

# Solubility of Isobutane and Propane in Polyethylene at High Temperatures and Low Pressures

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## Synopsis

A novel procedure was developed to measure the solubility of isobutane and propane in both low and high-density polyethylene at temperatures to 500°F (260°C) and vapor pressures from 1 to 1500 torr (33 psia). These measurements represent the first known solubility measurements at these combined extremes of pressure and temperature. Excellent agreement was found when our data were extrapolated to higher pressures and compared with data from another source. In the temperature and pressure regions of interest in this work, the linear isotherms were fit with a form of the Flory-Huggins equation. With the equation in that form we can now estimate the ratio of solubilities of two solutes in a given polymer from pure solute data only. We can also predict the absolute solubility of nonpolar solutes in polyethylene at various temperatures and pressures using only critical temperatures and acentric factors of the solutes.

## INTRODUCTION

For high-density polyethylene (HDPE) and low-density polyethylene (LDPE), manufacture occurs in solvents, slurries, or in the gas phase in the presence of hydrocarbon diluents. These low molecular weight substances function to remove heat of reaction during polymerization. For economic and safety reasons, solvents or diluent gases should be removed from the polymer before finishing.

Removal of volatile solvents or diluent gases during polymer manufacture depends on both kinetic and equilibrium factors. Equilibrium establishes the lowest attainable residual volatile level in the polymer; for a given polymer-solvent system, it is a function of temperature and pressure. Design of a process that achieves a fixed level of residual volatiles in the product requires knowledge of their distribution between the polymer and vapor phase at the temperature and pressure in the process equipment.

In the final stages of the manufacturing process, polymer melt devolatilizers typically operate at high temperatures (>200°C) and low pressures (<500 torr), conditions not reflected by the experimental data in the literature. To illustrate, Figure 1 shows a survey of published vapor/polymer equilibria experiments. Extrapolation of data taken at less severe conditions of temperature and pressure can be risky and may lead to serious errors. Direct measurement at these severe devolatilizer conditions would not only yield more reliable data but could be used as a test for the validity of extrapolation of other data and evaluation of current polymer solution models.

In 1975, Bonner summarized theory, experimental techniques, and available data for vapor-polymer equilibria in polymer melts.<sup>1</sup> A main thread in the development of polymer solution theory may be traced from the work of Flory<sup>2</sup> and

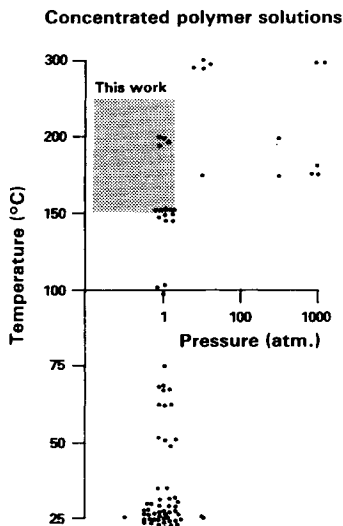


Fig. 1. Survey of published vapor/polymer equilibrium.

Huggins<sup>3</sup> to Maron,<sup>4</sup> Heil and Prausnitz,<sup>5</sup> to Flory and co-workers,<sup>6-9</sup> through Prausnitz and co-workers<sup>10-15</sup> including contributions by Patterson and co-workers.<sup>16-19</sup> Prausnitz and co-workers have continued to extend these ideas.<sup>20-24</sup> Several recent papers were concerned with polyethylene.<sup>14,25-30</sup> In spite of the effort in this field, no present theory can predict polymer-vapor thermodynamic equilibrium with any degree of accuracy unless experimental data for the binary pair are available. Furthermore, no theory is adequate for extrapolating data outside the temperature range over which the data were measured. A semiempirical relationship described in Ref. 26 is discussed in a later section. Finally, there are no published data for the specific systems of interest to this work at the temperatures and pressures investigated here, although data have been published for *n*-butane in LDPE to 300°C<sup>26</sup> and for isobutane in HDPE to 93°C.<sup>30</sup>

The most popular techniques for acquiring equilibrium data in polymer-vapor systems include gas chromatography, vapor pressure lowering, and isopiestic methods. However, these techniques are not useful at high temperatures and low pressures due to the very low solubilities being measured. The classic gravimetric method using a high-sensitivity microbalance for low solubilities is inadequate because of the high noise levels caused by convective currents around the sample pan. Convective currents increase markedly with temperature of measurement. Commercially available microbalances are not designed to handle organic vapors at high temperatures and a glaring void exists in the literature for a rapid, accurate technique for measuring vapor-polymer equilibrium at these conditions.

We have devised a new technique for measuring gas and vapor solubilities in polymers at extreme conditions of temperature (260°C) and pressure (1-150 torr) that fills this void and overcomes the inadequacies of other published techniques. Its effectiveness is a result of two novel additions to a classical isopiestic method. These are: invention of a unique sample vessel that can be utilized as a true, closed thermodynamic system, and development of a method

for quenching the molten polymer in equilibrium with the vapor at elevated temperatures such that no solute is lost.

