Gas Chromatographic Determination of Thermodynamic Properties of Polymer Solutions. I. Amorphous Polymer Systems

N. F. Brockmeier,*[1a] R. W. McCoy,[1b] and J. A. Meyer[1b]

Research and Development Department, Amoco Chemicals Corporation,
and Research and Development Department, Standard Oil Company, (Indiana),
Standard Oil Research Center, Naperville, Illinois 60540. *Received April 12, 1972*

ABSTRACT: A gas chromatographic (gc) method has been developed to measure solubility isotherms of a low molecular weight solvent in a high polymer. This method depends on the elution of the injected solvent on a concentration plateau of the same solvent in nitrogen carrier gas. The measured solubility is used to calculate the vapor–solid equilibrium ratio ($\Omega = a_1/w_1$), along with the solvent–polymer interaction parameter χ, as a function of solution composition. Based on the Flory–Huggins and Maron theories, a mathematical correlation permits computation of Ω values, usually with less than 5% deviation from those measured experimentally. The following polymer–solvent systems have been studied: polystyrene with benzene and ethylbenzene at 120° and with ethylbenzene at 185°, polyethylene with *n*-decane at 185°, and atactic polypropylene with hexane at 80°. The computed Ω values range from about 4 to 5.

The urgent need for reliable process design data has led us to develop a new gas chromatographic (gc) method for measuring the thermodynamic properties of polymer solutions and a mathematical model for correlating the results. Several investigators[2–5] have reported their gc measurements of activity coefficients and vapor–polymer equilibrium ratios at infinite dilution. By contrast, our method yields equilibrium values using finite concentrations of solvent vapor in the carrier gas.[6] We have determined distribution isotherms, activity coefficients rationalized by weight fraction (Ω value), and polymer–solvent interaction parameters for polystyrene, amorphous polyethylene, and atactic polypropylene with selected hydrocarbon vapors constituting up to 60 mol % of the carrier gas. In the limit of infinite dilution, our Ω values and interaction parameters essentially agree with those reported in the literature.[3,5]

Although the gc method has been used for some time in measuring the activity coefficient of a vapor over a low molecular weight stationary phase,[7,8] it has only recently been applied to a polymeric stationary phase. In 1969, the activity coefficients of acetic acid, butyl alcohol, and hexadecane were determined at infinite dilution in a polyamide of 50,100 molecular weight coated on Chromosorb packing.[2a] The equations for calculating a more useful form of the activity coefficient have been derived in another gc study. Patterson, *et al.*,[3] divide the activity coefficient by weight fraction of solvent to yield a logarithm that does not approach minus infinity for a polymer. They also report values for the interaction parameter of *n*-dodecane in branched polyethylene and *n*-decane in linear polyethylene at high temperatures (110–190°). In another investigation, gc was used to measure the activity coefficients at infinite dilution for polyisobutylene and polystyrene with 13 different hydrocarbon solvents.[5] Both polar and nonpolar solvents were included at temperatures of 25, 150, 175, and 200°.

Theory

Two factors have been important in facilitating the application of gc to polymer thermodynamics in solutions of finite concentrations: appropriate theoretical equations and polymer coating procedure. The first of these is discussed here, while the second is covered in the Experimental Section. The theoretical relations for computing the desired isotherms from gc data have been developed in a general form in a series of articles by Conder and Purnell.[9–11] They demonstrated the utility of their equations by accurately measuring the activity coefficients of *n*-hexane in squalane and *n*-heptane in di-*n*-nonyl phthalate at carrier gas concentrations ranging from zero to 70 mol %.[12] Their technique of elution on a plateau of finite concentration was the one chosen for all of our work. Their key equation yields the solubility isotherm: $q(P)$ moles of hydrocarbon solvent per unit mass of polymer in the stationary phase at mean pressure P. To calculate an accurate value for $q(P)$, corrections must be made to the experimental values for pressure, flow rate, and feed gas composition. These corrections will be discussed only briefly here because they have been derived in detail in the literature.[11]

The true value of the mole fraction of solvent vapor above the stationary phase is determined from

$$\psi = ajy_0 \tag{1}$$

where y_0 is the mole fraction measured at the detector outlet, j is a compressibility correction to compensate for the column pressure gradient, and a is a correction for gas nonideality. To correct for the pressure drop required to force the carrier gas through the column, a mean pressure for the isotherm is defined by

$$P = p_0 J_3^4 \tag{2}$$

The form of the J function is defined as

$$J_n^m = \frac{n}{m}\left[\frac{(p_i/p_0)^m - 1}{(p_i/p_0)^n - 1}\right] \tag{3}$$

---

(1) (a) Amoco Chemicals Corp.; (b) Standard Oil Co.

