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Solubilities of Ethylene and Other Organic Solutes in Liquid, Low-Density Polyethylene in the Region 124° to 300°C

Gas-liquid chromatography was used to measure the solubilities of ethylene, *n*-butane, vinyl acetate, *n*-hexane, benzene, toluene, and *n*-octane in three different samples of liquid, low-density polyethylene. Solubilities in the different samples are similar. A correlation is presented for estimation of solubilities of nonpolar solutes in liquid polyethylene.

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SCOPE

This year, as last year, worldwide sales of polyethylene are expected to reach several billion dollars. Most polyethylene is produced by the high-pressure process. Since ethylene is the starting material, and since conversion per pass in the reactor is only about 20%, each high-pressure polyethylene facility must include one or more separation stages where unreacted ethylene is removed from the product polyethylene. Low molecular-weight products and chain-transfer agents are also removed from the polyethylene in these separators. Rational equipment design requires equilibrium solubilities of these solutes in liquid polyethylene.

In this work, gas-liquid chromatography has been used to measure solubilities of seven solutes in liquid polyethylene in the range 124° to 300°C. The chromatographic technique has been applied to sparingly soluble components, in particular ethylene, which appear in the high-pressure polyethylene process. Special experimental precautions must be observed to obtain reliable solubilities of sparingly soluble solutes in polymers.

CONCLUSIONS AND SIGNIFICANCE

Solubility data have been obtained for ethylene, *n*-butane, vinyl acetate, *n*-hexane, benzene, toluene, and *n*-octane in liquid, low-density polyethylene between 124° and 300°C. These data can be used to calculate equilibrium compositions for solute-polyethylene mixtures at moderate pressure (typically to 25 atm) as encountered in separation operations in polyethylene production. Solubility data in three low-density polyethylenes are only slightly different. Agreement with data reported by other researchers is good. It appears that the solubility of solutes in liquid polyethylene is nearly independent of polymer molecular-weight distribution and degree of long-chain branching.

New and previously published solubility data are correlated with solute critical temperatures and acentric factors. The resulting correlation gives good estimates of solubilities for nonpolar solutes in liquid polyethylene.

To measure low solubilities using gas-liquid chromatography, it is important to determine accurately the time the solute spends in the gas phase. Therefore, it is necessary to measure the retention-time difference between the solute and an "inert" reference gas (nitrogen). Since nitrogen is not truly inert, corrections for finite nitrogen solubility are not negligible for those solutes (for example, ethylene) whose solubilities are small.

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Last year more polyethylene was produced than any other synthetic polymer: United States production in 1974 was over 4 million tons. Most polyethylene is low-density polyethylene; that is, its solid state density at 25°C is less than 0.93 g/cc. Since ethylene is the starting material, and since conversion is rarely complete, each low-density polyethylene facility must include one or more stages where unreacted ethylene is separated from the polyethylene product. These stages also separate from the polymer-rich phase, low-molecular-weight products, and chain-transfer agents. Rational equipment design requires quantitative estimates for phase equilibria in systems containing these solutes and molten polyethylene.

The equilibrium weight fraction w_i of a gaseous solute in liquid polyethylene is determined by the equation of equilibrium:

$$y_i\phi_i P = \Omega_i^* w_i H_i \exp \int_0^P \frac{\bar{v}_i^\infty dP}{RT} \tag{1}$$

For low solubilities, the weight-fraction activity coefficient Ω_i^* is near unity. (Superscript * indicates that $\Omega_i^* \rightarrow 1$, as $w_i \rightarrow 0$). As discussed by Prausnitz (1969), equations of state can be used to calculate the fugacity coefficient ϕ_i; reasonable estimates can also be made of the liquid-phase, infinite-dilution, partial molar volume $\bar{v}_i^\infty$. The parameter which cannot be accurately estimated is the weight-fraction Henry's constant H_i, formally defined by Equation (2):

$$H_i \equiv \lim_{w_i \rightarrow 0} \frac{f_i}{w_i} \tag{2}$$

This Henry's constant is the most important parameter in Equation (1), since at low pressures

$$w_i = \frac{Py_i}{H_i} \tag{3}$$

Rigorously, H_i in Equations (1) and (3) should be calculated at zero pressure. However, for the low experimental pressures in this work, less than 2 atm, the pressure effect on Henry's constants is negligible. Therefore, H_i is used to designate all weight-fraction Henry's constants measured at these low pressures.

The purpose of this research is to measure Henry's constants for ethylene, *n*-butane, vinyl acetate, *n*-hexane, benzene, toluene, and *n*-octane in low-density polyethylene from 124° to 300°C.

The use of chromatography to measure thermodynamic properties has been reviewed by Kobayashi et al. (1967) and by Young (1968) and by Guillet (1973). Measurement of the solubilities of solutes in polymer melts by gas-liquid chromatography has been discussed by Smidsrød and Guillet (1969), Hammers and de Ligny (1971), Patterson et al. (1971), Newman and Prausnitz (1972), and Brockmeier et al. (1972). The discussions in these articles provide the background for this work.

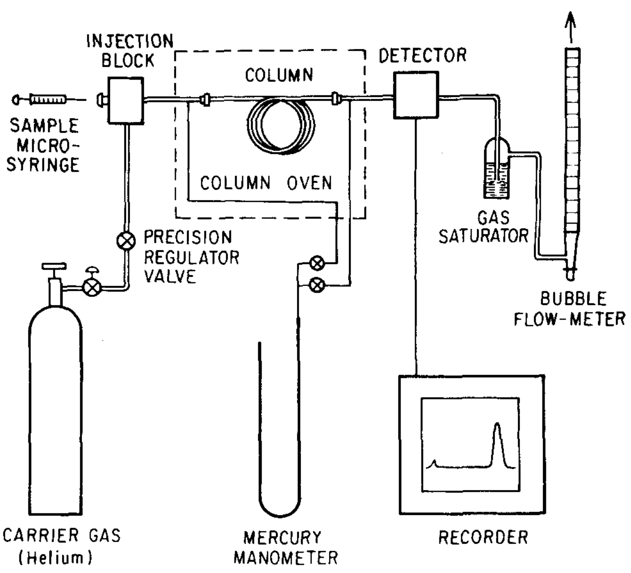

Fig. 1. Gas chromatographic apparatus.