Kubo and Dole<sup>31</sup> have reported a similar method to measure the solubility of H<sub>2</sub> in polyethylene. Their work was limited to lower temperatures (~25°C) and pressures near atmospheric. In addition, the gas-polymer interface is the last to cool during their quenching procedure and thus can absorb vapor during the relatively slow cooling of the polymer. Our quenching procedure is instantaneous since the polymer is immediately immersed in ice water during quenching thereby cooling the polymer melt uniformly on all surfaces and not just on the surface in contact with the glass.

Our new technique involves equilibrating a known weight of polymer with a known amount of vapor in a hermetically sealed pyrex vessel of known volume at a specific temperature. The quantity of polymer used dissolves only a small amount of solute vapor during an experiment. The pressure remains essentially constant during the time for equilibration. After equilibration the vessel and its contents are rapidly quenched to "freeze" the polymer as it existed at high temperature. Gas chromatographic analysis of the quenched polymer for its solute vapor content (along with the total amount of vapor added to the vessel) is then used to calculate the equilibrium ratio. It can be called a pseudo gravimetric technique in a constant pressure system.

The new technique was used to acquire equilibrium solubility data for isobutane and propane in both HDPE and LLDPE at temperatures up to 260°C and pressures from 1 to 1500 torr. Linear solubility isotherms were observed over this range. Excellent agreement was found when our data were extrapolated to higher pressures and compared with data from another source. In addition, Henry's law constants calculated from our data for isobutane and propane in polyethylene agree with Henry's constants calculated for the same solvents based on a published method utilizing data for other solvents in polyethylene. These comparisons affirm the validity of our new method.

## EXPERIMENTAL

Typical properties of the polymers used are shown in Table I. A diagram of the gas buret apparatus used to accurately measure and transfer quantities of gases and vapors is shown in Figure 2. It consists of a pyrex glass manifold line (D) to which is attached a gas or vapor storage vessel (A), calibrated volume vessel

TABLE I  
Typical Properties of Polymers Used in This Investigation

	HDPE	LLDPE
Density (g/cc)	0.951	0.919
Melt index (g/10 min)	5.8	2.0
Crystallinity at 93.3°C (%)	56	—
Izod impact strength (ft-lb/in.)	0.8	—
Tensile impact (ft-lb/in.)	27	99
Elongation (% at break)	600	600
GPC data:		
$M_n \times 10^{-3}$	14	18
$M_w \times 10^{-3}$	94	109

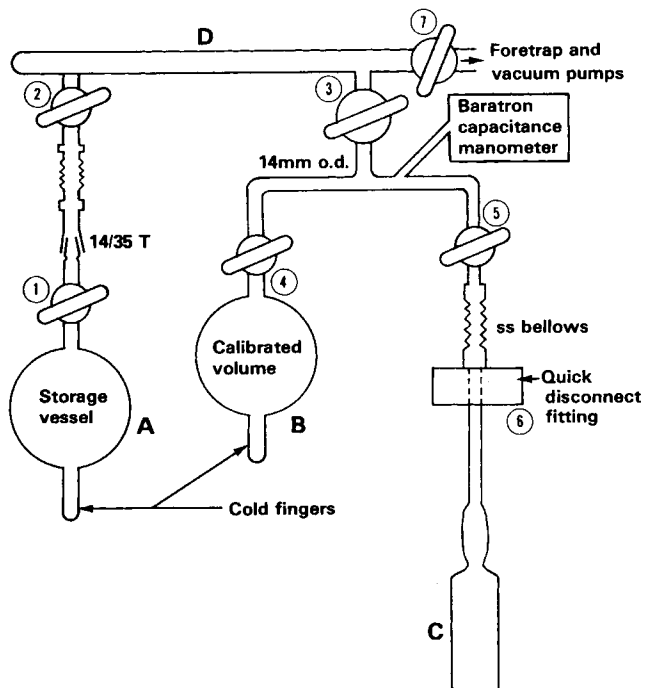


Fig. 2. Gas buret apparatus.

(B), and a 0.25-in. Quick Disconnect vacuum coupling (Veeco catalog number C-25) via Rotoflo TF2-18 high vacuum stopcocks.

Absolute pressures in the gas buret apparatus were measured using an MKS Instruments, Inc., Baratron, high accuracy, absolute sensor head (type 315BHS-100) with pressure range 0–100 torr and 5 decades of usable resolution. The system in Figure 2 was evacuated and maintained at high vacuum (<0.1 mtorr) with a Sargent-Welch Duo Seal Vacuum Pump (Model 1400) equipped with a Consolidated Vacuum Corporation Oil Diffusion Pump (Model VMF-10).

The equilibration vessels were fabricated from Wheaton Scientific, prescored, borosilicate glass ampules (catalog #176782). The dimensions of the 6-mm o.d. tubing on the neck was chosen to fit inside the Quick Disconnect fitting (#6) in Figure 2. Twenty of the fabricated vessels were randomly selected and volume calibrated at two points: at the point where the 6-mm o.d. tubing met the top of the ampule and at a point on the tubing 15 cm from the bottom of the vessel. Typical volumes were 27.6 cc and 28.3 cc, respectively, as shown in Figure 3.

