilities of 13 organic solutes in low-density polyethylene (LDPE) for temperatures from 50 to 175°C. Based on the principle of corresponding states, two simple correlation equations were developed for estimation of the solubility of nonpolar and slightly polar solutes in rubbery and molten LDPE.

INTRODUCTION

Exposure to residual volatile compounds during polymer processing has raised concern about potential health hazards and stimulated an interest in devolatilization processes used to remove unwanted volatile compounds. To improve the devolatilization process and to meet environmental and safety regulations, accurate thermodynamic properties such as solubility and the interaction between components of the polymer/solute system are essential. Inverse gas chromatography (IGC) is of value in gaining the required knowledge. Since most of the IGC data reported in the literature has been obtained for the case of infinite dilution of solutes in the low pressure range, the data are directly applicable to the devolatilization process. On the other hand, high pressure data are required for an understanding of the behavior of low molecular weight compounds in polymers during the extrusion process. Through proper thermodynamic treatment, low pressure data can be utilized to estimate the required high pressure data.

The solubility data of various compounds in low-density polyethylene (LDPE) have previously been determined for a number of gases and vapors at various temperatures and pressures by means of IGC with packed columns.[1-5] Vapor pressure equilibrium sorption studies using LDPE film[6] and using LDPE pellets[7] have also been reported. A piezoelectric sorption technique[8] and gas and vapor transport through LDPE membranes[9,10] have also been used.

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The application of IGC with open tubular column to the study of thermodynamic properties of polymer/solute systems is rare. The principal advantages of the open tubular column are that the pressure drop across the column can be minimized and the thickness and distribution of the polymer coating can be easily controlled. Lichtenthaler et al.[11] used both packed and open tubular columns to investigate thermodynamic properties of polyisobutylene, poly(vinyl acetate), and polydimethylsiloxane. A glass capillary column was used to study the interactions for polystyrene/solute systems.[12] Both studies indicated that packed and capillary IGC techniques may result in some differences in the thermodynamic properties for a given polymer/solute system. In light of their results, the open tubular column IGC technique has been utilized in the present work to measure the solubilities of thirteen solutes in rubbery and molten LDPE. In addition, available literature data have been included in the analysis to develop simple correlation equations for estimating the solubility of nonpolar and slightly polar organics in rubbery and molten LDPE.

PREVIOUS WORK

The solubility of a number of gases and vapors in rubbery LDPE and high-density polyethylene (HDPE) was studied by Rogers et al.[6] and Michaels and Bixler[7] using vapor pressure equilibrium sorption techniques. Both articles reported that solubility was independent of polymer molecular weight and mode of polymer synthesis, but that solubility was a linear function of the volume fraction of the amorphous portion of polymer. Michaels and Bixler[7] suggested a correlation equation relating the solubility constant to the Lennard–Jones potential force constant. Stern et al.[13] used transport through membranes to measure the solubility of carbon dioxide in LDPE at 0.4, 9.0, and 40.5°C and at pressures up to 54.4 atm. Based on the principle of corresponding states, a relationship between logarithmic solubility and the square of the inverse reduced temperature was proposed.[13] Later, using thermodynamic considerations, Stern and Shiah[14] proposed a correlation between the quantity solubility times critical pressure, P_c, of organic compounds and the inverse reduced temperature for several gases and vapors in silicone rubber, rubber, and other media. The correlation equation presented by van Krevelen and Hoftyzer[15] for evaluating the solubility of gases and vapors in polymers required additional information at the glass transition temperature. Kulkarni and Stern[10] determined the solubility for carbon dioxide, methane, ethylene, and propane in LDPE at temperatures of 5, 20, and 35°C and gas pressures up to 40 atm. Durill and Griskey[9,16] reported the solubility of several gases in LDPE using transport through membranes at 188°C and studied the relationship between the Henry's constants and the Lennard–Jones potential force constant. For molten LDPE at finite solute concentrations, the solubility data available in the literature are n-pentane at 109.9°C by van der Waals and Hermans[17]; nitrogen and methane for temperatures from 126 to 277°C by Lundberg et al.[18]; nitrogen at 125°C by Bonner and Chang[8]; and ethylene at temperatures of 126, 140, and 155°C and at gas pressures up to 69 atm by Chang and Bonner.[19] For molten LDPE and organic compounds at infinite dilution