EXPERIMENTAL

Apparatus

Figure 1 shows the essential features of the experimental apparatus. The flow rate of the helium carrier gas is controlled with a Negretti & Zambra pressure regulator. Solute vapor samples are injected into a Hamilton injection block with a 100 μl Precision Sampling syringe. A Carle Model 100 Micro Detector thermal conductivity meter and a Honeywell 1 mv recorder are used to detect and record solute concentrations in the carrier gas. A stopwatch and a 10 or 50 ml bubble flowmeter are used to measure flow rates. Temperatures are measured with mercury in glass thermometers.

The column oven is a 7-liter air bath from a Varian Aerograph 1520 chromatograph equipped with a Hallikainen Thermotrol temperature controller. Although the temperatures near the middle of the air bath appeared to be well controlled, there was a severe temperature gradient from the middle to the front of the bath at the highest experimental temperatures. At 300°C the front of the oven adjacent to the wall was 11°C cooler than the middle of the oven. However, at 124°C, this gradient was only 0.6°C. The temperature of the column is essentially the same as that of the bath's center, since the bulk of the column is placed at the bath's center. Nevertheless, it is important to include in an error analysis the consequences of temperature gradients.

Materials

All chemicals were used as received from suppliers. Except for *n*-octane, advertised purities ranged from 99 to 99.998 mole %. Since the resulting chromatographic elution peaks were single and symmetric for each chemical, there is no reason to suspect significant impurities. Practical grade *n*-octane with about 98% purity was used. Normal size injections of *n*-octane also gave single, symmetric elution peaks. However, during sample size studies, injections of liquid *n*-octane greater than 5 μl yielded two small peaks before the larger *n*-octane peak. Comparison with the specific-retention-volume data of Schreiber et

TABLE 1. POLYMER PROPERTIES

Polyethylene designation	M_N	M_W	M_z	CH_3/1 000 *C* atoms	Melt index*	Density	Supplier
PE1408.5	16 600	82 300	273 000	25.5	27	0.924†	Gulf
DXH 28	42 300	325,800	2 238 000		0.1	0.921**	Union Carbide
DYN I	35 000	235 000					Union Carbide

* See ASTM D1238-65T, g/10 min.
† ASTM D1505-63T, g/cm³.
** ASTM D1505-57T, g/cm³.

Table 2. Chromatographic Columns

Column	Polymer	Mass of polymer, g	Mass of antioxidant, g	Mass of Chromosorb, g	Apparent film thickness, Å	Percent polymer
I	PE1408.5	1.328	0.002	15.393	1 160	8
II	PE1408.5	3.059	0.004	13.953	2 940	18
III	PE1408.5	5.621	0.006	15.842	4 750	26
IV	DXH 28	3.248	0.004	14.411	3 020	18
V*	DYN I	2.115	None	13.056	540	14

* Column V used 60/80 mesh, Chromosorb-P, AW-DMCS and was prepared and used by Newman and Prausnitz (1973).

al. (1973) for octane isomers suggests that our sample contains less than 1% of 2-methylheptane and 2,2,4-trimethylpentane. However, measured retention times were unaffected by impurities in any of our chemicals.

Three samples of low-density, branched polyethylene were used in this work. The properties, as furnished by the suppliers, are shown in Table 1. These polymers are typical of polyethylenes made by the high-pressure process.

Column Preparation

Columns were prepared by dissolving a weighed amount of polymer, with about 0.15% of Irganox 1010 antioxidant and thermal stabilizer, into 50 ml of *m*-xylene. After about 3 hr. in a nitrogen oven at 130°C, the polyethylene had dissolved completely. A weighed amount of preheated 60/80 mesh Chromosorb W (acid washed, DMCS treated) was stirred into the polymer solution. The mixture was returned to the nitrogen oven and occasionally stirred until all visible solvent had evaporated. Then it was placed into a vacuum oven at 140°C. After 2 days, all solvent had evaporated as determined by weighing. The packing was then charged into a 10-ft length of ¼-in. stainless steel tubing that had been washed with cyclohexane and acetone. During filling, the columns were slightly agitated to pack the support; column ends were stuffed with glass wool to prevent packing loss.

The amount of polyethylene inside each packed column is known to ½% or better. Table 2 lists the columns used in this work. Apparent film thicknesses were calculated assuming surface areas of 1 m^2/g for Chromosorb W and 4 m^2/g for Chromosorb P as reported by Ottenstein (1963).

DATA REDUCTION

The gas-liquid chromatograph experiment uses an insoluble carrier gas, helium, flowing through a column packed with a polymer-coated, inert support. A solute sample is injected into the carrier gas stream, and the time from injection to the elution of the peak maximum is recorded. This retention time (t_i) can be separated into two parts: the time the solute spends in the gas phase (t_g) and the time the solute spends in the liquid phase ($t_i - t_g$). Assuming that the vapor phase inside the chromatograph behaves as an ideal gas, that fugacities of solutes in the liquid phase are proportional to their weight fractions, and that partitioning of solute molecules between liquid and gas is only determined by thermodynamic equilibrium between the bulk fluids, the time a solute spends in the liquid phase can be directly related to its Henry's constant:

$$H_i = \left(\frac{m_2}{M_i \dot{n}(t_i - t_g)}\right)\left(\frac{P_0}{j}\right) \qquad (4)$$

