Thermodynamics of Concentrated Polymer Solutions Containing Polyethylene, Polyisobutylene, and Copolymers of Ethylene with Vinyl Acetate and Propylene

Gas-liquid chromatography is used to measure polymer-solvent interactions in polymer solutions where the solvent is at infinite dilution. Experimental data are presented for 24 binary polymer-solvent systems in the temperature range 50° to 150°C. A simple relation exists between the experimental retention volume data and the infinite dilution volatility; this volatility can be used to calculate the solvent vapor pressure over the polymer solution up to about 0.1 weight fraction solvent. Using concepts from the Prigogine-Flory theory of polymer solutions, Flory-Huggins χ parameters for some polymer-hydrocarbon systems were correlated with the hydrocarbon's normal boiling temperature.

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SCOPE

Fundamental data for polymer-solvent interactions are rare for highly concentrated polymer solutions. However, it is precisely such solutions which are of primary interest in polymer technology, especially in devolatilization of highly concentrated polymer solutions and polymer films. In this work experimental data are reported for 24 binary polymer-solvent systems containing the polymers given in the title and the solvents benzene, toluene, *p*-xylene, *n*-hexane, *n*-heptane, *n*-octane, cyclohexane, and trans-decalin.

The experimental technique used was infinite-dilution, gas-liquid chromatography. This technique is particularly useful for chemical engineering work because it uses only standard, commercially-available equipment, can be applied over a wide range of temperature, and because of the rapidity of chromatographic measurements, can yield a large body of data in a short time.

CONCLUSIONS AND SIGNIFICANCE

Thermodynamic data on polymer-solvent interactions at infinite dilution of solvent were obtained for polyethylene, ethylene-propylene copolymer, ethylene vinyl acetate copolymer, and polyisobutylene with several hydrocarbons. Good agreement was obtained with published results based on static methods or gas chromatography in other laboratories.

Polyethylene and the two ethylene copolymers showed almost identical behavior with the solvents. New and previously obtained data indicate that polymer-solvent interactions for polyethylene-hydrocarbon systems are independent of concentration; a similar conclusion probably applies also to the two ethylene copolymers. Polyisobutylene was found to have substantially larger polymer-solvent interactions than the other polymers; these interactions show considerable concentration dependence.

The chromatographic method for characterizing polymer-solvent interactions provides a convenient tool for rapid determination of fundamental design data. It is particularly useful for polymer solutions containing only trace amounts of solvent where classical experimental methods are slow and difficult to operate.

Several authors have discussed the use of gas chromatography to obtain infinite-dilution activity coefficients of volatile fluids in nonvolatile liquids (Porter et al., 1956; Cruickshank et al., 1966; Kobayashi et al., 1967; Young, 1968). Smidsrød and Guillet (1969) applied gas chromatography to polymer-solvent systems and more recently, several other investigators have studied polymer-solvent interactions using infinite-dilution gas chromatography (Hammers and de Ligny, 1971; Patterson et al., 1971; Summers et al., 1972; Newman and Prausnitz, 1972).

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Recently, Brockmeier et al. (1972) have extended this experimental method to finite solvent concentrations. Brockmeier's extended technique has the advantage of providing information on the concentration dependence of polymer-solvent interactions, but it is much more time consuming than infinite-dilution chromatography.

In this work we have used infinite-dilution gas chromatography to study concentrated solutions of low-density polyethylene, polyisobutylene and two ethylene copolymers, each with several hydrocarbon solvents.

EXPERIMENT

The experimental apparatus used has been described previously by Newman and Prausnitz (1972); only a brief summary is given here. Figure 1 shows a schematic diagram of the chromatographic apparatus. The chromatograph (Varian Aerograph 1520) was modified to provide better oven-temperature control and to enable measurement of pressure drop through the column. The column is packed with a polymer-coated diatomaceous earth support. A small amount of solvent is injected as a liquid, vaporized in the injector, and swept through the column by the carrier gas. Solvent concentration in the effluent carrier gas is monitored by a thermal conductivity detector and recorded. As the solvent sample is eluted from the column the detector produces a peak on the recorder chart.

Materials

All polymers were commercial samples and were used as received from the supplier. Table 1 shows the polymers, their sources, and available characterization data. The solvents were reagent-grade materials obtained from standard laboratory supply sources.