(2) (a) O. Smidsrød and J. E. Guillet, *Macromolecules*, **2**, 272 (1969); (b) J. E. Guillet and A. N. Stein, *ibid.*, **3**, 102 (1970).

(3) D. Patterson, Y. B. Tewari, H. P. Schreiber, and J. E. Guillet, *ibid.*, **4**, 356 (1971).

(4) W. E. Hammers and C. L. DeLigny, *Recl. Trav. Chim. Pays-Bas*, **90**, 912 (1971).

(5) R. D. Newman and J. M. Prausnitz, *J. Phys. Chem.*, **76**, 1492 (1972).

(6) N. F. Brockmeier, R. W. McCoy, and J. A. Meyer, *Macromolecules*, **5**, 130 (1972).

(7) F. I. Stalkup and H. A. Deans, *AIChE J.*, **9**, 106 (1963).

(8) K. T. Koonce, H. A. Deans, and R. Kobayashi, *ibid.*, **11**, 259 (1965).

(9) J. R. Conder and J. H. Purnell, *Trans. Faraday Soc.*, **64**, 1505 (1968).

(10) J. R. Conder and J. H. Purnell, *ibid.*, **64**, 3100 (1968).

(11) J. R. Conder and J. H. Purnell, *ibid.*, **65**, 824 (1969).

(12) J. R. Conder and J. H. Purnell, *ibid.*, **65**, 839 (1969).

The arithmetic mean pressure in a column is p_0/J_2^1. Accurate measurements of inlet and outlet column pressures are required for eq 2 and 3.

With the inclusion of a term to compensate for gas nonideal P–V behavior, the full compressibility correction takes the form

$$j = J_3^2\left[1 + \frac{y_0^2 p_0 B_{22}(J_3^2 - 1)}{RT}\right] \tag{4}$$

where B_{22} is the second virial coefficient of the solvent vapor at the column operating temperature, T. Values of B_{22} are either estimated from a correlation in the literature[13] or obtained from tabulated results.[14]

Sorption into the solid phase can have a significant effect, causing the gas velocity in the column to differ at each end. A common measure of sorption is the solvent distribution coefficient, given approximately by

$$k = (t_R - t_M)/t_M \tag{5}$$

where t_R and t_M are, respectively, the retention times of the solvent and of an air peak. One of the relationships needed to correct the retention volume for sorption is

$$b_n^m = 1 + k(1 - J_n^m y_0) \tag{6}$$

The composition correction factor for gas nonideality is defined as

$$a = \frac{b_2^1}{b_3^2}\left[1 + \frac{2y_0 p_0 B_{22}(1 - J_2^1 y_0)}{RT}\right] \tag{7}$$

Calculations demonstrate that b_2^1/b_3^2 is within 1% of unity if the pressure ratio over the column is less than 1.1, a fact that simplifies some of the computations. The solvent concentration in the gas above the polymer is calculated from a virial equation of state, dropping all terms after the second virial coefficient. This approximation introduces less than 1% error at our conditions. Solving this equation for concentration gives

$$c = p_0\psi/(ajRT + \psi^2 B_{22} p_0) \tag{8}$$

The effect of sorption causes a difference between the retention times of air (nonsorbed) and of hydrocarbon. This is expressed classically as a difference in retention volumes

$$V_R - V_M = (t_R - t_M)TF(y)/T_F \tag{9}$$

The temperature ratio, T/T_F, is included to correct the flow rate, $F(y)$, measured at the flowmeter temperature to that of the column. It has been shown[11] that the distribution isotherm at pressure P is given by the integral

$$q(P) = \frac{j}{V_2}\int_0^{y_0} \frac{V_R - V_M}{1 - \psi}\,dc \tag{10}$$

For our method, elution on a plateau of constant solvent concentration in the carrier, the above integral is evaluated by finding the area under the curve generated by plotting $(V_R - V_M)/(1 - \psi)$ *vs.* concentration. The criterion for constant concentration as given by Conder and Purnell is[11]

$$y_0(p_i - p_0)/p_0 \leq 0.01 \tag{11}$$

where 0.01 is the experimental uncertainty in V_R. If reliable data are to be obtained at high solvent mole fraction, the column pressure drop must be held to a very low value. However, this restriction on pressure drop can be relaxed somewhat for the special case of a nearly straight distribution isotherm. With a straight isotherm, the contribution to retention time at the inlet of the gc column (high c) is exactly offset by the loss at the outlet (low c). The pressure gradient must be nearly linear ($p_i/p_0 < 1.7$). We were able to tolerate about 5% error caused by changing concentration, so the limit set by eq 11 was extended to 0.08. Beyond this limit, the curvature of the distribution isotherms contributed more than 5% error.