The j factor was introduced by James and Martin (1952) to correct the column's outlet pressure P_0 and inlet pressure P_I to an average column pressure, thus accounting for gas-phase compressibility and pressure drop through the column:

$$j \equiv \frac{3}{2}\,\frac{[(P_I/P_0)^2 - 1]}{[(P_I/P_0)^3 - 1]} \qquad (5)$$

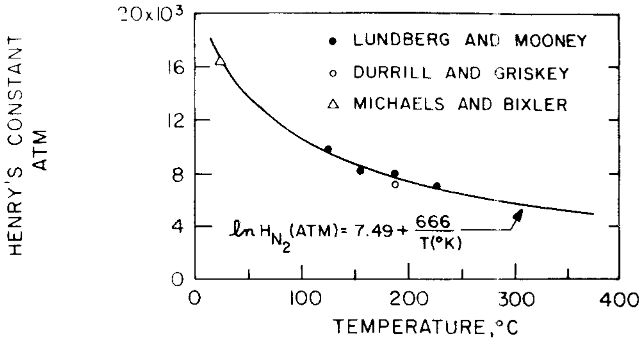

Fig. 2. Weight-fraction Henry's constant for nitrogen in amorphous polyethylene.

At experimental conditions prevailing in this work, the term (P_0/j) differs from the naive assumption $P_{\text{average}} = (P_I + P_0)/2$ by less than 1%. Lenoir et al. (1971) have used an equation similar to Equation (4).

The time a solute spends in the gas phase is determined by injecting an "inert" gas, nitrogen, and measuring its retention time. Equation (4) can be solved for t_g in terms of nitrogen's Henry's constant H_{N_2} and molecular weight M_{N_2}:

$$t_g = t_{N_2} - \left(\frac{m_2}{M_{N_2}\dot{n}H_{N_2}}\right)\left(\frac{P_0}{j}\right) \qquad (6)$$

When we use the data of Durrill and Griskey (1966) and of Lundberg and Mooney (1969), Henry's constant for nitrogen in liquid polyethylene is

$$\ln H_{N_2}(\text{atm}) = 7.49 + \frac{666}{T(°\text{K})} \qquad (7)$$

as shown in Figure 2. An estimate of nitrogen's Henry's constant in amorphous polyethylene, as deduced by Michaels and Bixler (1961) from their experimental data on semicrystalline polyethylene at 25°C, is included to show that Equation (7) appears to be valid also at lower temperatures.

When we know ambient pressure P_a and ambient temperature T_a, the molar flow rate of the carrier gas is easily calculated with the ideal-gas law from measurements of volumetric flow rates $\dot{V}_s$ with the bubble flowmeter:

$$\dot{n} = \frac{P_a \dot{V}_s}{RT_a}\left[\frac{P_a - P_{H_2O}}{P_a}\right] \qquad (8)$$

The presence of water vapor in the gas flowing through the bubble flowmeter is accounted for by P_{H_2O}, the vapor pressure of water at T_a.

The apparent specific retention volume is defined by

$$V_g{}^0 \equiv \frac{(273.15°\text{K})R\dot{n}(t_i - t_{N_2})}{m_2(P_0/j)} \qquad (9)$$

The adjective apparent is used to stress that the quantity

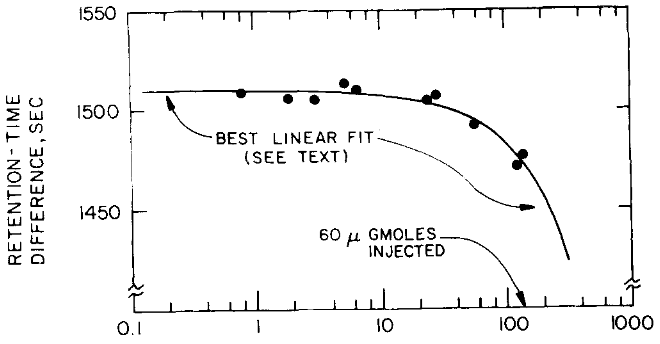

Fig. 3. Effect of sample size on *n*-octane—air, retention-time difference.

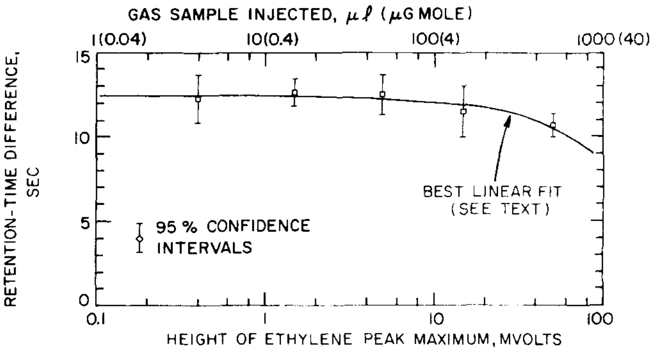

Fig. 4. Effect of sample size on ethylene—nitrogen, retention-time difference.

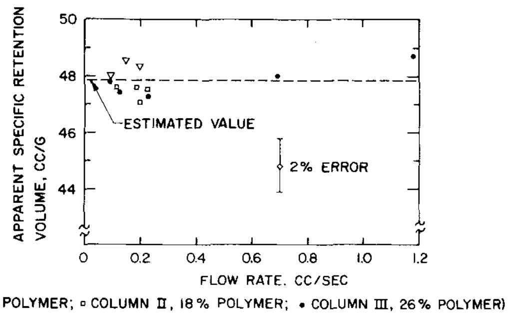

Fig. 5. Apparent specific retention volumes for *n*-octane at 124°C.

is based on the assumption that nitrogen is totally insoluble in the liquid phase. If the assumptions leading to Equation (4) are valid, then the apparent specific retention volume is independent of polymer loading and flow conditions. This quantity, therefore, is useful for comparing results measured under different experimental conditions.