Column Preparation

Columns were prepared by coating the polymer onto Chromosorb-P, AW-DMCS, 60/80 mesh from solution and loading the coated support into a 0.5 cm stainless steel tube. The coating procedure is discussed by Littlewood (1970) and by Purnell (1962). Table 2 shows details of column preparation. Earlier work with polystyrene (Newman and Prausnitz, 1972) has shown that special precautions must be taken when polar systems are studied; in the present work, however, all solvents were nonpolar.

The coverage ratio is defined as the weight ratio of polymer to support in the column. Polymer-solvent interactions often vary with coverage ratio when that ratio is small. Schreiber et al. (1972) have shown for polyethylene systems that the results are independent of coverage ratio when that ratio is greater than 0.05 and we have found the same result for polyisobutylene systems above 50°C. In this work all experiments were made with a coverage ratio of at least 0.15.

DATA REDUCTION

Patterson et al. (1971) have discussed the relation between chromatographic data and activity coefficients. When the solvent, component 1, is infinitely dilute, this relation is

$$\ln \Omega_1^\infty = \ln\left(\frac{a_1}{w_1}\right)^\infty = \ln \frac{RT}{V_g P_1^s M_1} - \frac{P_1^s(B_{11} - V_1)}{RT} \qquad (1)$$

In Equation (1) the activity coefficient Ω_1^∞ is defined as the ratio of activity to weight fraction. The standard state in Equation (1) is pure liquid solvent at system temperature and zero pressure.

The specific retention volume V_g is given by

$$V_g = Q(t_g - t_r)\frac{f_p}{W_2} \qquad (2)$$

The corrected retention time $(t_g - t_r)$ is measured directly from the recorder chart as the difference between the air-peak maximum and the solvent-peak maximum. Air is always injected along with the sample as an inert marker; since air is not dissolved in the polymer, it is swept directly through the column providing a convenient measure of the column holdup volume. Subtracting the air retention time from the apparent solvent retention time gives the corrected solvent retention time. To correct for

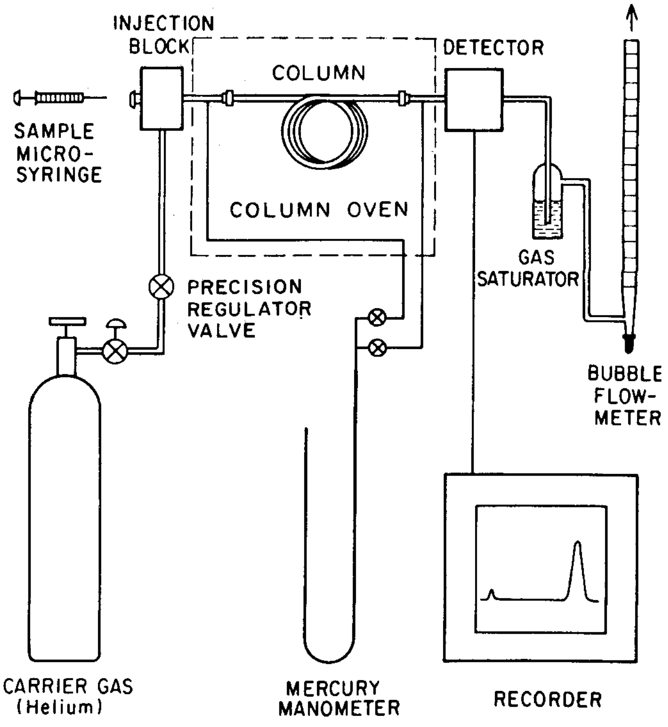

Fig. 1. Gas chromatographic apparatus.

TABLE 1. DESCRIPTION OF POLYMERS

Polymer	Source	Industrial name	Characterization
Low density polyethylene	Union Carbide Corp.	DYN I uncompounded	$\overline{M}_n = 35{,}000$ $\overline{M}_w = 235{,}000$
Ethylene-vinyl acetate copolymer	Union Carbide Corp.	DXM-228 uncompounded	4% Vinyl Acetate Melt Index 0.8 $\overline{M}_n = 30{,}000$ $\overline{M}_w = 105{,}000$
Ethylene-propylene copolymer	Enjay Chemical Co.	Vistalon-404	40 ± 3.0 wt % ethylene $\overline{M}_v = 250{,}000$
Polyisobutylene	Enjay Chemical Co.	Vistanex-LM	$\overline{M}_v = 53{,}000$

TABLE 2. CHROMATOGRAPHIC COLUMNS

	Polyethylene	Ethylene vinyl acetate	Ethylene-propylene	Polyisobutylene
Weight of polymer, g	2.1153	2.0243	2.6330	2.0995
Weight of support, g*	13.056	13.069	12.995	10.000
Coverage ratio, g/g	0.162	0.155	0.202	0.21
Coating solvent	*p*-xylene	*p*-xylene	*p*-xylene	chloroform
Coating temp., °C	110.0	110.0	110.0	50.0
Column length, *m*	1.52	1.52	1.52	1.21
Column internal diam., cm	0.25	0.25	0.25	0.25

* Chromosorb-P, AW-DMCS, 60/80 mesh.