using the packed column IGC technique, considerable low pressure solubility data are available at various temperature.[1-5] Maloney and Prausnitz[3] proposed a correlation equation for nonpolar substances in molten LDPE with 12% average error in Henry's law constant. They also performed high pressure IGC experiments up to 600 atm to calculate Henry's law constants in the temperature range from 130 to 300°C for the ethylene/LDPE system at infinite dilution. They presented equations for estimating the Henry's law constant of nitrogen and ethylene in LDPE.

All of the above IGC studies were carried out using packed columns. Lichtenthaler et al.[11] utilized both packed and open tubular columns to study the effect of polymer film thickness on thermodynamic properties of solutes with poly(isobutylene), poly(vinyl acetate), and poly(dimethyl siloxane) and suggested that polymer-solute interactions for a bulk polymer might be different from those for a thin film absorbed on granular packing. The different results obtained by packed and capillary techniques has also been attributed to the different morphology or degree of ordering in thin films absorbed onto a surface and in bulk polymer.[20] Factors such as polymer loading, injection sample size, carrier gas flow rate, carrier gas solubility, polymer molecular weight, and molecular weight distribution have been associated with the accuracy of IGC measurements.[3,4,21-27] Several review articles on the application of IGC to measure thermodynamic properties are available in the literature.[28-32]

EXPERIMENTAL

Apparatus

A Tracor Model 565 gas chromatograph (Tracor Instruments, Austin, TX) equipped with flame ionization detector was modified to facilitate the measurement of carrier gas flow rate and pressure drop across the column. Nitrogen was utilized as the carrier gas. Methane was used as a noninteractive marker. Oven temperature was controlled to within ±0.1°C. The pressure drop across the column was determined to within ±0.05 mm Hg with a calibrated Validyne Model DP215-46 pressure transducer (Validyne Engineering Corp., Northridge, CA) connected to a Hewlett-Packard 3467A Logging Multimeter. The flow rate of nitrogen gas was measured to within ±0.5% error by means of a Tylan Model FC-260 mass flow controller (Taylan Corp., Carson, CA). A Fisher Recordall chart recorder was used to record the peak maximum elution time and the time difference between probe and marker peaks was taken as the net retention time of the probe molecule.

Column Preparation

The preparation of open tubular columns has been described in detail.[33] In the present work, a 15-m-long stainless-steel column with 1/16-in. inner diameter was used. Prior to coating, the column was cleaned following the procedures suggested by Mon.[34] The polymer solution was prepared by dissolving a known weight of LDPE in p-xylene, with 0.15 wt% 4,4'-thio-bis(6-tert-butyl-M-cresol) antioxidant, at 85°C for 48 h. The polymer solution was

introduced into a 10 cc coating reservoir (Glass Engineering, Inc., Austin, TX) by a short vacuum line. By using the dynamic coating technique, nitrogen was used to push the solution through the column at a pressure of approximately 0.5 atm and temperature about 85°C. Then the column was placed in a vacuum oven at 90°C until the weight of the column reached a constant value. The weight of polymer coated inside the column was determined by weighing the column before and after coating. This procedure was repeated as many times as required until the desired film thickness was attained. A balance accurate to within ±0.5 mg was used; therefore, the amount of polymer inside the column was known to within ±0.5%. The weight of LDPE inside the column was determined to be 0.0977 g.