Sample Size Effect

To assure that our measurements are at infinite dilution, as required by Equation (2), sample sizes were kept small, generally less than 2 μgmoles of solute. Occasionally larger sample sizes were used to check if there was any variation in retention-time difference with sample size. Figure 3 shows the result of one study with Column III at 124°C with a flowrate, measured at the soap-bubble meter, of 0.22 cm^3/s. The experiments were conducted by injecting 1 μl of air with various amounts of *n*-octane, by measuring the retention-time difference between air and *n*-octane peaks, and by noting the height of the *n*-octane peak maximum. Since most samples were saturated *n*-octane vapor, no accurate sample size could be determined. However, an estimate of sample size can be made since the height of the peak maximum is nearly proportional to sample size and a 10 μl (60 μgmoles) liquid *n*-octane sample gave a recorder response of about 120 mV. When retention-time difference is plotted against height of peak maximum on linear coordinates, not with the logarithmic abscissa shown in Figure 3, a straight line fits the data within experimental error. The smooth line, shown in Figure 3, is the best linear fit of retention-time difference with peak height. It appears that for this column, under these conditions, the use of sample sizes as large as 20 μgmoles would give retention-time differences within 1% of the infinite-dilution estimate.

Figure 4 shows a similar plot for ethylene as the solute. Column II at 150°C was used with a flow rate of 0.13 cm^3/s. Since pure gaseous ethylene was injected, sample sizes could be accurately determined; therefore, three scales of sample size are presented. The size of nitrogen-gas injections were the same as those for ethylene. Since ethylene is sparingly soluble in liquid polyethylene at atmospheric pressure, retention-time differences for ethylene are very short. Because of noninstantaneous injections, inaccuracies in determining peak maxima, and other random errors, the standard deviation in determining the retention-time difference between one ethylene peak and one nitrogen peak was about 1 s. Thus, one ethylene-nitrogen pair did not give the retention-time difference with high accuracy. For each point on the graph, four to six ethylene-nitrogen pairs were measured and the mean retention-time difference determined. The 95% confidence intervals were calculated using a *t* distribution, with the measured standard deviation as outlined by Dixon and Massey (1969). The solid line is the best linear fit of retention-time difference with sample size. From this line, a 2 μgmole injection is estimated to have a retention-time difference about 2% below the infinite-dilution value, while experimentally a higher value was observed. This illustrates the difficulty in measuring retention times of sparingly soluble gases. Random errors can mask trends unless exhaustive data are taken. This one sample size study took 8 hr. of laboratory time.

Effects of Flowrate and Polymer Loading

Figure 5 shows the effect of carrier gas flow rate on the apparent specific retention volume for *n*-octane. As shown by the filled-in circles, Column III, there does not seem to be any clear trend of retention volume with flow rate. The lack of flow-rate dependence suggests that these measured values are equilibrium values.

To check the data for signs of adsorption, results from Columns I, II, and III are compared. Since adsorption is proportional to surface area, it becomes relatively less important as the ratio of polymer to support rises; the amount of bulk polymer increases, while the surface area remains nearly constant. As shown in Figure 5, the apparent specific retention volumes of Column I are somewhat higher than those for Columns II and III, at least in the low flow-rate region. Agreement between Columns II and III seems to indicate that adsorption plays an insignificant role in these two columns. However, a deviation of 2% is the estimated maximum error due to random temperature fluctuations, inaccurate flow-rate measurements, etc. This random error is close to the 1.5% deviation noted by Lichtenthaler et al. (1974) in their thorough interlaboratory comparison for hydrocarbon solutes in polydimethylsiloxane. Since all data fall within 1.9% of the mean value, the variation of values is probably due to random errors and slight inaccuracies in weighing the polymer loadings. Within experimental error, the mean of the apparent specific retention volumes is the equilibrium value due only to the retention of *n*-octane molecules in the bulk, liquid polyethylene.

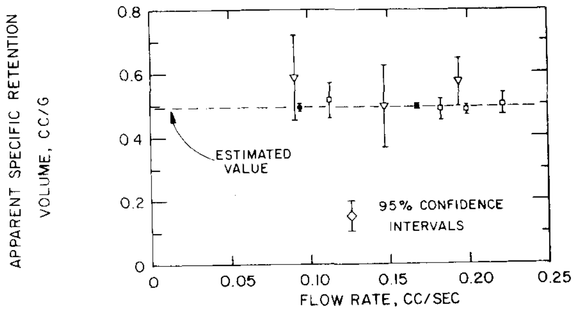

Fig. 6. Apparent specific retention volumes for ethylene at 124°C.

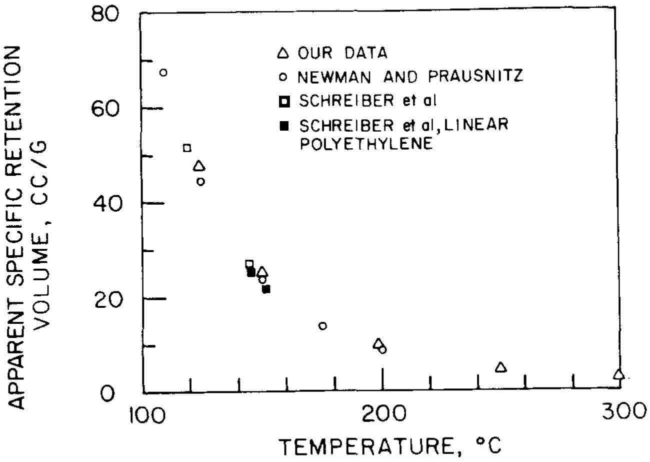

Fig. 8. Comparison of apparent specific retention volumes for *n*-octane.