Equation 10 provides the key information from which equilibrium values are calculated. One equilibrium ratio commonly used in work with polymers is

$$\Omega = \frac{P_1}{P_1^0 w_1} = \frac{P\psi}{P_1^0 w_1} \tag{12}$$

The weight fraction of solute in the polymer phase is

$$w_1 = \frac{q(P)M_1}{1 + q(P)M_1} \tag{13}$$

Since the solvent activity a_1 is $p\psi/p_1^0$, Ω is identical with a_1/w_1 the activity coefficient rationalized by weight fraction. This definition of Ω obviates the need to know the polymer molecular weight and has other advantages discussed by Patterson, *et al.*[3]

Although the Ω values computed from eq 12 are completely independent of any polymer solution theory, they can be correlated with solution composition using one or more of the classical theories. The Flory–Huggins equation, which is based on the lattice theory of solutions, provides an accurate correlation of solvent activity above an amorphous polymer

$$\ln a_1 = \ln \phi_1 + \phi_2 + \chi\phi_2^2 \tag{14}$$

where ϕ_1 and ϕ_2 are the volume fractions of solvent and polymer, respectively. The interaction parameter χ is often a constant for compatible solvents in an amorphous polymer. For those systems in which χ varies, it is convenient to refer to the Maron theory of nonelectrolyte solutions.[15,16] One of the most useful features of the Maron theory is the result that χ is a linear function of composition

$$\chi = \psi^{(0)} - \psi^{(1)}\phi_1 \tag{15}$$

where $\psi^{(0)}$ and $\psi^{(1)}$ are constants at a given temperature. Equation 14 is converted to the equilibrium ratio form by dividing a_1 by the weight fraction

$$w_1 = \frac{\phi_1}{\phi_2/r + \phi_1} \tag{16}$$

where r is the ratio of the specific volume of the polymer to that of the solvent, v_2/v_1, at the column operating temperature. The resulting equation

$$\ln \Omega = \ln[\phi_2/r + \phi_1] + \phi_2 + \chi\phi_2^2 \tag{17}$$

is extremely useful for interpolating Ω values over the range where χ is known. The limiting Ω value for a pure polymer (plateau concentration of solvent equal to zero) is

$$\ln \Omega = -\ln r + 1 + \chi \tag{18}$$

At the other end of the range ($\phi_1 = 1$), Ω equals unity.

Because our gc method gives data over a range of solution compositions, we can compare the behavior of χ with the predictions of any theory. Starting with eq 14, the value of χ can be calculated directly from

$$\chi = [\ln(\Omega w_1/\phi_1) - \phi_2]\phi_2^{-2} \tag{19}$$

---

(13) K. C. Pitzer and R. F. Curl, Jr., *J. Amer. Chem. Soc.*, **79**, 2369 (1957).

(14) M. L. McGlashan and D. J. B. Potter, *Proc. Roy. Soc., Ser. A*, **267**, 478 (1962).

(15) S. H. Maron, *J. Polym. Sci.*, **38**, 329 (1959).

(16) S. H. Maron and N. Nakajima, *ibid.*, **40**, 59 (1959).

Table I
Description of Gas Chromatographic Columns[a]

Column no.	Polymer	Mesh size	Polymer, %	Loading, g
1	Polystyrene	70–80	1.00	0.1450
2	Polystyrene	70–80	5.00	0.7900
3	Polyethylene	80–100	1.78	0.3336
4	Polyethylene	80–100	0.834	0.1552
5	Atactic polypropylene	100–120	0.409	0.0709
6	Atactic polypropylene	60–80	1.30	0.2010

[a] O.d. 0.25 in., in length 10 ft, acid-washed Chromosorb W support.

Equation 19 is a counterpart to eq 12 of Patterson, *et al.*,[3] with one important difference: ours is not limited to infinite dilution ($\phi_1 = 0$).

Although solution theories generally use volume fraction as the composition variable, it is more convenient for design purposes to express Ω values as a function of weight fraction. Therefore, for our correlations eq 17 is converted to

$$\ln \Omega = -\ln\left[(1 - w_1)r + w_1\right] + \frac{1 - w_1}{(1 - w_1) + w_1/r} + \chi\left[\frac{1 - w_1}{(1 - w_1) + w_1/r}\right]^2 \quad (20)$$

Experimental Section

The experimental procedure comprised three principal steps: preparation of the gc columns, preparation of the carrier gases, and collection and treatment of the gc data.

Preparation of Gc Columns. The characteristics of the gc columns are summarized in Table I. Each column consisted of a 10-ft length of 0.25-in. o.d. copper tubing packed with a support of acid-washed Chromosorb W that had been coated with a thin layer of polymer—polystyrene, polyethylene, or atactic polypropylene. The coating procedure, designed to produce free-flowing packings, was based on previous work,[17] which has shown that coating thickness must be controlled to minimize gc data errors arising from either too slow or too rapid elution rates.