Analysis of polyethylene for isobutane or propane content was by gas chromatography using a 4 ft  $\times$  0.125 in. stainless steel column packed with 80/100 mesh Porapak QS.

## PROCEDURE

The general procedure for making solubility measurements of isobutane or propane solute in polyethylene is shown schematically in Figure 4. Three to five pellets of polyethylene sample are weighed and added to the vessel. The vessel

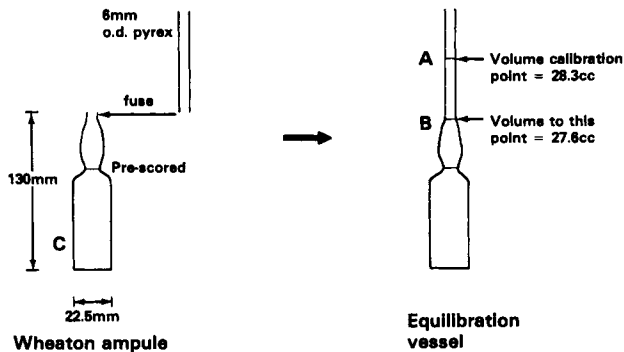


Fig. 3. Volume-calibrated equilibrium vessels.

is attached to the gas buret apparatus (Fig. 2) at the Quick Disconnect fitting (#6). It is evacuated to ultimate vacuum ( $10^{-4}$  torr). An accurately known amount of solute is transferred to the vessel from the calibrated volume (B). Once transfer of the vapor is complete the vessel is sealed off by collapsing the 6-mm glass tubing at the volume calibration mark with a natural gas/ $O_2$  torch. Now the hermetically sealed vessel contains known amounts of polymer and solute in a known volume and the pressure can be calculated at any temperature. A large number of vessels can be prepared in this manner and the isobutane pressures can be easily varied.

The vessels are equilibrated at elevated temperatures by placing them in a forced-air oven. They are placed in the oven on their sides as shown in Figure

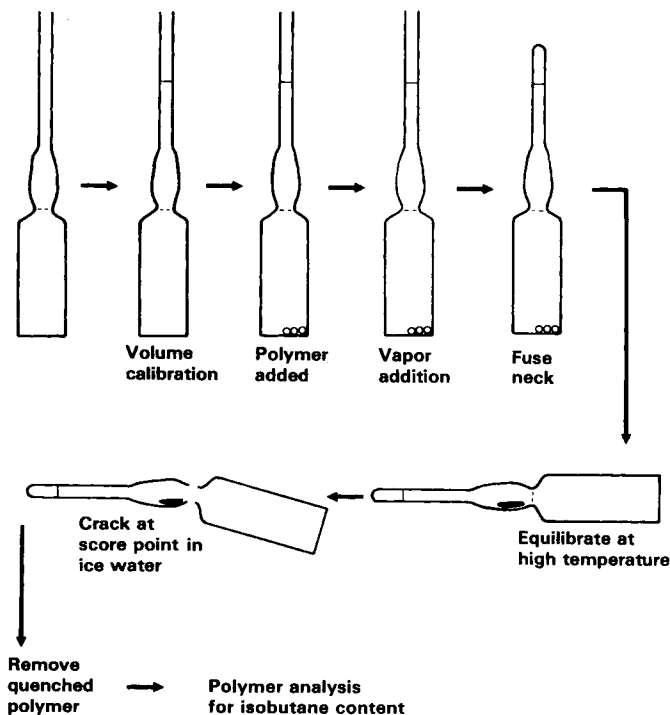


Fig. 4. Solubility measurement sequence.

4 with the polymer pellets located at the flared part of the neck just above the score point. In this way, as the pellets melt and fuse, they form a relatively compact melt.

Quenching the vessels to maintain the amount of solute in the polymer melt that existed at elevated temperature is the critical step. This is done by opening the oven door, removing a vessel, and quickly dipping it in ice water while simultaneously cracking the vessel at the score point. The whole quenching step takes no more than 1–2 s. The ice water rushes into the vessel and quenches the melt surfaces, preventing any loss of solute. The quenched melt is then immediately removed from the ice water for solute determination.

Knowing accurately the vessel volume permits calculation of solute partial pressure from the amount of vapor added to the vessel with the gas buret apparatus, less the amount of vapor recovered from the quenched polymer melt. This latter quantity is usually a small correction. Corrections for the volume of the polymer melt and non-ideality of solute vapor are likewise negligible. The amount of solute in the equilibration vessels was varied over a wide range by altering calibrated volume B (Fig. 2).