TABLE 3. WEIGHT-FRACTION HENRY'S CONSTANTS AT 1 ATM (ATMOSPHERES)

	Temperature, °C				
Solute	124	150	200	250	300
Ethylene	1 390	1 550	1 830	2 050	2 260
n-butane	118	162	264	366	489
Vinyl acetate	34.3	52.0	99.7	168	231
n-hexane	20.0	32.8	67.7	115	176
Benzene	12.6	20.6	44.1	78.5	119
Toluene	5.22	9.40	22.6	45.5	75.2
n-octane	4.10	7.88	20.5	42.9	72.7

Figure 6 shows similar results for ethylene; however, random errors are larger due to difficulty in measuring small retention-time differences. Each datum represents five to eight nitrogen-ethylene pairs. The values for Column III are accurate to about 2%. For these two, most accurate, measurements there is no significant flow-rate dependence. Since all the 95% confidence intervals overlap the mean value of Column III measurements, it cannot be concluded with a high degree of confidence that either Column I or Column II gives results different from Column III. The estimated apparent specific retention volume, shown in Figure 6, is mainly determined by the results of Column III, since these are the most precise.

RESULTS

Figures 5 and 6 represent some of the more extensive measurements taken for polyethylene PE1408.5, listed first in Table 1. However, the data for all solutes, at all temperatures, were plotted as in Figures 5 and 6 to determine if any trends could be observed. No definite flow rate dependence occurred; however, results for Column I were usually 1 or 2% higher than the others. Above 150°C, Column I was no longer used, since retention-time differences with ethylene were too small to measure accurately. After the measurements at 300°C, Columns II and III were retested at 124°C to determine if any polymer had volatilized or degraded during the experiments. No significant difference was noted between data taken before and after the high-temperature measurements.

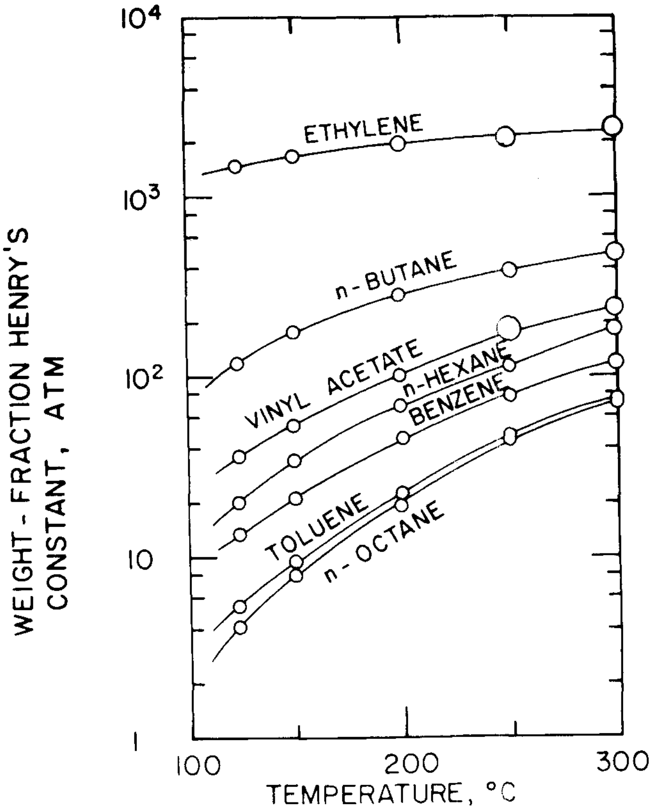

Fig. 7. Henry's constants for solutes in liquid polyethylene.

Experimental retention times for Columns, I, II, and III were used to calculate Henry's constants from Equations (4) through (8). Results are presented in Table 3 and in Figure 7.

Solubilities in Other Polyethylenes

Measurements of Henry's constants with Column IV were conducted with all solutes at 150°C and for ethylene, vinyl acetate, and *n*-octane at 124°C. The Henry's constants were always slightly lower than those reported in Table 3, with the average difference about 1.7%. Column V was used to measure Henry's constants for ethylene from 124° to 250°C. Some values were higher than those in Table 3 and some were lower, but the average difference was 1.6% higher. Measurements with benzene and Column V between 150° and 250°C gave Henry's constants that averaged 1.7% lower than those in Table 3. Random errors could explain these small differences, or there could be real differences in solute solubilities in the three low-density polyethylene samples. Further studies with other polyethylenes may yield larger differences. However, the differences among the low-density polyethylene samples seemed to be too small to measure accurately or to correlate with fundamental molecular parameters. It is likely that the Henry's constants in Table 3 are good estimates for all low-density molten polyethylenes.

Figure 8 compares our apparent specific retention volumes for *n*-octane with those measured by Schreiber et al. (1973). Also shown are values calculated from Equation (9) with the unpublished raw data of Newman and Prausnitz (1973) used. Our values are the highest, while those for a linear polyethylene sample are lowest. It is reason-

TABLE 4. CONTRIBUTIONS TO THE PERCENT ERROR IN HENRY'S CONSTANTS

Error source	Ethylene 124°C	Ethylene 300°C	*n*-octane 124°C	*n*-octane 300°C
Random errors	2.0	7.0	1.9	2.0
Henry's constant for nitrogen	1.4	3.9	0.0	1.0
Column temperature	0.2	1.1	0.7	3.4
Other systematic errors	1.0	1.2	1.3	1.6
	4.6%	13.2%	3.9%	8.0%

able to expect that solutes have a lower solubility (higher Henry's constant) in linear polyethylene, but at a given temperature, none of the solubilities differ by more than 10%. Solubilities in all low-density polyethylenes differ by less than 5%. Comparison of solubility data for toluene from Schreiber et al. (1973) and from Newman and Prausnitz (1973) gives similar results.

The maximum deviation of Newman and Prausnitz's (1973) benzene solubility data is 4%, while for *n*-hexane the difference is as much as 9% at 200°C. Because of the low polyethylene loading in their column (Column V in Table 2), Newman measured retention-time differences of only 23 s; the error in such measurement is likely to be high. Also, since Newman did not correct for finite nitrogen solubility, our results for *n*-hexane are probably more accurate.