TABLE 3. ACTIVITY COEFFICIENTS AT INFINITE DILUTION (WT. FRACTION) AND, IN PARENTHESES, FLORY χ PARAMETERS FOR SOLVENTS IN LOW-DENSITY POLYETHYLENE

	Ω_1^∞ (χ)				
Solvent	*t*, °C 110	125	150	175	200
Benzene	4.39(0.45)	4.32(0.43)	4.25(0.39)	4.27(0.37)	4.13(0.29)
Toluene	3.95(0.35)	3.94(0.35)	3.94(0.33)	3.91(0.31)	3.87(0.28)
p-Xylene	3.73(0.30)	3.71(0.28)	3.76(0.28)	3.75(0.30)	3.71(0.25)
n-Hexane	5.65(0.39)	5.73(0.39)	5.91(0.39)	5.97(0.36)	6.10(0.33)
n-Heptane	5.08(0.35)	5.10(0.34)	5.26(0.34)	5.37(0.32)	5.40(0.28)
n-Octane	4.71(0.31)	4.74(0.30)	4.85(0.31)	4.93(0.29)	4.94(0.26)
Cyclohexane	3.88(0.21)	3.86(0.19)	3.95(0.19)	4.04(0.18)	4.04(0.13)
Trans decalin	2.67(0.02)	2.70(0.03)	2.77(0.04)	2.78(0.03)	2.75(0.02)

finite pressure drop through the column, the correction factor f_p is given by Purnell (1962):

$$f_p = \frac{3}{2}\,\frac{\left[\left(\frac{P_i}{P_o}\right)^2 - 1\right]}{\left[\left(\frac{P_i}{P_o}\right)^3 - 1\right]} \tag{3}$$

The infinite-dilution weight-fraction activity coefficient Ω_1^∞ has an important advantage over other activity coefficients: it is independent of any polymer-solution theory and it can be found directly from the chromatographic data without knowledge of fluid densities and without specification of polymer molecular-weight distribution.

When Equation (1) is combined with the Flory-Huggins equation, (Flory, 1953), we obtain for the Flory parameter χ:

$$\chi = \ln \Omega_1^\infty + \ln \frac{v_2}{v_1} - \left(1 - \frac{1}{m}\right) \tag{4}$$

In polymer solutions the quantity $1/m$ is very small compared to unity and can be neglected.

If the parameter χ is assumed to be independent of polymer concentration, the vapor pressure of the solvent over the solution can be calculated at any concentration once χ is known, using the relation:

$$\ln \frac{P_1}{P_1^s} = \ln \phi_1 + \left(1 - \frac{1}{m}\right)\phi_2 + \chi\,\phi_2^2 + \frac{P_1^s\,(B_{11} - V_1)}{RT} - \frac{P_1\,B_{11}}{RT} \tag{5}$$

However, to calculate the partial pressure at very low solvent concentrations it is not necessary to assume any model; the solvent's pressure can be calculated directly from the specific retention volume by the remarkably simple equation:

$$\left(\frac{P_1}{w_1}\right)^\infty = \frac{RT}{V_g M_1} \tag{6}$$

Equation (6) gives the volatility (Henry's constant) of the solvent at very low weight fractions. To find this volatility it is necessary only to know the temperature, the molecular weight of the solvent, and the specific retention volume as given by Equation (2).

RESULTS

Tables 3 to 6 show infinite-dilution activity coefficients calculated by Equation (1) and Flory parameters calculated by Equation (4). Second virial coefficients for the solvents were estimated by the correlation of Pitzer and Curl (1957). Solvent saturation vapor pressures and specific volumes were obtained from standard sources, including the compilation of Timmermans (1950, 1960). Specific volumes for polyethylene were taken from the compilation of Orwoll and Flory (1967) and specific volumes for polyisobutylene were obtained from Eichinger and Flory (1968a). The specific volume of the ethylene-propylene copolymer was estimated by the method of Bondi (1968) and the specific volume of the ethylene-vinyl acetate copolymer was assumed to be the same as that of polyethylene.