## RESULTS AND DISCUSSION

### Investigation of Experimental Variables to Assess Accuracy

Figure 5 shows the results of a set of experiments to measure the solubility of isobutane vapor in HDPE at 300–500°F and isobutane pressures ranging from 200 to 1800 torr. These data are in Table II. The data show excellent linear correlation over this pressure range with no apparent trends in the variability of the numbers with increasing pressure. The average values of the isobutane solubility per torr of isobutane pressure for each temperature show a slightly increasing relative standard deviation ( $\sigma_{rel}$ ) with temperature. This may reflect increasing random errors during the quenching step for the hot polymer melt since at higher temperatures the diffusion rate is greater and, depending on the

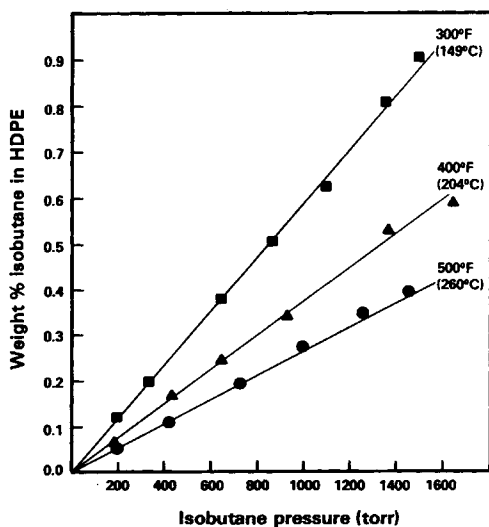


Fig. 5. Solubility of isobutane in HDPE (medium pressure).

TABLE II  
Solubility of Isobutane in HDPE

Temp (°F)	<i>i</i> -C <sub>4</sub> pressure (torr)	wt % <i>i</i> -C <sub>4</sub> in HDPE	Wt %/torr × 10 <sup>4</sup>
300	197	0.118	5.99
	335	0.202	6.03
	646	0.376	5.82
	867	0.513	5.92
	1095	0.650	5.94
	1351	0.818	6.05
	1496	0.911	6.09
			$\bar{X} = 5.98 \pm 0.10$ $\sigma = 2.7\%$
400	185	0.0663	3.58
	438	0.165	3.77
	654	0.246	3.76
	926	0.344	3.70
	1369	0.528	3.78
	1649	0.591	3.58
			$\bar{X} = 3.70 \pm 0.10$ $\sigma = 2.7\%$
500	200	0.053	2.66
	421	0.112	2.66
	727	0.196	2.70
	1015	0.276	2.72
	1262	0.353	2.80
	1454	0.395	2.72
	1722	0.434	2.52
			$\bar{X} = 2.68 \pm 0.10$ $\sigma_{rel} = 3.7\%$

geometry of the melt, there may be random losses of vapor. This can be minimized with a fast quench procedure.

The validity of these data was inferred by determining the effects of several experimental variables. The variables studied were polymer sample size, time required for equilibrium, melt geometry, and method of quenching.

Selection of polymer sample size in the equilibration vessels was based on several factors. These included, giving a melt thick enough to minimize solute loss during quenching, and small enough to require negligible corrections to vessel volume and solute pressure. The data below show the results of an experiment at constant temperature (149°C) and partial pressure (274 torr) of isobutane vapor:

No. of polymer pellets	Weight (mg)	Wt %/(torr)
1	18.3	4.42
2	39.1	5.65
3	54.2	5.77
4	74.8	6.01
5	101	6.09
6	121	5.87
7	149	5.83

Comparison of these data to those in Table II, which were taken using ap-

proximately 765 mg of sample, shows that the (wt %/torr) values start to level out at about 50–60 mg of sample. Lower values for smaller sample sizes probably indicate that the polymer melt is too thin and there is isobutane loss during or after the quenching step. Based on this, the sample size was chosen to be in the 60–70 mg range, or 3–4 typical polymer pellets. This amount gives a circular polymer melt approximately 2.5 mm thick at the middle and 8 mm in diameter. In addition, the volume correction ( $\sim 0.05$  cc) to the equilibration vessel volume (28.3 cc) due to this small amount of sample was insignificant (0.2%).

During an experiment the pressure is nearly constant, as a result of the small sample size used. Less than 1% of the total amount of isobutane added to the vessel dissolves in the polymer phase. This was accounted for when calculating the final pressure.

Next, the time required for equilibrium was investigated by preparing 10 vessels, each containing the same amount of polymer and isobutane vapor. In this case we chose 149°C and an isobutane pressure of approximately 280 torr. We chose the lower temperature since it will give the maximum time for diffusion of isobutane into polymer until equilibrium is attained. Experiments at the higher temperatures all have shorter equilibration times because of the effect of temperature on the diffusivity.