ERROR ANALYSIS

The error analysis assumes that the apparent specific retention volume had no flow-rate dependence, that negligible adsorption occurred in Columns II and III, and that sufficiently small sample sizes were used so that a solute's liquid phase fugacity is proportional to its weight fraction. The data obtained justify these assumptions.

Four sources of error were identified: random error, error in estimating H_{N_2} with Equation (7), inaccurate column-temperature measurement, and other systematic errors. The random errors were estimated from observed scatter in the data. For example, in Figure 6, the 95% confidence intervals for Column III data, the most accurate, are about 2%. For Figure 5, a random error of 1.9% is used, since this error would account for all the observed scatter.

For ethylene and *n*-butane, a 10% error in estimating H_{N_2} with Equation (7) was assumed. For the other solutes, a 20% error was used, since their retention-time differences were referenced to air, and it is estimated that the solubility of air in polyethylene differs by about 10% from that of nitrogen.

The major source of column-temperature error was due to the gradient across the oven as noted in "Apparatus." The inherent inaccuracies in the mercury-in-glass thermometers and the imprecise stem correction are also taken into account. Small systematic errors arose from neglecting gas-phase nonidealities in Equation (4), imprecise pressure measurements, uncertainty in the amount of polymer in a column, and uncertainties in other quantities appearing in Equation (4).

Table 4 lists the contributions from each error source for ethylene and *n*-octane at the extreme experimental temperatures. *N*-octane is the more sensitive to uncertainty in column temperature, while ethylene, or any other sparingly soluble gas, tends to have larger random errors and is more affected by inaccuracy in the nitrogen-solubility estimate. For all the solutes, worst-probable-case errors averaged 4, 5, 6, 9, and 10% at 124°, 150°, 200°, 250°, and 300°C, respectively. Ethylene and vinyl acetate errors are larger than these mean values, while *n*-octane always has lower errors. The worst error expected, 15%, is for vinyl acetate at 250°C. The size of the data circles in Figure 7 illustrates the estimated worst-probable-case errors.

CORRELATION OF HENRY'S CONSTANTS FOR NONPOLAR SOLUTES IN LIQUID POLYETHYLENE

There are three correlations in the literature for prediction of solubilities in polyethylene. The one by Michaels and Bixler (1961) is applicable to low-molecular-weight solutes near 25°C; it is based on solubilities of gases in semicrystalline polyethylene. Since the experimental data suggest that solute absorption only occurs in the amorphous regions, Michaels and Bixler (1961) extrapolate their data to 100% amorphous polyethylene. These solubilities, in 100% amorphous polyethylene, are similar to those predicted by extrapolating solubilities in liquid polyethylene to lower temperatures. The correlation of Durrill and Griskey (1969) is of similar form but is only applicable to low-molecular-weight gases in liquid polyethylene near 188°C.

The correlation of Stern et al. (1969), although presented in a form applicable for all temperatures and solute critical temperatures, is mainly based on solubility data for semicrystalline polyethylene near 25°C. The only data for liquid polyethylene are the five light-gas data of Durrill and Griskey (1966). This correlation typically underestimates solute solubilities in liquid polyethylene by a factor of 3.

To provide more accurate solubility predictions when no data are available, a new correlation is presented here. It is based on the Flory-Huggins equation for a single solute *i* in a polymer solution:

$$\ln\left(\frac{f_i}{f_i^0}\right) = \ln \Phi_i + \left(1 - \frac{v_i}{v_p}\right)(1 - \Phi_i) + \chi_i(1 - \Phi_i)^2 \tag{10}$$

The interaction parameter χ_i reflects dissimilarities in the free volumes and potential energies of the solute and polymer.

By using Equation (2), the definition of Henry's constant, the Flory-Huggins equation can be rewritten in the limit as $\Phi_i \rightarrow 0$:

$$\ln\left(\frac{H_iM_i}{v_i}\right) = \ln f_i^0 - \ln\frac{v_p}{M_p} + 1 - \frac{v_i}{v_p} + \chi_i \tag{11}$$

For solutes of interest, $v_p >> v_i$; therefore the term (v_i/v_p) is neglected. For our purposes, the molar volume of solute is assumed to be independent of temperature and proportional to the ratio (T_c/P_c), where T_c is the critical temperature and P_c is the critical pressure. Incorporating these assumptions into Equation (11), we get

$$\ln\left(\frac{HM}{T_c}\right) = \ln(f^0/P_c) + C + \chi \tag{12}$$

The subscript *i* has been dropped, since polymer properties only appear in the unknown factors C and χ. To find f^0, the solute standard state fugacity, the correlation of Lyckman et al. (1965) was used:

$$\log_{10}(f^0/P_c) = h^{(0)} + \omega \cdot h^{(1)} \tag{13}$$

where ω is the acentric factor and $h^{(0)}$ and $h^{(1)}$ are known functions of reduced temperature (T/T_c) for the range $0.56 \leq T/T_c \leq 1.0$. Based on the correlation of Lyckman et al., we propose to use for all reduced temperatures

$$h^{(0)} = 0.924278 - \frac{0.677546}{(T/T_c)} - \frac{0.491313}{(T/T_c)^2} \tag{14}$$