Materials

Low-density polyethylene was obtained from the Cities Service Company (Tulsa, OK). The density of the LDPE was 0.918 g/cc at room temperature as measured by pycnometer. The degree of crystallinity per gram of sample and the melting temperature as measured by Differential Scanning Calorimetry (DSC) were 27.5% and 112°C, respectively. Regent-grade solvents were received from standard laboratory sources and used without treatment.

Procedure

After a column was placed in the IGC oven, it was conditioning for 12 h at 205°C with nitrogen flowing at 10 cc/min. Then the oven temperature was adjusted to the desired value. The temperature of the injector block was kept in the range from 150 to 180°C. To obtain the maximum sensitivity, the detector temperature was set at 250°C, the flow rate of air and hydrogen which provided the flame were approximately 30 and 20 cc/min, respectively. The solute sample size was as small as possible to obtain a sharp peak and to avoid operating in the nonlinear sorption-isotherm range, which could give rise to skewing of elution peaks and corresponding anomalous values of the net retention time.[22] The retention time at a given temperature was measured at several flow rates ranging from 8 to 20 cc/min for a variety of solutes. Each measurement was repeated at least three times and averaged. The pressure drop recorded by the digital logger was between 1 and 3 psi.

DATA REDUCTION

The specific retention volume, V_g, is given by

$$V_g = \frac{273.15 (t_g - t_r)Q}{TW_2\bar{P}}$$

(1)

where the symbols are defined in the nomenclature section at the end of this article. To account for the finite pressure drop through the column, the average pressure, $\bar{P}$, across the column was introduced. The average pressure drop can be calculated by

$$\bar{P} = P_0 \cdot J_2^3 \tag{2}$$

where J_2^3 is the pressure correction factor[35]

$$J_2^3 = \frac{2}{3} \cdot \frac{(P_i/P_0)^3 - 1}{(P_i/P_0)^2 - 1} . \tag{3}$$

By assuming ideal gas behavior, the Henry's law constant $1/K_p$ as defined by Stiel and Harnish[23] is obtained from Eq. (1) as

$$1/K_p = \frac{V_g^0}{P_1} = V_g . \tag{4}$$

ERROR ANALYSIS

Estimation of the standard deviation of V_g, S_{V_g}, can be obtained from the standard deviations of the individual parameters by[36]

$$S_{V_g} = \left[\Sigma \left(\frac{\partial V_g^2}{\partial x} \right) S_x^2 \right]^{\frac{1}{2}} . \tag{5}$$

Applying this formula to eq. (1), the standard deviation of V_g can be estimated. One example of the error analysis performed on the data generated in the current study is presented in Table I as an illustration. Obviously, the largest error resulted from the flow rate measurement. In this case, the estimated standard deviation and percentage error of V_g were ±0.79 cc/g and 3.9%, respectively. For all solutes, worst-probable-case errors in V_g averaged 8, 6, and 5% at 175°, 150°, and 125°C, and 4% at temperatures below the melting point of LDPE (with few exceptional cases at 50°C). For those solutes possessing carbon number greater than 8, broad peaks were detected which might result from the slow diffusion of larger solutes in the stationary phase; hence, thermodynamic equilibrium might not have been established. The expected worst error for this group of solutes is 10% at 50°C.

TABLE I
Source of Errors in IGC Measurement of LDPE/Octane at 150°C

Variables	Measured values x	Standard deviation S_x	$100\ S_x/x$	Variance $(\partial V_g/\partial x)^2\ S_x^2$
Q	0.1440 cc/s	±0.0005	0.35	0.50
t_g	79.83 s	±0.20	0.25	0.033
t_r	57.53 s	±0.20	0.35	0.033
J_2^3	1.044	±0.001	0.10	0.040
P_0	1.0 atm	±0.0001	0.10	0.0004
w_2	0.0977 g	±0.0005	0.51	0.011
T	423.15 K	±0.1	0.02	0.00003
v_g	20.27 cc/g	±0.79	3.9	0.617

RESULTS AND DISCUSSION

The specific retention volumes for all solutes studied are listed in Table II. Extrapolation to zero flow rate was required to obtain the specific retention data in all cases. Comparison of Henry's Law constants with literature data is given in Table III. It was observed that the results obtained in this work were consistently lower by less than 14% when compared with the average literature data. Similar results were observed and explained by Lichtenthaler et al.[11] as well as Lipatov and Nesterov[20] who attributed the different results obtained by packed and capillary techniques to the different morphology or degree of ordering in thin films adsorbed onto the surface and in bulk polymer.