The data below show that at the conditions of temperature, pressure, and sample size listed above, equilibrium is probably achieved within 2 h:

<u>Time</u>	<u>Wt %/(torr)</u>
10 min	4.03
20 min	4.80
30 min	4.27
60 min	5.75
120 min	5.70
180 min	5.85
18 h	5.84
24 h	5.90
48 h	5.83

Next, we investigated the effect of melt geometry on the data. In this experiment, we again chose 149°C and an isobutane pressure of approximately 280 torr with a polymer sample size of approximately 70 mg. The vessels were then equilibrated in three ways: first, with the vessel on its side and the polymer in the vessel neck just above the score point. This is how the previous experiments were run, and it gave a circular polymer melt of approximate dimensions 2.5 mm thick and 8 mm diameter. After quenching, the polymer was easy to retrieve. Second, with the equilibration vessel again on its side, the polymer was placed below the score mark in the vessel proper. Now, when the polymer melted, it gave a long (40 m), thin ( $\sim 0.5$  mm) melt that was difficult to remove from the glass surface after quenching. During this time and because the polymer melt was so thin, there was isobutane loss from the polymer, and the apparent solubilities were approximately 30% lower than those in Table II. Third, at the other extreme the vessel was inverted and the polymer allowed to melt into a small cylindrical form at the 27.6-cc volume calibration point in Figure 3. This gave a polymer melt of lower surface area, approximately 4 mm thick, that minimized isobutane loss. The measured isobutane solubility was identical (within ex-



perimental error) to those in Table II. The main disadvantage here was in the difficulty in removing the quenched polymer melt from the vessel for analysis.

The other variable studied was the method of quenching the hot polymer melt in equilibrium with isobutane vapor such that no significant amounts of isobutane vapor were added or lost from the polymer during quenching. The first method we tested was to remove the hot equilibration vessel from the oven and immerse it quickly in ice water. This is similar to the method used by Kubo and Dole.<sup>31</sup> After a few minutes the vessel was removed, broken, and the quenched melt removed for isobutane determination. However, the isobutane concentration in the polymer was approximately 25% higher than predicted from extrapolation of data from high pressure or comparison to the data in Table II. When the sealed equilibration vessel is plunged into cold water, polymer in direct contact with the glass surface is cooled quickly while the polymer in contact with the vapor space is cooled more slowly. Thus, as the melt cools, there is opportunity for additional solubility of isobutane into the melt and polymer nearest the vapor-solid interface is higher in solute content. The method of quenching we finally settled on was described previously.

Figure 6 shows the results of another set of experiments to measure the solubility of isobutane in HDPE from 300–500°F but at much lower pressures than those shown in Figure 5. Here the isobutane pressure in the equilibration vessels varied from 2 to 200 torr. Again, the data show excellent linear correlation. Comparison of these data in Table III to those at the higher pressure in Table II shows agreement within experimental error. Overall linearity of isobutane solubility in HDPE at 300–500°F is thus established over the partial pressure range 2–1700 torr or 0.003–2.2 atm.

Isobutane solubility measurements at 200°F (93.3°C) require careful analysis because the measurements were made well below the crystalline melting point of the polymer (~137°C). The apparent isobutane solubility isotherm was between those for the 400°F and 500°F isotherms. However, once the solubility has been corrected for polymer crystallinity (56% as measured by X-ray diffraction), the solubility isotherm is in line with the expected variation of isobutane solubility in HDPE with temperature. Data are shown in Figure 7 and in Table IV.

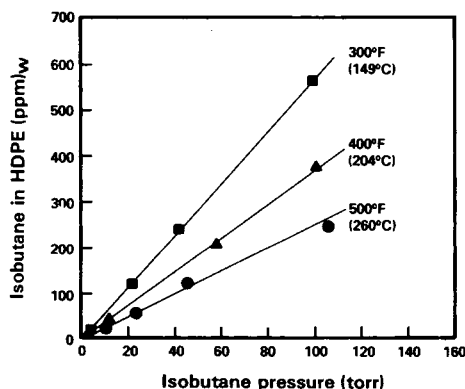


Fig. 6. Solubility of isobutane in HDPE (low pressure).

TABLE III  
Isobutane Solubility in HDPE at Low Pressure

Temp (°F)	<i>i</i> -C <sub>4</sub> pressure (torr)	Wt % <i>i</i> -C <sub>4</sub> in HDPE	Wt %/torr × 10 <sup>4</sup>
300	3.79	0.0020	5.28
	21.3	0.0135	6.34
	41.8	0.0239	5.72
	99.9	0.0561	5.62
	129.	0.101	7.83
			$\bar{X} = 6.16 \pm 1.0$
			$\sigma_{\text{rel}} = 1.6\%$
400	2.86	0.0011	3.85
	11.7	0.0046	3.93
	58.1	0.0206	3.55
	101.	0.0380	3.76
	202.	0.0790	3.91
			$\bar{X} = 3.80 \pm 0.15$
			$\sigma_{\text{rel}} = 3.9\%$
500	5.22	0.0012	2.30
	10.5	0.0028	2.67
	23.6	0.0057	2.42
	45.0	0.0122	2.71
	106.	0.0249	2.35
			$\bar{X} = 2.49 \pm 0.19$
			$\sigma_{\text{rel}} = 7.6\%$

As a further test of the procedure, we measured the solubility of propane in HDPE from 300°F to 500°F and propane partial pressures from 100 to 1400 torr. The data are shown in Figure 8 and in Table V. Again, a linear correlation exists and the data show excellent precision. Comparison of the data to those in Table II for isobutane over the same pressure range shows propane to be less soluble by a factor of 0.55 at 400°F.