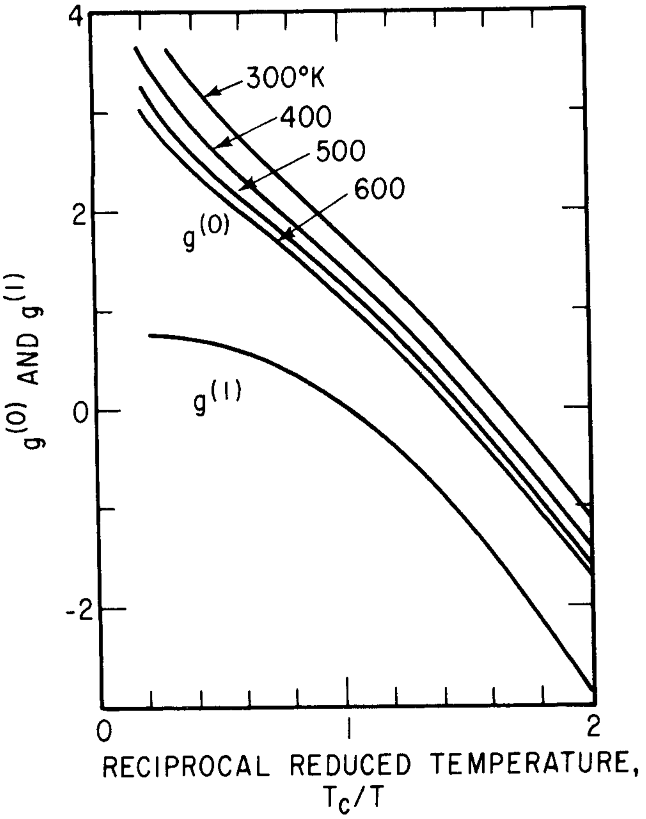

Fig. 9. Functions $g^{(0)}$ and $g^{(1)}$ for Henry's constants in polyethylene.

$$h^{(1)} = 0.689857 + \frac{0.48134}{(T/T_c)} - \frac{1.13278}{(T/T_c)^2} \qquad (15)$$

Experimental Henry's-constant data from this work and other sources listed in Table 5 were fitted to Equation (12) to solve for the correlating parameter $(C + \chi)$. Further, the χ parameter is assumed to be linear in reciprocal temperature

$$(C + \chi) = a_1 + \frac{a_2}{T} \qquad (16)$$

Parameters a_1 and a_2 were then correlated with critical temperature. The Henry's constant for helium in 100% amorphous polyethylene at 25°C, from Michaels and Bixler (1961), was included to cover a wider range of solute critical temperatures. The final correlation has the form

$$\log_{10}\left(\frac{HM}{T_c}\right) = g^{(0)} + \omega \cdot g^{(1)} \qquad (17)$$

where

$$g^{(0)} = 2.401 - \frac{1.3833}{(T/T_c)} - \frac{0.4913}{(T/T_c)^2} + 2.006 \exp(-0.0148T_c) + \frac{371.4}{T} \qquad (18)$$

and

$$g^{(1)} = 0.690 + \frac{0.4813}{(T/T_c)} - \frac{1.1328}{(T/T_c)^2} \qquad (19)$$

with T and T_c in kelvins. Solute molecular parameters were either obtained from Appendix A or Chapter 2 of Reid and Sherwood (1966).

For 84 experimental data, covering the 24 different solutes in Table 5, the average error in (predicted) Henry's constants [Equation (17)] is 12%. The worst error is 52% for vinyl acetate (a polar fluid) at 124°C.

TABLE 5. CORRELATED SOLUBILITY DATA

Source	Solutes
Durrill and Griskey (1966)	Nitrogen, carbon dioxide, monochlorodifluoromethane, argon, and helium
Lundberg and Mooney (1969)	Methane and nitrogen
Schreiber et al. (1973)	3-methylheptane, 2,2,4-trimethylpentane, *n*-decane, *n*-dodecane, ethylbenzene, tetralin, and cis-decalin
Newman and Prausnitz (1973)	*p*-xylene, *n*-heptane, cyclohexane, and trans-decalin
Michaels and Bixler (1961)	Helium
This work	Ethylene, *n*-butane, vinyl acetate, *n*-hexane, benzene, toluene, *n*-octane

The correlation shown in Figure 9 is useful for estimating solubilities of nonpolar solutes in liquid polyethylene. Large errors are to be expected for highly polar compounds, such as water and alcohols. For such solutes the calculated Henry's constants are too low. Although function $g^{(0)}$ is shown in Figure 9 even for temperatures where polyethylene is semicrystalline, these Henry's constants apply to the amorphous region only.

CONCLUSIONS

Gas-liquid chromatography provides a simple and rapid method for obtaining solubility data. However, one must be extremely careful that the data so quickly obtained are not affected by rate phenomena, adsorption, or finite-concentration effects. Only by careful design of experiments can these effects be minimized, and only by varying experimental conditions can one obtain confidence that these effects have been eliminated. The usefulness of the chromatographic technique is illustrated in Figure 7, which shows Henry's constants that vary by three orders of magnitude.

All chromatographic measurements rely on an estimate of the time a solute molecule remains in the gas phase. If an injection of "inert" gas such as nitrogen or air is used, an estimate of that gas's solubility must be made to correct the apparent retention-time differences or to justify the assumption that it has insignificant solubility. For measurements with *n*-octane at 124°C, this correction is indeed insignificant, but for ethylene at 300°C, neglecting this correction produces a 65% error in Henry's constant.

Polyethylene samples are often characterized by their solid density at 25°C; for low-density polyethylene, $0.91 < \rho_{25°C} < 0.93$ g/cc. Different polyethylene samples can vary widely in molecular-weight distribution and extent of long-chain branching. While molecular-weight distribution and extent of long-chain branching have profound effects on rheological, and solid-state, properties, the thermodynamic equilibrium properties of liquid polyethylene seem to be relatively unaffected. From this study and the experimental data of Schreiber et al. (1973) and of Newman and Prausnitz (1973), it appears that the solubilities of a solute in various low-density polyethylene melts do not differ by more than 5 or 10%. Solutes may have about 10% lower solubilities in linear polyethylene than in commercial low-density polyethylene, but there are few data to support this conclusion. Henry's constants in Table 3 provide good estimates for all types of low-density polyethylene, where $\overline{M}_N \cong 10\,000$.