A column prepared with polyisobutylene (Enjay Vistanex L-100) with $\overline{M}_v = 1.1 \times 10^6$ gave results essentially identical to those obtained with the lower molecular-weight polyisobutylene shown in Table 6.

When the air and solvent are swept from the column by the carrier gas, the concentration of each one in the carrier gas is represented by a peak on the recorder chart. All peaks obtained in this work were symmetric (Gaussian) in shape as required by equilibrium chromatographic theory. There was no dependence of specific retention volume on carrier-gas flow rate except for polyisobutylene at 50°C. In this case measurements were made at several

Table 4. Activity Coefficients at Infinite Dilution (Wt. Fraction) and, in Parentheses, Flory χ Parameters for Solvents in Ethylene-Vinyl Acetate Copolymer

	Ω_1^∞ (χ)				
Solvent	t, °C 110	125	150	175	200
Benzene	4.30(0.44)	4.26(0.41)	4.20(0.37)	4.18(0.34)	4.09(0.28)
Toluene	3.88(0.33)	3.86(0.33)	3.86(0.31)	3.89(0.31)	3.85(0.28)
p-Xylene	3.64(0.27)	3.64(0.26)	3.67(0.29)	3.74(0.29)	3.76(0.26)
n-Hexane	5.66(0.39)	5.73(0.39)	5.87(0.38)	5.97(0.36)	6.01(0.32)
n-Heptane	5.09(0.35)	5.11(0.34)	5.14(0.31)	5.37(0.32)	5.62(0.32)
Cyclohexane	3.87(0.21)	3.86(0.19)	3.91(0.18)	3.95(0.15)	4.01(0.13)

Table 5. Activity Coefficients at Infinite Dilution (Wt. Fraction) and, in Parentheses, Flory χ Parameters for Solvents in Ethylene-Propylene Copolymer

	Ω_1^∞ (χ)				
Solvent	t, °C 100	125	150	175	200
Benzene	4.47(0.46)	4.33(0.40)	4.31(0.37)	4.35(0.35)	4.30(0.30)
Toluene	3.98(0.34)	3.89(0.30)	3.85(0.28)	3.87(0.27)	3.80(0.24)
p-Xylene	3.70(0.27)	3.63(0.23)	3.61(0.21)	3.62(0.20)	3.60(0.17)
n-Hexane	5.11(0.28)	5.25(0.27)	5.37(0.26)	5.68(0.27)	5.80(0.26)
n-Heptane	4.80(0.27)	4.75(0.23)	4.80(0.22)	4.89(0.19)	4.90(0.16)
Cyclohexane	3.83(0.18)	3.80(0.14)	3.87(0.14)	4.06(0.15)	4.03(0.13)

Table 6. Activity Coefficients at Infinite Dilution (Wt. Fraction) and, in Parentheses, Flory χ Parameters for Solvents in Polyisobutylene

	Ω_1^∞ (χ)				
Solvent	t, °C 50	75	100	125	150
Benzene	6.56(0.82)	6.46(0.78)	6.36(0.74)	6.26(0.70)	6.15(0.66)
Toluene	5.86(0.70)	5.76(0.66)	5.66(0.65)	5.54(0.59)	5.43(0.55)
n-Hexane	6.96(0.58)	7.12(0.57)	7.28(0.56)	7.43(0.55)	7.59(0.54)
Cyclohexane	5.04(0.43)	5.13(0.42)	5.22(0.42)	5.31(0.41)	5.40(0.40)

flow rates and extrapolated to zero flow rate to insure that equilibrium was attained. The accuracy of the activity coefficients is estimated to be ± 0.1. However, since calculation of χ by Equation (4) is achieved by subtraction of two numbers of about the same size ($\ln v_2/v_1$ is usually close to zero), small errors in Ω_1^∞, are magnified. Flory χ values are accurate to about ± 0.03.

Figures 2 and 3 show solvent vapor pressures as a function of composition for concentrated solutions of polyethylene and ethylene-propylene copolymer; the results shown were calculated by Equation (5). Figures 4 and 5 show infinite-dilution volatilities calculated as a function of temperature for highly concentrated solutions of polyethylene and polyisobutylene. These volatilities were found using Equation (6).