For polystyrene, about 1 g of the polymer (Amoco General Purpose R3 Grade) dissolved in benzene was stirred with a known weight of support (99 g for a 1% polymer coating), and then the benzene was evaporated.

For polyethylene, about 350 g of decalin and 0.2–0.3 g of Santonox R, an antioxidant, were brought to reflux under nitrogen in a 1000-ml round-bottomed, three-necked flask equipped with a stirrer. About 5 g of the polymer (high-density polyethylene of 0.5 melt index) was then added to the flask, and refluxing was continued for 4 hr to ensure complete solution. The flask was then cooled to break the reflux, and a known weight of support was added slowly while stirring was continued. After the resultant slurry had cooled to about 40–60°, it was passed through a coarse sintered-glass filter and the antioxidant was washed away with decalin to leave an almost pure polymer coating. Finally, the packing was placed in a vacuum oven at 170° overnight to remove the last traces of decalin.

For atactic polypropylene, the polymer (a commercial by-product) was dissolved in hexane at room temperature. Any isotactic impurity, which is insoluble in hexane, remained as a swollen gel. The suspension was passed through an analytical filter paper, the filtrate was slurried with the support in hexane, and the hexane was evaporated to leave a free-flowing packing.

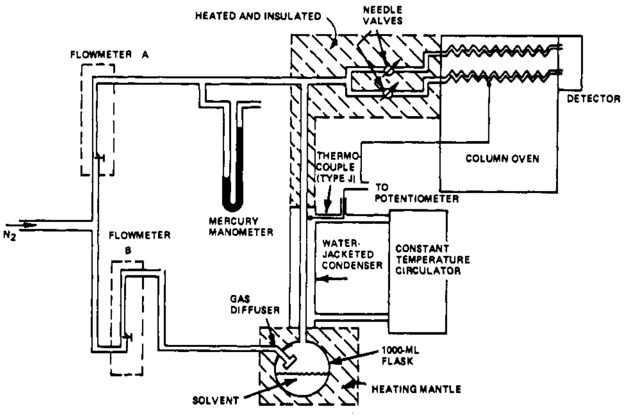

Figure 1. Schematic diagram of apparatus.

The gc columns were filled by a vibration technique, and the packing container was weighed before and after to determine the total weight of packing within a column. Samples of the packing were analyzed for total organic carbon, and the per cent carbon was multiplied by the ratio of total polymer to carbon—1.08 for polystyrene and 1.17 for polyethylene and polypropylene—to obtain the per cent loading of polymer on the support. This number, in turn, was multiplied by the total weight of packing to obtain the column loading in grams of polymer. The loading on the polystyrene columns was also calculated from the weights of polymer and packing used to compose the recipe. This technique gave somewhat more precise results than the other, but it can be utilized only for a solvent that is removed by evaporation, thereby depositing all of the polymer.

Preparation of Carrier Gases. Figure 1 shows the apparatus for preparing carrier gases and controlling their flow through the gc columns. It permits the option of using either pure nitrogen or nitrogen containing a known concentration of solvent vapor up to about 60 mol %.

The nitrogen (Baker, prepurified) is obtained from a standard cylinder through two regulators—a two-stage (50-psig outlet) and a single-stage (25-psig outlet)—connected in series. Flow rates from the cylinder are controlled and monitored by Gilmont compact flowmeter–valve assemblies. Flow distribution between the two columns is controlled by a pair of Nupro fine-metering needle valves, Model 2SA. Equipment for mixing the nitrogen with solvent vapor includes a 1000-ml round-bottomed flask equipped with a gas diffuser and attached to a water-jacketed condenser.

The carrier gases are split and passed through two gc columns which are matched as closely as possible in flow rate and packing composition so that the gas composition in both arms is nearly equal. The columns are maintained in an oven at a controlled temperature that is monitored by an iron–constantan thermocouple connected to a Leeds and Northrup potentiometer, Model 8691-2.

For operation with pure nitrogen, flowmeter B is closed and A is adjusted to give a suitable inlet pressure, as measured with the mercury manometer, and suitable column flow rates, as measured with a soap-bubble flowmeter at the detector outlet (not shown in Figure 1).

For a mixed carrier gas, flowmeter A is closed and B is opened to allow nitrogen to enter the flask that contains the solvent (analytical reagent grade), which is maintained at a temperature above its boiling point by the heating mantle surrounding the flask. The incoming nitrogen passes through the gas diffuser, sweeps the vapor space above the solvent but does not bubble through the solvent itself, and subsequently enters the condenser. The temperature of the condenser, which dictates the vapor pressure of the solvent, is measured with a Type J thermocouple located in the flowing water stream, and is controlled by a Haake 1277, Model FK, constant-temperature circulator.