Estimation of the solubility of untested probes in LDPE would be possible if a suitable correlation were developed using the existing solubility data. There are four correlation equations in the literature for estimation of solubility in LDPE. The applicability of correlation equations suggested by Michaels and Bixler[7] and Durill and Griskey[16] is limited at 25 and 188°C, respectively. In addition, the required Lennard–Jones potential force constant of the low-molecular weight compound[7] is usually not available. Solubility data above and below the melting point of LDPE were utilized in correlations by Stern et al.[13] and Maloney and Prausnitz.[3] In general, the one by Stern et al.[13] is useful for gases at low temperatures. On the other hand, the equation by Maloney and Prausnitz[3] is applicable for nonpolar solutes above the melting point of LDPE. It seems that the need to correlate separately the solubility data above and below the melting point of LDPE is indicated. At temperatures below the melting point, the solubility in a semicrystal polymer is normally expressed and reported in terms of 100% amorphous polymer base. By using the data and procedures reported by Charlesby and Callagham,[37] the volume fractions of amorphous LDPE used in the present study were estimated to be 0.628, 0.704, and 0.888 at 50, 75,

TABLE II
Specific Retention Volumes V_g (cm³/g) Data

Probes	50°C[a]	75°C[a]	100°C[a]	125°C	150°C	175°C
Tetrahydrofuran	33.86	19.24	14.40	11.92	—	—
1-Octene	175.38	76.57	49.08	35.70	19.24	10.24
1-Nonene	446.30	174.77	99.40	67.45	33.47	17.81
Heptane	79.08	37.77	26.73	21.69	12.27	—
Octane	207.47	87.73	54.91	39.45	21.96	12.55
Nonane	542.19	198.00	112.21	74.04	36.73	19.17
Decane	1434.85	452.90	233.71	139.22	63.97	31.26
Benzene	58.01	32.52	22.59	18.96	11.79	—
Toluene	169.47	81.46	50.92	40.17	22.18	12.94
Chlorobenzene	347.65	150.76	93.35	64.65	34.71	19.43
p-Xylene	481.42	188.26	112.99	74.37	38.56	21.50
Cumene	626.61	246.15	142.37	94.99	49.38	25.11
n-Butylbenzene	2172.69	729.39	380.05	221.75	100.61	49.15

[a] Data presented in Table II are without conversion to 100% amorphous LDPE.

TABLE III
Comparison of Henry's Law Constants with Literature Data at Various Temperatures

Probes	Temp (°C)	$1/K_p$	Reference
Heptane	125	23.28	2
		21.69	This study
	150	13.26	2
		12.27	This study
Octane	150	23.62	2
		24.90	3
		21.76	This study
1-Octene	135	31.50	5
		27.63	This study
Decane	135	115.55[a]	1
		110.81	5
		100.85[a]	This study
Toluene	150	24.59	2
		25.88	3
		21.96	This study
	175	13.80	2
		16.20[a]	3
		12.94	This study

[a] Values obtained by linear interpolation from a plot of $\ln(1/K_p)$ vs. reciprocal temperature.

and 100°C, respectively. Based on the solubility data available in the literature and the data from this study, the results of correlations are shown in Figures 1 and 2. For the sake of clarity, not all of the available data are plotted in these figures.