COMPARISON WITH OTHER EXPERIMENTAL RESULTS

Polyethylene-hydrocarbon solutions have been studied by van der Waals and Hermans (1950) using an isobaric vapor pressure apparatus and by Schreiber et al. (1972) and Brockmeier et al. (1972) using gas chromatography. Solutions of polyisobutylene in benzene and cyclohexane have been studied by Bawn and Patel (1956) in the range 25° to 65°C using isobaric vapor pressure measurements and by Hammers and de Ligny (1971) in the range 25° to 125°C using gas chromatography. Studies for polyisobutylene-benzene and polyisobutylene-cyclo-

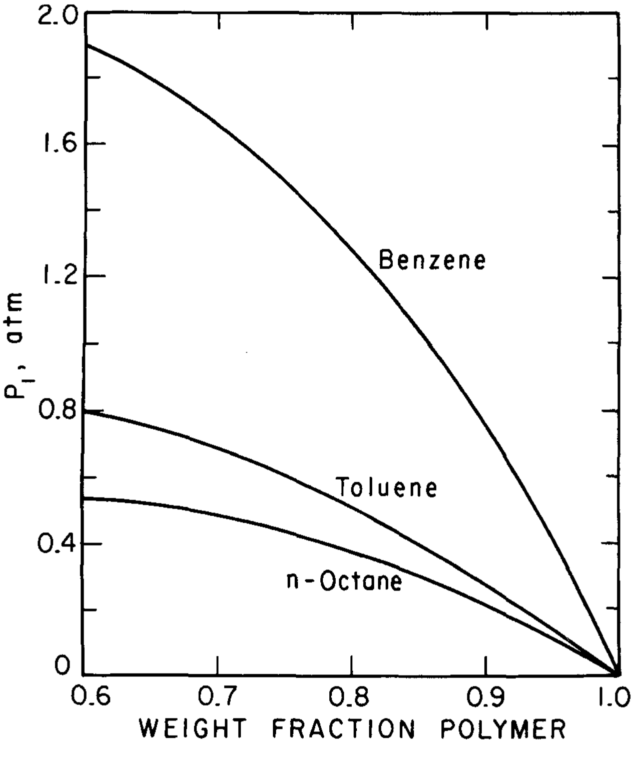

Fig. 2. Solvent vapor pressure for polyethylene-hydrocarbon solutions at 110°C.

hexane systems by Eichinger and Flory (1968b) were restricted to temperatures below 40°C.

The results of all investigations are summarized in Table 7. The values shown in the static column were obtained by extrapolation to infinite dilution of solvent. For polyethylene-hydrocarbon systems there is excellent agreement between our results and those reported by others except for the system polyethylene-*n*-decane. The lack of agreement between our result and that reported by Brockmeier et al. (1972) appears to be due to a difference in data reduction. In the analysis of their results, Brockmeier et al. (1972) neglected the correction of activity for vapor-phase nonideality. When Brockmeier's χ value for the polyethylene-*n*-decane system is corrected for vapor-phase nonideality, it is 0.22, in good agreement with ours.

For polyisobutylene systems there is fair agreement between static and chromatographic results, but the static Flory parameters are somewhat larger. The small discrepancy may be due to uncertainties in extrapolation to infinite dilution as indicated in the next section.

EFFECT OF CONCENTRATION

It has been found experimentally (Flory, 1953) that χ is, in general, a function of concentration. However, the work of van der Waals and Hermans (1950) in the range 0 to 0.8 volume fraction polymer and Brockmeier et al. (1972) in the range 0.85 to 1.0 weight fraction polymer suggests that χ is independent of concentration for polyethylene-*n*-alkane systems. Since the binary systems in Table 3 are very similar chemically, we expect that χ is nearly independent of concentration for all systems listed in Table 3. We also expect that the χ values for systems containing the two ethylene copolymers shown in Tables 4 and 5 are nearly independent of concentration.

However, there is strong evidence that χ is not constant with concentration in the polyisobutylene-benzene system. Bawn and Patel (1956) and Eichinger and Flory (1968b) have shown that χ increases by about 50% as polymer fraction goes from 0.5 to 0.95. For the polyisobutylene-cyclohexane system the same investigators find that χ