The composition of the carrier gas leaving the condenser is determined by the vapor pressure of the solvent and the total pressure measured by the manometer. At the operating temperature and

---

(17) W. A. Aue and C. R. Hastings, *J. Chromatogr.*, 56, 295 (1971).

pressure (~1.3 atm) the solubility of nitrogen in the solvent and the gas imperfections were assumed negligible for this calculation. To change the composition, the temperature of the condenser is raised or lowered as necessary. To ensure a gas mixture of identical composition at both the condenser exit and the column inlet, all connecting tubing is wrapped with heating tape maintained well above the highest operating temperature of the condenser.

Collection and Treatment of Gc Data. Our gc data are obtained on a Bendix gas chromatograph, Model 2110, equipped with a dual thermal conductivity detector and a Dohrmann 1-mV recorder.

Adjusted retention volume, the gc parameter of chief importance, is obtained by difference (retention volume of the solvent peak minus retention volume of the nonsorbed peak). To measure the retention volume of the nonsorbed peak, about 100 μl of helium is injected into the gc column with a 500-μl Hamilton gas-tight syringe, and the time between injection and the apex of the peak is measured to the nearest 0.1 sec with a stopwatch. The solvent peak is measured in the same way after the injection of about 0.2 μl of solvent with a Unimetrics 1.0-μl syringe.

For each polymer–solvent system, the retention time difference is used to calculate the solubility isotherm, the interaction parameter χ, and the equilibrium ratio Ω. For example, Figure 2 shows the experimental gc data obtained for the polystyrene–benzene system in column no. 1 at 120° plotted so that the area under the curve is equal to the integral in eq 10. The product of the area and j/V_2 gives the solubility $q(P)$ at each concentration c of solvent in the carrier gas. The thermodynamic properties χ and Ω are calculated from such $q(P)$ data. Volume fractions were calculated from pure solvent densities reported in the literature[18] and polymer densities measured in the Amoco Chemicals laboratories.

Error Analysis

The solubility isotherms calculated from gc data are affected by three sources of systematic errors, all related to the column packings: (1) thickness of the polymer coating on the support, (2) diffusion of gas within the coating, and (3) kind and size of packing.

The thickness (loading) of the polymer on the support can cause errors arising from two extremes: too light a loading leads to a high variability in measurements of $t_R - t_M$, whereas too heavy a loading requires excessive elution time and the peak is too broad to pinpoint the maximum. A coating may also be so thick that the inner layers of polymer do not participate in the sorption, thereby causing a systematic error in addition to peak dispersion. A high-surface-area support and a uniform coating minimize these errors. The purpose of a very light loading is to permit equilibrium measurements with a single experiment in a dynamic system.

The thickness in ångströms of a uniform film on a support is represented by

$$\delta = \frac{\nu\omega \times 10^8}{A(1 - \omega)} \qquad (21)$$

where $A \cong 10^4$ cm^2/g for 80–100 mesh Chromosorb W. At a typical coating level in our columns, $\omega = 0.01$ weight fraction polymer and the thickness is about 100 Å. Scanning electron micrographs of a series of loadings from 1 to 20% revealed a gradual smoothing of detail with an increase in polymer and showed no evidence of lumps.

It is reasonable to question whether such a thin polymer layer can exhibit bulk properties accurately. Experimental results with layers of from 40 to 250 Å average thickness yielded identical results. We have assumed that this demonstrates that in fact bulk properties are being measured.

To determine the extent to which diffusion in a 100 Å coating could cause dispersion and error in the measurements, the van Deemter equation[19] is used in a simplified form

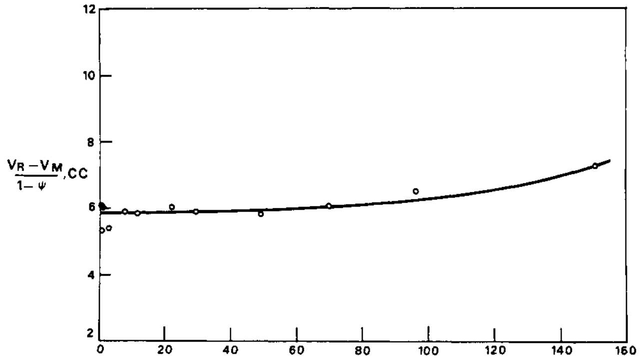

Figure 2. Corrected retention volume difference for benzene–polystyrene at 120°.