In Figure 1, the largest deviations were observed for gases such as methane, oxygen, argon, carbon monoxide, and carbon dioxide and for polar vapors such as chloroform, tetrahydrofuran, and chlorobenzene. The solubility data of helium and nitrogen by Michaels and Bixler[7] were too low to be shown in Figure 1. The quadrapole effect might be responsible for the deviations of carbon dioxide and nitrogen while the anamolous low solubility of helium might be due to the nature of the quantum gas. The thermodynamic behavior of quadrapoles and quantum gases has been discussed by Prausnitz.[38] A similar situation was found in Figure 2. Since the effect of polarity decreases as temperature increases, the deviations of polar substances such as acetone, methyl ethyl ketone, isopropyl alcohol, vinyl acetate, tetrahydrofuran, and chlorobenzene become less prominent as indicated in Figure 2. It was also found that at the same reduced temperature the solubility of polar substance was lower than that of nonpolar ones. This is expected and supported by the general rule of thumb, likes dissolve likes. Consequently, in the regression analysis, the light gases and polar substances were eliminated.

The general correlation model applicable to both rubbery and molten LDPE is

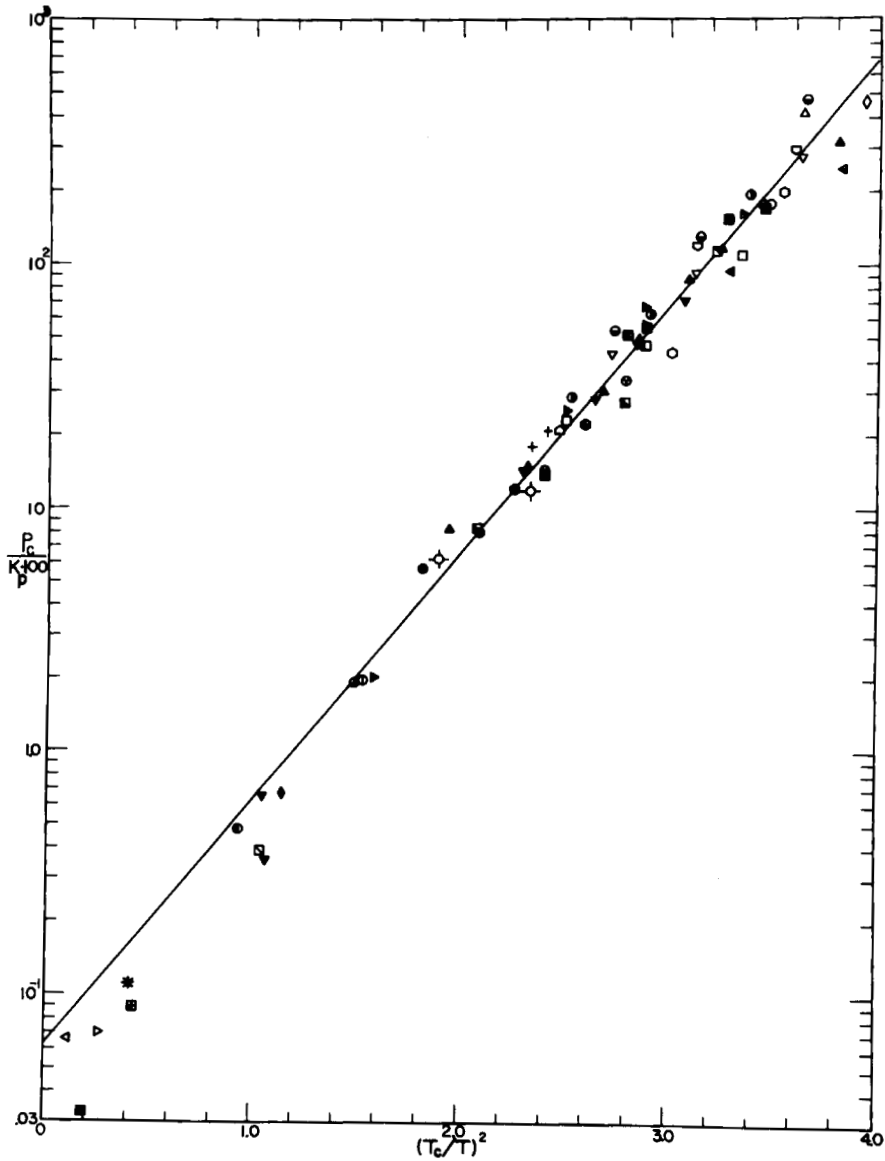$$\ln\left(\frac{P_c}{K_p \cdot 100}\right) = a + b\left(\frac{T_c}{T}\right)^2 \tag{6}$$