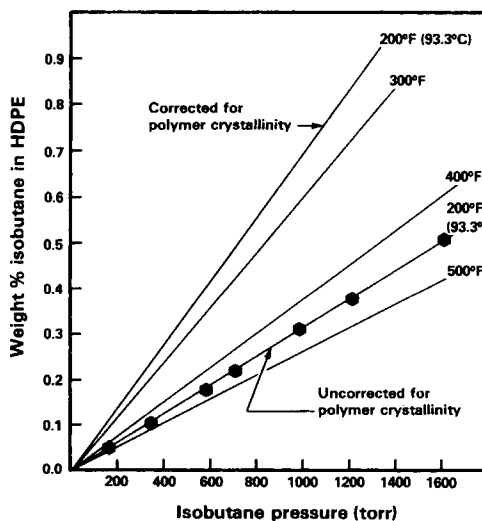


Fig. 7. Effect of polymer crystallinity on isobutane solubility.

TABLE IV  
Isobutane Solubility in HDPE at 200°F Corrected for Polymer Crystallinity of 56%

Temp (°F)	<i>i</i> -C <sub>4</sub> pressure (torr)	Wt % <i>i</i> -C <sub>4</sub> in HDPE	Wt %/torr × 10 <sup>4</sup>
200 (uncorrected)	170	0.0507	2.98
	343	0.103	3.00
	587	0.178	3.03
	708	0.217	3.06
	987	0.310	3.14
	1213	0.376	3.10
	1609	0.509	3.16
200 (corrected)	170	0.115	6.76
	343	0.234	6.82
	587	0.405	6.90
	708	0.493	6.96
	987	0.704	7.13
	1213	0.855	7.05
	1609	1.16	7.21
			$\bar{X} = 6.97 \pm 0.16$
			$\sigma_{rel} = 2.3\%$

The success with HDPE prompted evaluation of the procedure with another polymer, linear low-density polyethylene (LLDPE). The two polymers differ primarily in density and the amount of ethyl-chain branches. Data for 300–500°F and pressures from 70 to 1700 torr are shown in Figure 9 and in Table VI. The data again show a good linear correlation but the precision of the data is 3–7 times worse than that for HDPE. However, the mean solubility data for each temperature are in near agreement with those for HDPE. We believe the decrease in precision is primarily due to random errors in recovery of the quenched polymer melt from the equilibration vessel. The quenched polymer clings tenaciously to the glass surface and its quantitative removal is difficult. On the other hand, HDPE does not stick to the glass after the quenching step and is easily recovered.

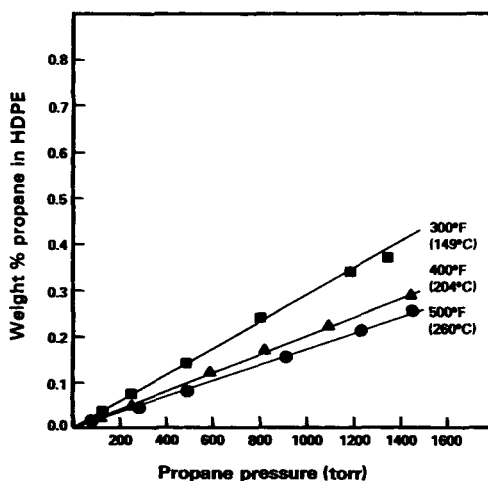


Fig. 8. Solubility of propane in HDPE (medium pressure).

TABLE V  
 Solubility of Propane in HDPE

Temp (°F)	<i>i</i> -C <sub>4</sub> pressure (torr)	Wt % <i>i</i> -C <sub>4</sub> in HDPE	Wt %/torr × 10 <sup>4</sup>
300	124	0.0357	2.89
	250	0.0730	2.92
	479	0.140	2.92
	793	0.242	3.05
	1182	0.338	2.86
	1337	0.370	2.77
			$\bar{X} = 2.90 \pm 0.10$
			$\sigma_{rel} = 3.4\%$
400	119	0.0232	1.95
	250	0.0492	1.97
	589	0.120	2.03
	815	0.169	2.07
	1093	0.226	2.07
	1443	0.291	2.02
			$\bar{X} = 2.02 \pm 0.05$
			$\sigma_{rel} = 2.5\%$
500	84.5	0.0132	1.56
	280	0.0476	1.70
	487	0.0823	1.69
	905	0.155	1.71
	1233	0.215	1.74
	1447	0.261	1.80
			$\bar{X} = 1.70 \pm 0.10$
			$\sigma_{rel} = 5.9\%$

### Comparison with High-Pressure Data

It is difficult to assess the accuracy of these solubility measurements by comparison to similar investigations using other methods of measurement because there are few literature data at the high temperature and low pressures

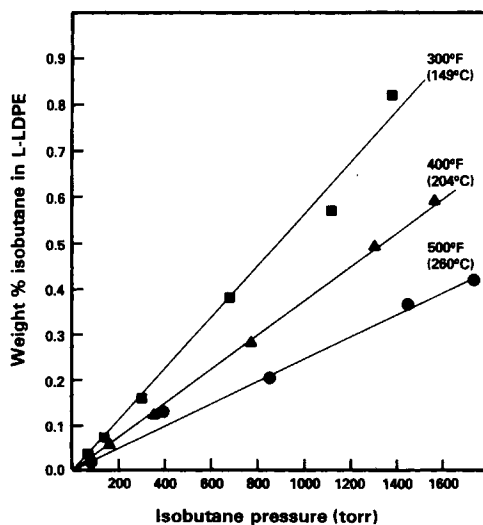


Fig. 9. Solubility of isobutane in L-LDPE (medium pressure).