$$H = A_1 + A_2/u + A_3u \qquad (22)$$

where H is the column height equivalent to a theoretical plate. The number of plates in one of our 10-ft columns is about 3600, calculated by the classical method from a chromatogram. Therefore, H is about 0.08 cm. The linear gas velocity is about 2 cm/sec, and the constant A_3 is given by

$$A_3 = \frac{8}{\pi^2}\frac{k}{(1 + k)^2}\frac{\delta^2}{D_1} \qquad (23)$$

where D_1 is the diffusivity of the solvent vapor in the polymer film. A reasonable value for a C_6 hydrocarbon in a polymer at 80° is $D_1 = 4 \times 10^{-9}$ cm^2/sec. When a value of $k = 0.1$ (typical in our work) is used in eq 23, the third term in eq 22 is about 10^{-4} cm, a negligible value. When eq 23 is used to evaluate the contribution to H of a 500-Å coating, the third term in eq 22 is a few per cent of the total. The second term in eq 22, which represents gas-phase dispersion, is given by

$$A_2/u \approx 2D_g/u \qquad (24)$$

Typical gas-phase diffusivities are about 10^{-1} cm^2/sec, so this second term accounts for nearly all of the peak broadening observed in our system. The first term, attributed to eddy dispersion in the gas, is estimated to be 0.01 cm. The conclusion from the van Deemter equation is that there is negligible diffusion limitation to interfere with establishing equilibrium between vapor and polymer at the 1% loading level. Experiments with polyethylene columns of different loadings indicate that there is no diffusion limitation below 1.8% loading.

A detailed flow study with gc columns no. 1 and 2 (Table I) at 120° and with several carrier gas flow rates from 8.6 to 60.6 cm^3/min showed no diffusion limitation to cause error at a 1% loading of polystyrene. The value of k was constant at 0.076 over the range of flow rates, and the retention volume per cubic centimeter of polystyrene was constant at 20.3. However, at 5% loading, both parameters increased somewhat as flow was decreased.

The correction to the flow rate to compensate for the sorption effect is given by

$$\frac{F(y)}{F(0)} = \frac{1 + k}{1 + k(1 - yJ_3^2)} \qquad (25)$$

where $F(0)$ is the gas rate with no solvent vapor and $F(y)$ is the rate with a vapor mole fraction of y.[10] This correction was not necessary because the rate $F(y)$ was measured at the

---

(18) "Technical Data Book-Petroleum Refining," American Petroleum Institute, New York, N. Y., 1966, Chapter 6.

(19) A. B. Littlewood, "Gas Chromatography," Academic Press, New York, N. Y., 1970, p 169 ff.

Table II
Estimate of Average Error in Computation for 10-ft Gc Column with 1% Polymer Loading

Parameter	Deviation from true value, %
$\Delta V_c = (V_R - V_M)/(1 - \psi)$	2.3
$q(P)$	5.7
Ω value	6.7
χ value	40

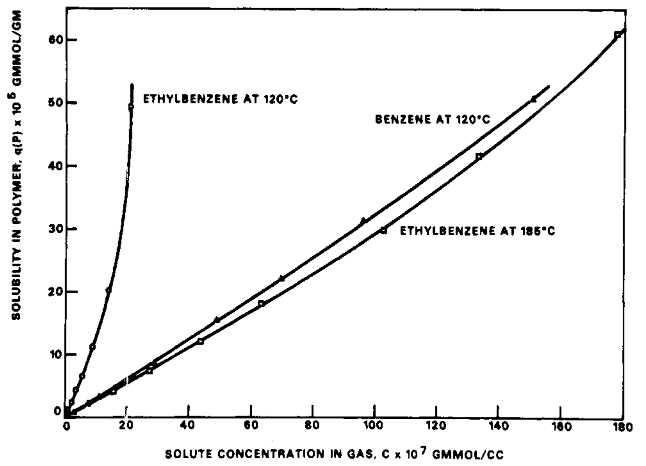

Figure 3. Distribution isotherms in polystyrene at 1.3 atm total pressure.

column outlet at each plateau concentration. The error caused by eluting a small peak of slightly higher concentration is negligible because k is about 0.1 for this system. At the highest plateaus used ($y \sim 0.7$), the required sample size was large enough to cause about 1% error in t_R due to the sorption effect.

Table II lists the average deviations from the true values estimated for our computed values. The estimated deviation for χ is so large because computation of χ involves the subtraction of two terms that are often nearly equal. One term (ϕ_2 in eq 19) is of the order of unity and has less than 3% error. For some polymer–solvent systems, the other term is so close to the same value that a very considerable relative error can be produced in the result. Consequently, it is more useful to state the absolute error in χ, which is limited to ± 0.05, with a precision of ± 0.03.