Fig. 1. Relationship between $\ln(P_c/100 \cdot K_p)$ and $(T_c/T)^2$ for low-density polyethylene in the rubbery state. Data taken from Ref. 6: (◇) isobutylene; (□) n-pentane; (⊠) n-hexane; (■) n-heptane; (△) n-octane; (○) carbon tetrachloride; (+) methyl bromide; (▽) ethyl bromide; (⊗) cyclohexane; (◎) benzene; (◇) toluene; (▲) ethylbenzene; (▲) chloroform; (⊞) carbon monoxide; (▷) oxygen; (◁) argon; (✳) methane; (◨) carbon dioxide; (⊕) sulfur hexafluoride; (▼) ethane; (⊕) propylene; (◍) propane; (●) methyl acetylene. Data taken from Ref. 10: (▼) carbon dioxide; (◐) ethylene; (▶) propane; (⊞) methane. Data from this study: (◨) tetrahydrofuran; (⊘) heptane; (△) octane; (▽) 1-octene; (◑) nonane; (▷) 1-nonene; (◒) decane; (⊕) benzene; (◁) chlorobenzene; (□) toluene; (▽) p-xylene; (△) cumene; (▽) n-butylbenzene.
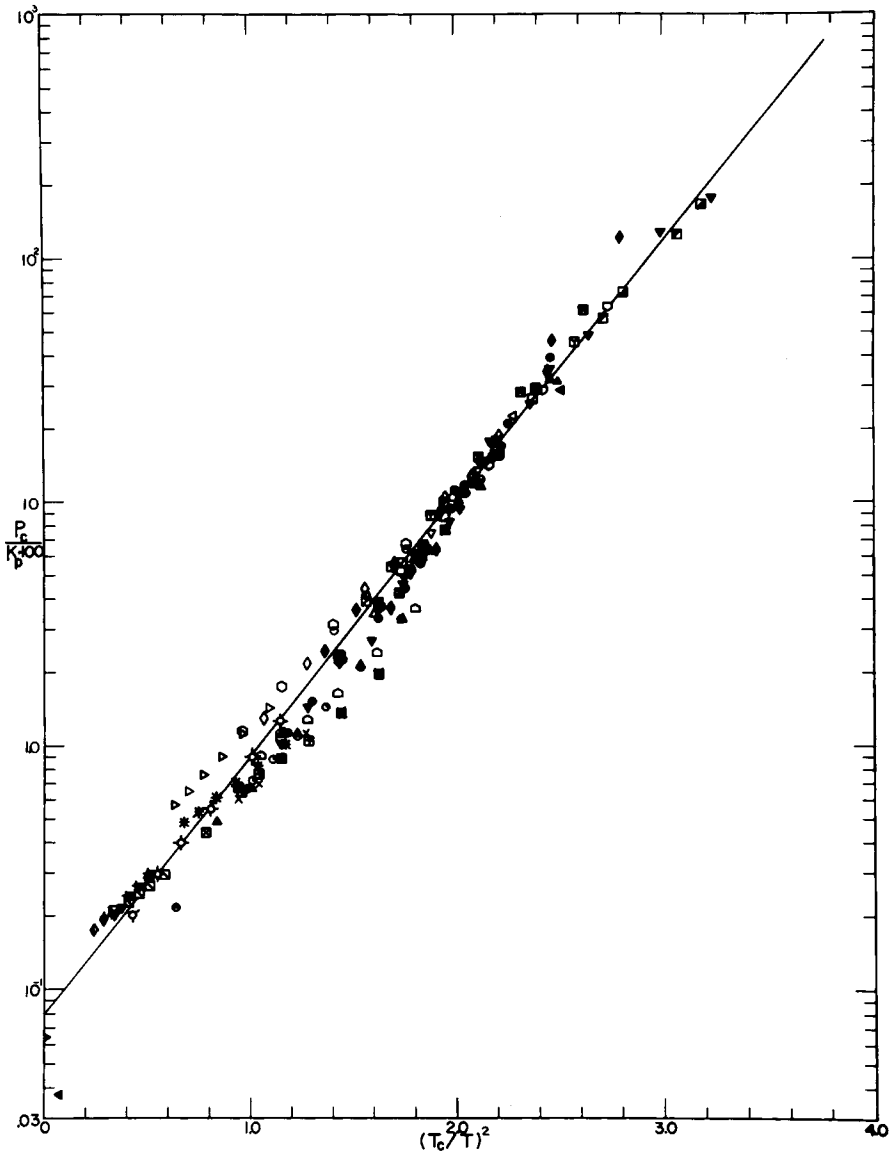