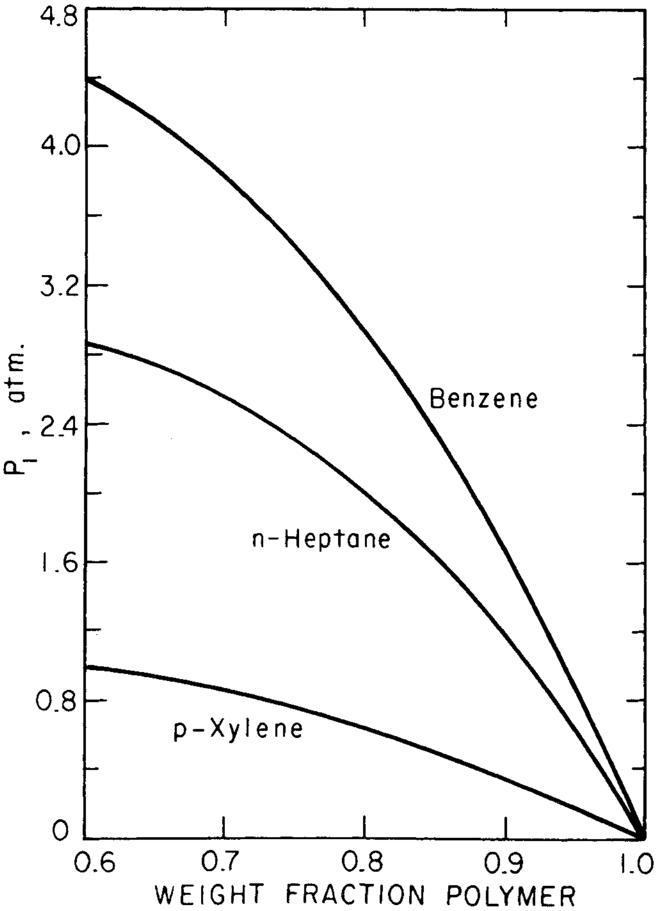

Fig. 3. Solvent vapor pressure for ethylene-propylene copolymer-hydrocarbon solutions at 150°C.

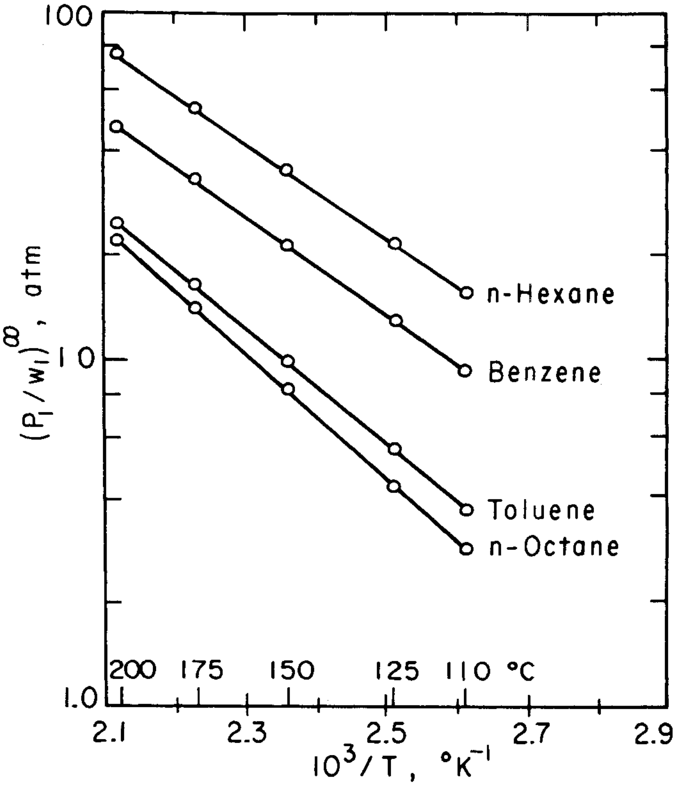

Fig. 4. Volatilities of solvents at infinite dilution in polyethylene.