TABLE VI  
 Isobutane Solubility in LLDPE

Temp (°F)	<i>i</i> -C <sub>4</sub> pressure (torr)	Wt % <i>i</i> -C <sub>4</sub> in HDPE	Wt %/torr × 10 <sup>4</sup>
300	67.6	0.0367	5.42
	139	0.0720	5.18
	300	0.168	5.60
	682	0.388	5.69
	1120	0.579	5.17
	1380	0.820	<u>5.94</u>
			$\bar{X} = 5.50 \pm 0.30$
			$\sigma_{\text{rel}} = 5.5\%$
400	72.5	0.0239	3.30
	162	0.0537	3.31
	350	0.125	3.57
	774	0.280	3.62
	1310	0.491	3.75
	1566	0.595	<u>3.80</u>
			$\bar{X} = 3.56 \pm 0.21$
			$\sigma_{\text{rel}} = 5.9\%$
500	83.2	0.0220	2.64
	179	0.0560	3.13
	387	0.131	3.39
	859	0.203	2.36
	1453	0.365	2.51
	1745	0.420	<u>2.41</u>
			$\bar{X} = 2.74 \pm 0.42$
			$\sigma_{\text{rel}} = 15\%$

investigated here. However, there are data<sup>32</sup> available at high pressures (>1 atm) and 400°F that overlap the high pressure end of our experiments (2 atm). These data were obtained over the pressure range 23–830 psia using classical pressure-difference techniques. The experiment involved placing a known amount of HDPE in a cylindrical metal vessel and injecting known volumes of isobutane. After thorough mixing, the amount of isobutane in the polymer phase was calculated from the amount of isobutane charged to the vessel minus the estimated amount in the vapor phase from final pressure readings. These types of measurement become less accurate at lower pressures due to lower solubilities and are generally limited to pressures above atmospheric.

High pressure solubility data for isobutane in HDPE at 400°F are given in Table VII. To facilitate comparison to our data, the isobutane solubilities are given in wt %/torr. Comparison of Wilson's data in Table VII to ours in Table II shows remarkable agreement in view of the different experimental techniques used.

Comparison of the propane solubility of Wilson<sup>32</sup> to ours at 400°F shows even better agreement. Wilson's data in Table VIII can be compared to our data in Table V. Here the agreement is within the standard deviation of both sets of data.

### Comparison with Dilute Solution Models

No theory is available to predict solubilities of solutes in polymers from pure component data alone. However, the dilute solution form of the Flory–Huggins

TABLE VII  
High Pressure, Isobutane Solubility in HDPE at 400°F from Wilson<sup>32</sup>

<i>i</i> -C <sub>4</sub> pressure		Wt % <i>i</i> -C <sub>4</sub> in HDPE	Wt %/torr × 10 <sup>4</sup>
torr × 10 <sup>-3</sup>	psia		
1.19	23	0.38	3.20
1.60	31	0.55	3.43
10.3	200	3.27	3.16
17.1	330	6.03	3.53
26.7	517	8.68	3.25
34.7	672	11.3	3.25
42.9	830	14.0	3.26
			$\bar{X} = 3.30 \pm 0.13$
			$\sigma_{\text{rel}} = 3.9\%$
Comparison of Data 400 psia and 400°F			
		Isobutane solubility in HDPE	
Wilson		6.82%	
Meyer and Blanks (linear extrapolation)		7.65%	

equation can be used to estimate the relative solubility of two solvents in a given polymer, or to estimate the solubility of a solvent in a polymer from data on the solubility of another solvent in the same polymer, as shown below.

In the low concentration range, where a plot of pressure versus concentration is linear, a modified form of the Flory-Huggins equation<sup>2,3</sup> may be used to relate solute partial pressure to the concentration of solute dissolved in the polymer melt at a given temperature

$$p_i = \frac{p_i^s \rho_p}{\rho_i} [\exp(1 + \chi)] c_i \quad (1)$$

In eq. (1),  $p_i$  and  $p_i^s$  are solute partial pressure and vapor pressure, respectively. The density of polymer and that of solute are  $\rho_p$  and  $\rho_i$ . The parameter  $\chi$  is the

TABLE VIII  
High Pressure Propane Solubility in HDPE at 400°F from Wilson<sup>32</sup>

Propane pressure		Wt % propane in HDPE	Wt %/torr × 10 <sup>4</sup>
torr × 10 <sup>-3</sup>	psia		
1.23	239	2.20	1.78
2.53	490	4.77	1.89
3.71	717	7.19	1.94
5.04	975	9.47	1.88
6.22	1205	11.95	1.92
7.50	1450	14.83	1.98
90.0	1740	17.75	1.97
			$\bar{X} = 1.91 \pm 0.07$
			$\sigma_{\text{rel}} = 3.7\%$
Comparison of Data at 400 psia and 400°F			
		Propane solubility in HDPE	
Wilson		3.95%	
Meyer and Blanks (linear extrapolation)		4.18%	

Flory-Huggins interaction parameter and  $c_i$  is weight fraction solute in the polymer phase.