Fig. 2. Relationship between $\ln\left(\dfrac{P_c}{100 \cdot K_p}\right)$ and $(T_c/T)^2$ for low-density polyethylene at molten state: Data taken from Ref. 1: (●) 3-methylhexane; (⊞) n-octane; (⏺) 2-methylheptane; (⊖) 3-methyl heptane; (▼) 2,4-dimethylhexane; (⊠) 2,5-dimethyl hexane; (⊠) 3,4-dimethyl hexane; (◆) 2,2,4-trimethyl pentane; (◁) n-nonane; (▲) 2,2,4-trimethyl hexane; (◑) decane; (◈) n-dodecane; (⊗) toluene; (△) ethylbenzene; (◈) p-xylene; (▽) m-xylene; (◪) mesitylene; (◪) cis-decalin; (◼) trans-decalin. Data taken from Ref. 2: (⊕) cyclohexane; (△) octane; (▽) hexane; (⊕) heptane; (○) benzene; (▱) toluene; (⌑) p-xylene; (▽) trans-decalin. Data taken from Ref. 3: (◌) octane; (○) benzene; (⊠) hexane; (◇) butane; (◆) ethylene; (▲) vinyl acetate; (◇) toluene. Data taken from Ref. 4: (×) acetone; (▷) methyl chloride; (◪) carbon dioxide; (◕) vinyl acetate; (✳) sulfur dioxide; (+) ethylene; (▽) ethane; (▢) methylethylketone; (⊞) isopropyl alcohol. Data taken from Ref. 9: (◀) nitrogen; (▽) carbon dioxide; (◕) monochlorodiflouromethane; (▶) argon. Data from this study: Symbols are the same as in Figure 1.