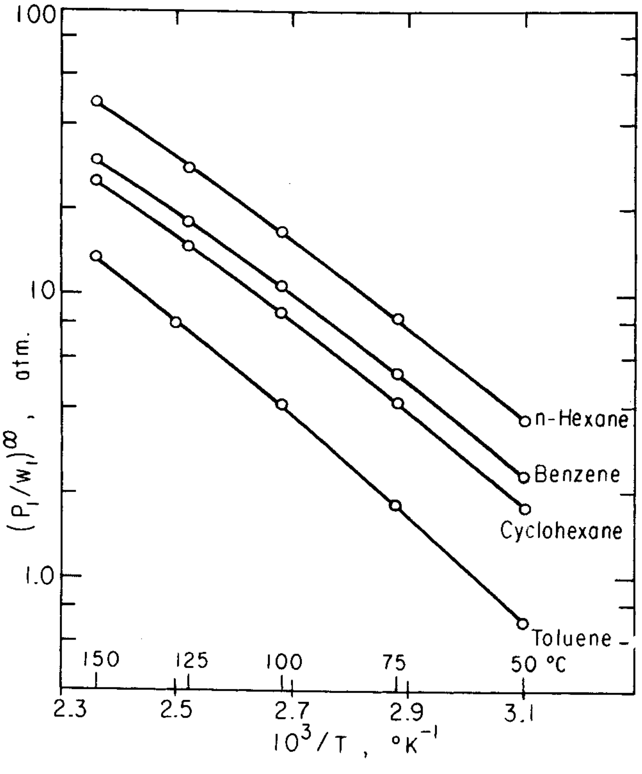

Fig. 5. Volatilities of solvents at infinite dilution in polyisobutylene.

TABLE 7. COMPARISON WITH PUBLISHED RESULTS

Polymer	Solvent	t, °C	χ glc		static*
Polyethylene	n-Heptane	110	0.35		0.345[a] (109°)
	n-Octane	125	0.30	0.31[b] (120°)	
		150	0.31	0.30[b] (145°)	
	p-Xylene	125	0.28	0.27[b] (120°)	
		150	0.28	0.28[b] (125°)	
	n-Decane	185	0.25	0.11[c]	
Polyisobutylene	Benzene	50	0.82	0.84[d] (40°)	0.90[e] (40°)
		75	0.78	0.81[d] (60°)	0.80[e] (65°)
		100	0.74	0.77[d]	
	Cyclohexane	50	0.43	0.45[d] (40°)	0.50[e] (40°)
		75	0.42	0.47[d] (60°)	0.50[e] (65°)
		100	0.42	0.49[d]	

[a] van der Waals and Hermans (1950).
[b] Schreiber, Tewari and Patterson (1972).
[c] Brockmeier, McCoy and Meyer (1972).
[d] Hammers and de Ligny (1971).
[e] Bawn and Patel (1956).
* Extrapolated from data at finite solvent concentration to infinite dilution.

increases by about 10 to 20% as polymer volume fraction goes from 0.5 to 0.9.

It is not clear that χ is always a monotonic function of polymer concentration and, therefore, in systems where χ varies with concentration, it is not possible to make an unambiguous comparison between χ found from chromatography and χ found from extrapolation of static data. However the theory of Eichinger and Flory (1968b) suggest that χ usually increases with polymer concentration and in that event the χ value obtained from gas chromatographic measurements represents an upper limit.

EFFECT OF DIFFERENCES IN FREE VOLUME

Tables 3 to 5 show that there is little difference between the activity coefficients of a given solvent in polyethylene and in the two ethylene copolymers. The variation from one solvent to another is greater but still not large. The difference in activity coefficients can be qualitatively explained by consideration of the state of expansion of the polymer and solvent. Recent work of Eichinger and Flory (1968b) indicates that χ consists of two contributions: one due to differences in the extent of volumetric expansion of polymer and solvent, and the other due to differences in intermolecular forces. The first contribution is called the free-volume contribution and is related to the difference in α, the thermal expansion coefficient. In the systems studied here, since all polymers and solvents are chemically similar, the intermolecular force contribution probably is small. Thus χ varies from one solvent to another primarily because of differences in free volume. Following similar arguments, Patterson et al. (1972) have correlated χ values for polyethylene-solvent systems with the value of α of the solvent. We have here prepared a similar correlation.

Wall and Krigbaum (1949) have shown that α for hydrocarbons is approximately proportional to the reciprocal of the normal boiling point of the hydrocarbon. Using this relation, we have plotted Flory χ parameters as shown in Figure 6. This plot represents our data as well as those of Schreiber et al. (1972) for polyethylene-hydrocarbon systems and of Hammers and de Ligny (1971) for polyisobutylene-hydrocarbon systems. Figure 6 shows that a fair correlation is obtained; however, in both plots the cycloparaffins give anomalously low χ values indicating that differences in free volume do not make the only contribution to χ in the systems studied. Cycloparaffins contain only methylene (CH_2) groups and no methyl (CH_3) groups; this difference could, perhaps, account for a lower energy of mixing. However, this possibility is difficult to reconcile with the observation that there is no significant difference in behavior between normal and branched paraffins.