Results and Discussion

Polystyrene. Figure 3 shows the solubility isotherms calculated for polystyrene in column no. 1 with benzene at 120° and with ethylbenzene at 120 and 185°. The lower temperature was selected to be above the glass transition of polystyrene, while the upper temperature is close to the operating limit of our apparatus. The plots for all three systems have an upward curvature, characteristic of an anti-Langmuir isotherm. The benzene isotherm at 120° is nearly straight. If the line in Figure 2 were horizontal, the isotherm would be perfectly straight. The close similarity between the benzene isotherm and the one for the ethylbenzene at 185° is not surprising, because the solvent vapor pressures are nearly equal (~3 atm) at these temperatures and the two systems are closely analogous. Thus it is possible to estimate with reasonable accuracy the thermodynamic properties of systems such as toluene–polystyrene or styrene–polystyrene at a temperature such that the vapor pressure of the pure solvent is equal to that of one of the above-measured solvents. This estimation method is not reliable if the new temperature involves crossing a polymer transition temperature, but it can be especially helpful in estimating the properties for an unstable monomer such as styrene.

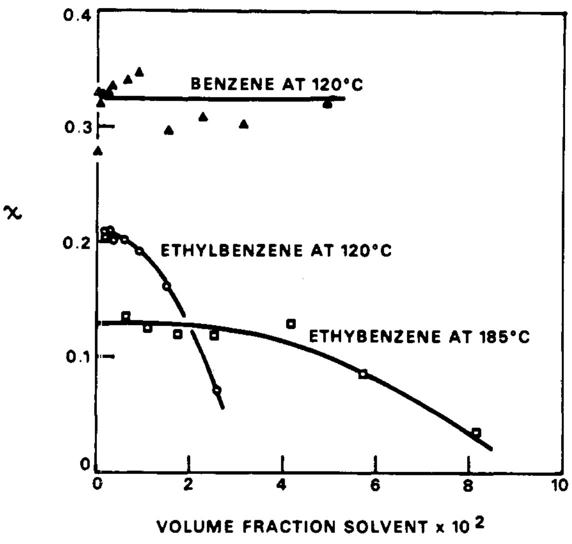

Figure 4. Interaction parameters in polystyrene.

Table III
Maron Theory Parameters for Polystyrene

Solvent	Temp, °C	r	$\psi^{(0)}$	$\psi^{(1)}$
Benzene	120	0.768	0.325	0
Ethylbenzene	120	0.777	0.220	3.8
Ethylbenzene	185	0.735	0.136	0.81

Figure 4 shows χ values plotted for each system as a function of volume fraction of solvent, assuming volume additivity for the components. These data, based on the specific volumes of polymer and solvent at the operating temperature, were calculated from eq 19. Although Maron theory indicates that this relationship should be linear, the ethylbenzene data have a noticeable curvature. The last two points at 120° indicate such a sharp curvature that an error is suspected. The Maron theory can be used to correlate these data even though there is some curvature. The parameters $\psi^{(0)}$ and $\psi^{(1)}$ were calculated from the coordinates of the best straight line through the ethylbenzene points. The decrease of 0.08 in χ is typical for this system with the 65° temperature rise. These parameters, together with the ratio of specific volumes r, are shown in Table III.

The Ω values are plotted in Figure 5, where the separate points are calculated from the solubility data using eq 12 and 13. The smooth curves were computed from eq 15 and 17 using the parameters in Table III. One of the biggest advantages of using Ω as defined is that the Ω values for a system do not change much, even with a 65° increase in temperature that causes a fivefold increase in the vapor pressure of the pure solvent. The Ω curve for ethylbenzene at 120° drops more rapidly than the one at 185° primarily because the solubility increases so sharply. For pure solvent, $\Omega = 1$ from eq 18.

Amorphous Polyethylene. Polyethylene that is completely amorphous (*i.e.*, at a temperature well above its crystalline melting point) behaves much like polystyrene in sorption. The solvent for this system, *n*-decane, was chosen for its favorable vapor pressure and linear, saturated character. Figure 6 shows the solubility isotherm at 185° for two separate gc columns, one with 1.7 and the other with 0.8% load-