The results shown in Table 3 can be used to calculate the compositions of equilibrium phases in low-pressure separators typically found in high-pressure polyethylene plants. Equation (1), including corrections for gas-phase nonidealities and the Poynting correction for the effect of pressure on liquid-phase fugacities, may be used to calculate solubilities at pressures up to about 25 atm. The weight-fraction activity coefficient Ω_i^* can probably be assumed to be unity as long as the total solute weight fraction in the polymer is only 2% or less. Vapor-phase corrections are discussed by Prausnitz (1969, Chapter 5), and the correlation of Lyckman et al. (1965) can be used for a rough estimate of the partial molar volume needed in the Poynting correction. Solubility parameters (square root of the cohesive energy density) for liquid polyethylene, required in Lyckman's correlation, have been previously estimated by Maloney and Prausnitz (1974).

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NOTATION

a_1, a_2 = correlating constants for each solute calculated from Equation (16)
C = constant in Equation (12)
f_i = fugacity of solute i in the liquid, atm
f^0 = fugacity of pure liquid solute, hypothetical standard state for supercritical solutes, atm
$g^{(0)}, g^{(1)}$ = correlating functions defined in Equations (18) and (19)
$h^{(0)}, h^{(1)}$ = functions used in reference state fugacity, Equations (13), (14), and (15)
H = weight-fraction Henry's constant defined by Equation (2), atm
j = pressure correction factor defined by Equation (5)
m_2 = polymer mass in column, g
M_i = molecular weight of solute i
M_p = polymer molecular weight where (v_p/M_p) = polymer specific volume
$\overline{M}_N$ = number-average molecular weight
$\overline{M}_W$ = weight-average molecular weight
$\overline{M}_Z$ = z-average molecular weight
n = molar flow rate of carrier gas calculated with Equation (8), gmole/s
P = pressure, atm
P_c, P_{ci} = critical pressure for solute i, atm
P_{H_2O} = vapor pressure of liquid water at ambient temperature, atm
R = gas constant, 82.06 cm^3 atm/gmole/kelvin
t_i = retention time for solute i measured from injection to peak maximum, s
T_c, T_{ci} = critical temperature for solute i, kelvins
t_g = time an average solute molecule spends in the gas phase from injection to detection, s
T = absolute temperature, kelvins
v = molar volume, cm^3/g mole
$\bar{v}_i^\infty$ = infinite-dilution, partial-molar volume of component i in liquid phase, cm^3/g mole
V_g^0 = apparent volume of ideal gas, corrected to 1 atm and 0°C, which dissolves in 1 g of polymer, defined by Equation (9), cm^3/g
$\dot{V}_s$ = volumetric flow rate of carrier gas, saturated with water vapor, measured at bubble flowmeter, cm^3/s
w_i = weight fraction of component i in liquid phase
y_i = mole fraction of component i in gas phase

Greek Letters

ϕ_i = fugacity coefficient of component i in gas phase
Φ_i = volume fraction of solute $i \equiv \dfrac{v_i w_i/M_i}{v_i w_i/M_i + v_p w_p/M_p}$
χ = Flory-Huggins interaction parameter
ω = acentric factor of solute
Ω_i^* = weight-fraction activity coefficient of component i in liquid phase

Subscripts

a = at ambient temperature and pressure
I = at column inlet
i = arbitrary solute i
0 = at column outlet
p = polymer

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Friction Coefficients for Bubbly Two-Phase Flow in Horizontal Pipes

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Friction coefficients determined from an experimental study of the flow of bubbly two-phase mixtures in horizontal pipes are used, together with a homogeneous theory, to establish a method for the prediction of the static pressure drop in this class of flows.

SCOPE

The results of experiments on high velocity flows of bubbly two-phase mixtures, that is, mixtures in which the gas phase is dispersed as bubbles throughout a continuous liquid phase, are presented. A simple mathematical model describing this class of flows has been developed by Huey and Bryant (1967), which depends for its application on the availability of experimentally determined average friction coefficients. Huey and Bryant concluded, on the basis of restricted experimental data for air-water mixtures, that friction coefficients could be correlated satisfactorily by a suitably defined Reynolds number alone. They also suggested that, as a first approximation, friction coefficients for single phase flows at the same equivalent Reynolds number could be adopted. The effect of Mach number on the coefficients was thought to be small.

The purpose of this investigation was to obtain reliable experimental data over a wider range of the flow variables and thereby to confirm or disprove these hypotheses and to develop a method for predicting the static pressure drop. A statistical examination of the results obtained was undertaken to establish working formulae correlating friction coefficients with the Reynolds number Re, the pipe diameter D, and the mixture quality χ which would be applicable more generally in the experimental range. These equations were used to predict the static pressure which could then be compared with the experimentally observed results.

CONCLUSIONS AND SIGNIFICANCE

The experimentally determined average friction coefficients $\overline{C}_f$ are shown to be dependent on the mass flow ratio and the pipe diameter, as well as Reynolds number. Therefore, the suggestion of Huey and Bryant (1967) is not substantiated by the experimental evidence reported.

With the correlation equations presented, the average friction coefficients can be predicted, within the experimental range, with an average error of the order of 2%.

The apparent variation of $\overline{C}_f$ with pipe length is shown to be primarily due to compressibility effects. If a high velocity and low pressure region exists, the void fraction can increase substantially, and large accelerations and high Mach numbers can occur. Under these conditions the homogeneous theory is shown to over-estimate the acceleration component in the pressure drop. This inadequacy is thought to be a consequence of the occurrence of slip between the phases. However, regions of high Mach number are of restricted extent in practical flows, and the validity of the homogeneous theory has therefore been substantiated.

When the equations given for $\overline{C}_f$ are used, together with the homogeneous theory, the average error in the prediction of the pressure drop is ±3% in the experimental range. It is shown, however, that the results can be more generally applied, subject to stated restrictions.

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