The quantities in brackets in eq. (1) depend only upon temperature for a given solute-polymer binary system. Thus eq. (1) may be considered in the Henry's Law form with  $H_i$  representing the Henry's constant:

$$p_i = H_i c_i \tag{2}$$

At a fixed solute partial pressure, the ratio of the solubility of two solutes in a given polymer, at any temperature and concentration region, where eq. (2) is valid, is the reciprocal of the ratio of Henry's constants. From eq. (1)

$$\frac{c_i}{c_j} = \frac{\rho_i P_j^s}{\rho_j P_i^s} \exp(\chi_j - \chi_i) \tag{3}$$

For solutes of similar structure and chemical nature the intermolecular free energies of interaction between solute and polymer should be similar. Therefore,  $\chi_i \cong \chi_j$ :

$$\frac{c_i}{c_j} = \frac{\rho_i P_j^s}{\rho_j P_i^s} \tag{4}$$

Because the temperatures of this work, 300-500°F, are above the critical points of the solutes propane and isobutane, eq. (4) may not be directly tested. As an approximation, however, the measured ratio of propane to isobutane solubility may be compared with predictions of eq. (4) based upon the densities evaluated at a reduced temperature of 0.7 and based upon linear extrapolations of log vapor pressure versus temperature. Table IX shows good agreement between this calculation and the data.

Maloney and Prausnitz have published solubility data for butane in low-density polyethylene, obtained by gas-liquid chromatography.<sup>26</sup> They also present a semiempirical relation for Henry's constant of solutes in liquid low-

TABLE IX  
Relative Solubility of Propane and Isobutane at Several Temperatures

Temperature (°F)	c(propane)/c(isobutane)	
	calcd	Measured
200	0.42	—
300	0.51	0.48
400	0.55	0.55
500	0.59	0.63

Experimental Data Used in Eq. (4) to Calculate the Solubility Ratios Shown<sup>33</sup>

	Propane				Isobutane			
Density (lb/ft <sup>3</sup> ) at $T_R = 0.7$	34.170				35.423			
Vapor Pressures Extrapolated								
$P_i^s$ (atm)	200°F	300	400	500	200°F	300	400	500
	40	86	162	263	17	45	92	160

TABLE X  
Henry's Constants for Solutes in Liquid Polyethylene

Temp (°F)	n-Butane			Isobutane			Propane		
	300	400	500	300	400	500	300	400	500
Henry's constants (atm/wt fraction):									
$H_{\text{calcd}}$	195	308	432	225	343	469	456	632	800
$H_{\text{exptl}}$	180	300	425	220	356	490	454	651	774

density polyethylene which requires only the solute acentric factor and critical temperature in its application.

The agreement between the Maloney–Prausnitz relation and the data in their work for butane and this work for propane and isobutane is good, as shown in Table X and Figure 10.

### CONCLUSIONS

The excellent agreement between our work and that of Wilson<sup>32</sup> and Maloney and Prausnitz<sup>26</sup> supports the accuracy of all three investigations since they were obtained at widely varying conditions using different experimental methods. Our method is precise at the conditions of low pressure and high temperature. In addition, it is much easier and less time-consuming to use than other published methods.

In the temperature and pressure regions of interest in this work, the isotherms are linear and were fit with a form of the Flory–Huggins equation. With the equation in that form, we can now estimate the ratio of solubilities of two solutes in a given polymer from pure solute data only.

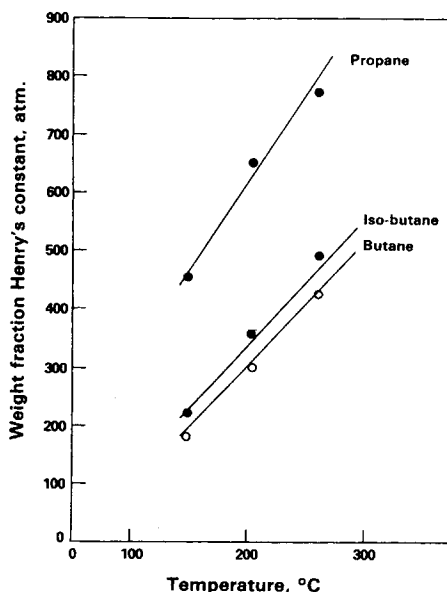


Fig. 10. Henry's constants for solutes in liquid polyethylene: (●) exptl, this work; (○) exptl, Ref. 26; (—) theoretical, Ref. 26.



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Received June 2, 1982

Accepted September 24, 1982