By plotting $\ln\left(\dfrac{P_c}{K_p \cdot 100}\right)$ vs. $\left(\dfrac{T_c}{T}\right)^2$ the coefficients a and b can be obtained

from the intercept and slope, respectively. By utilizing 57 data points of 21 different solutes for rubbery LDPE and 163 data points of 33 different solutes for molten LDPE the constants a and b were estimated; the statistical information of the regression analysis is given in Table IV. Comparison of the predicted Henry's constant by Maloney and Prausnitz[3], Stern et al.[13], this study, and average of all literature data at various temperatures is given in Table V. It must be pointed out that the compounds which appear in Table V are randomly chosen and given only as examples. Further comparisons can be made by referring to the original literature source. Within experimental error and recognizing the inherent differences among various experimental techniques, the proposed simple equations are useful for predicting the thermodynamic properties of LDPE/solute systems. The application of these correlations to estimate activity coefficient, heat of solution, and partial molar heat of mixing of solute at infinite dilution has been presented by Stiel and Harnish[23] and Tseng et al.[39,40]

The Henry's Law constant of a solute at elevated pressure is often required in extrusion process. The pressure dependence on the Henry's Law constant can also be estimated by using the considerations proposed by Stiel and Harnish.[23]

It has been reported by Maloney and Prausnitz[3] that solubility in LDPE is nearly independent of polymer molecular weight distribution and degree of long-chain branching. The study of interactions between linear or branched polystyrenes and solutes[26] also support this observation. Therefore, an attempt was made to justify the applicability of the suggested equations to HDPE/solute systems. The data of Schreiber et al.[1] agreed with the correlation by less than 12% error; however, the results by Varsano and Gilbert[41] show large deviations from the proposed equations. The applicability of the proposed equations to HDPE requires further study.

CONCLUSION

Solubility data of thirteen solutes in low-density polyethylene have been obtained for temperatures between 50 and 175°C by using inverse gas chromatography with open tubular column. The specific retention volumes reported in the present study were consistently lower by less than 14% when compared with literature data generated by packed IGC and other techniques. The reasons for this discrepancy were given by previous investigators.[11,20] However, within experimental error and in light of differences

TABLE IV
Statistical Information for the Regression Analysis of Solute Solubility

System	Intercept a in eq. (6)	Slope b in eq. (6)	Correlation coefficient R^2
Rubbery LDPE	-2.764 ± 0.210[a]	2.325 ± 0.071[a]	0.9874
Molten LDPE	-2.523 ± 0.066[a]	2.411 ± 0.036[a]	0.9912

[a] Within 95% confidence interval.

TABLE V
Comparison of the Predicted Henry's Law Constant by Maloney and Prausnitz,[3] Stern et al.,[13] This Study, and Average Literature Data at Various Temperatures

| Probes | T (°C) | Estimated values | | | Average experimental literature values |
		Ref. 3	Ref. 13	This study	
Ethane	25	—	0.81	1.50	1.35
	150	0.60	0.20	0.58	0.52
Pentane	25	—	34.56	60.57	63.75
Heptane	25	—	283.7	482.2	578.0
	125	21.15	6.44	25.14	22.49
p-Xylene	25		3801.5	3737.3	4010.0
	125	90.92	27.61	74.42	80.00
Cumene	150	62.97	17.60	53.90	49.38
Ethylbenzene	25	—	3928.2	3746.68	3208.99
1-Octene	135	29.60	8.08	32.26	29.57
Toluene	150	25.90	8.70	22.04	24.14
	175	15.78	4.99	13.21	14.31
cis-Decalin	120	468.88	222.45	566.38	540.10
2,2,4-Trimethylhexane	145.1	23.71	7.17	31.96	26.67

among various techniques, two simple, suitable correlation equations were developed by utilizing the solubility data available in the literature as well as the results from this study. For the molten LDPE, the applicability of the equation presented here is comparable to the one suggested by Maloney and Prausnitz[3]; for the rubbery LDPE, the equation presented here is better. These equations are useful in estimating thermodynamic properties when no data other than critical pressure and temperature are available.

Appendix: NOMENCLATURE

K_p Henry's law constant defined in eq. (4)
$1/K_p$ solubility at a total pressure of approximately 1 atm [cm³ (STP)/g · atm]
P average pressure in column (atm) defined in eq. (2)
P_1 vapor pressure of solute (atm)
P_i pressure at inlet of column (atm)
P_0 pressure at outlet of column (atm)
P_c critical pressure of solute (atm)
Q carrier gas flow rate at atmospheric pressure (cm³/s)
S standard deviation
T temperature (K)
T_c critical temperature (K)
t_g retention time of solute in column (s)
t_r retention time of reference gas in column (s)
V_g specific retention volume (cm³/g) corrected to 273 K and the average column pressure
V_g^0 specific retention volume [cm³(STP)/g]
W_2 weight of polymer in column (g)

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