A possible explanation for the cycloparaffin results may be related to their molecular structure. Due to their chair-and-boat forms and their cyclic nature, cycloparaffins will more readily fit into holes in the polymer network than the n-paraffins and the aromatics. Once in the polymer network the cycloparaffins' motion is more restricted since they have less symmetry than the n-paraffins and aromatics. The low activity coefficients of the cycloparaf-

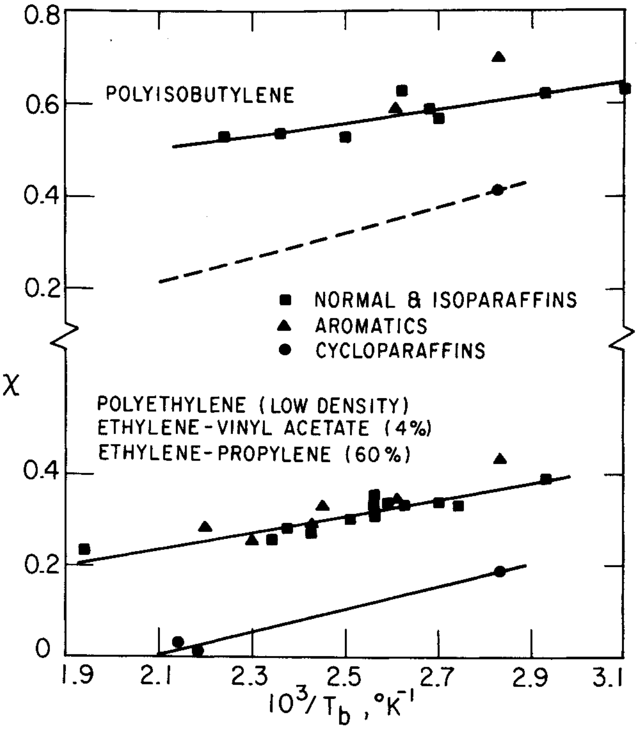

Fig. 6. Flory parameters for hydrocarbon-polymer systems at 120° to 125°C containing trace amounts of hydrocarbon.

fins may therefore be due to strongly hindered rotation of these molecules when infinitely dilute in the polymer.

Figure 6 also shows that χ values are substantially larger for polyisobutylene-hydrocarbon systems than for polyethylene-hydrocarbon systems. This is consistent with the large effect of the free-volume contribution because the value of α for polyisobutylene is substantially smaller than that for polyethylene at the same temperature.

APPLICATION OF RESULTS

Gas-liquid chromatography provides a rapid and convenient experimental method for obtaining solvent volatilities in concentrated polymer solutions.

Figures 2 and 3 show that when χ is constant, the solvent vapor pressure of a polymer solution is very nearly proportional to polymer weight fraction in the range 0.9 to 1.0. Volatilities presented in Figures 4 and 5 may be used directly to calculate solvent vapor pressure for highly concentrated polymer solutions.

For some polymer-hydrocarbon systems χ values may be obtained from Figure 6. For the ethylene-containing polymers shown in Figure 6, χ appears to be independent of polymer concentration and solution vapor pressures may be calculated by Equation (5).

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NOTATION

a_1 = activity of solvent in polymer-solvent mixture
B_{11} = second virial coefficient of pure solvent, cc/g mole
f_p = correction for pressure drop across column
m = ratio of polymer molar volume to solvent molar volume
M_1 = solvent molecular weight
$\overline{M}_n$ = number average molecular weight of polymer
$\overline{M}_v$ = viscosity average molecular weight of polymer
$\overline{M}_w$ = weight average molecular weight of polymer
P_1 = vapor pressure of solvent over polymer-solvent mixture, atm
P_1^s = saturation vapor pressure of pure solvent, atm
P_i = absolute column inlet pressure, mm Hg
P_o = absolute column outlet pressure, mm Hg
Q = volumetric flow rate of carrier gas at column outlet temperature and pressure, cc/min
R = gas constant
t = column temperature, °C
t_g = residence time of solvent sample in column, min
t_r = residence time of air sample in column, min
T = column temperature, °K
v_1 = solvent specific volume, cc/g
v_2 = polymer specific volume, cc/g
V_1 = solvent molar volume
V_g = solvent specific retention volume, cc/g
w_1 = weight fraction solvent
W_2 = weight of polymer in column, g

Greek Letters

ϕ_1 = volume fraction solvent
ϕ_2 = volume fraction polymer
χ = Flory parameter
Ω_1^∞ = infinite-dilution, weight-fraction activity coefficient

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