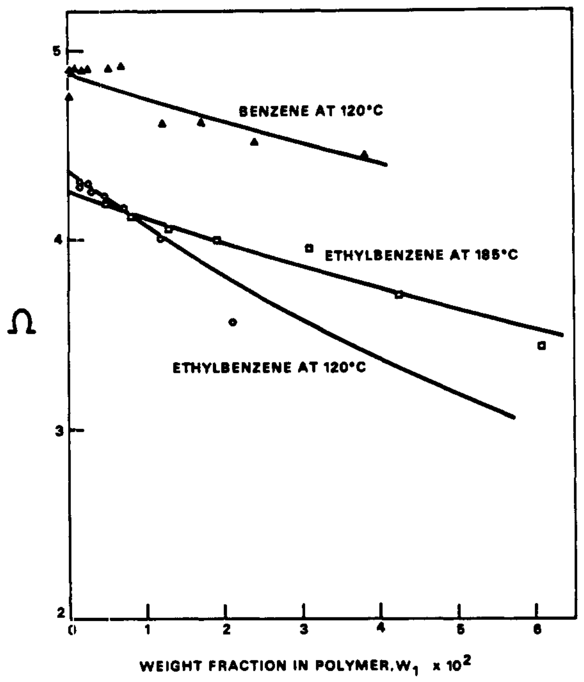

Figure 5. Equilibrium ratios in polystyrene.

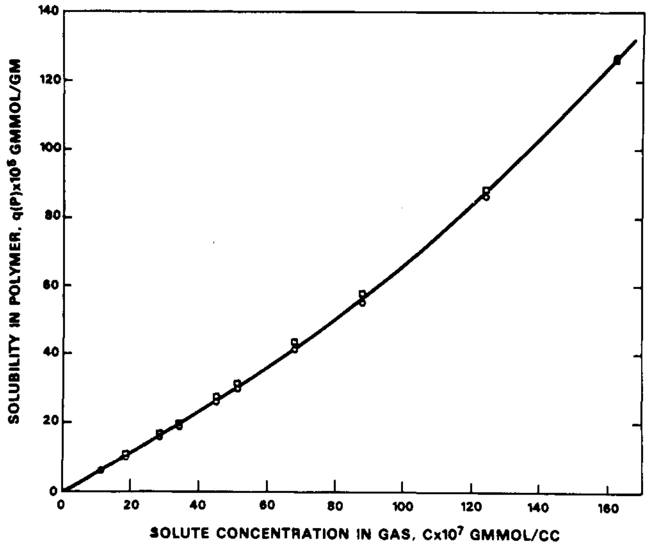

Figure 6. Distribution isotherm in polyethylene at 185° and 1.3 atm total pressure.

ing (columns no. 3 and 4, respectively, in Table I). Both columns produced the same isotherm, a necessary condition if equilibrium is attained. The anti-Langmuir curvature is quite similar to that obtained with polystyrene in Figure 3.

The χ values for decane computed from eq 19 are plotted in Figure 7 as a function of volume fraction. The results, which have been reported previously,[6] indicate that χ equals 0.12 up to at least 19% solvent. The χ value agrees with one reported by Patterson, *et al.*,[3] for the same system, within experimental uncertainty (± 0.05).

Figure 8 shows the equilibrium Ω values calculated from the gc data for decane and polyethylene. In addition, a smooth curve is drawn through the data using eq 20 with the following parameters: $r = 0.785$, $\psi^{(1)} = 0.12$, $\psi^{(1)} = 0$. Obviously, this form of the Flory-Huggins equation provides an excellent correlation of the data. The benzene-polystyrene curves for χ and Ω are similar to the decane-amorphous polyethylene curves. This is to be expected from the relationship of the solvent molecule to the polymer molecule—selected for similarity.

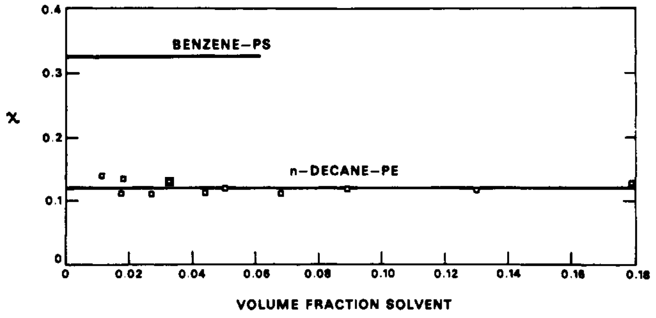

Figure 7. Interaction parameters in polyethylene.

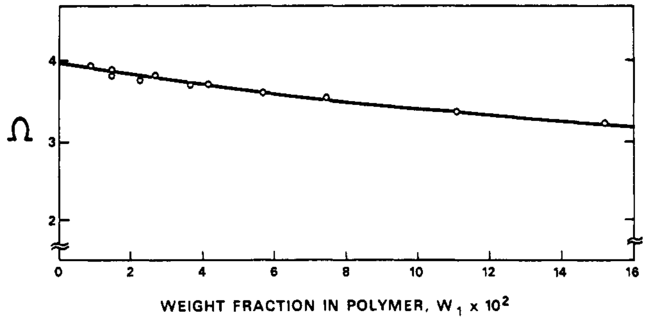

Figure 8. Equilibrium ratios in polyethylene.

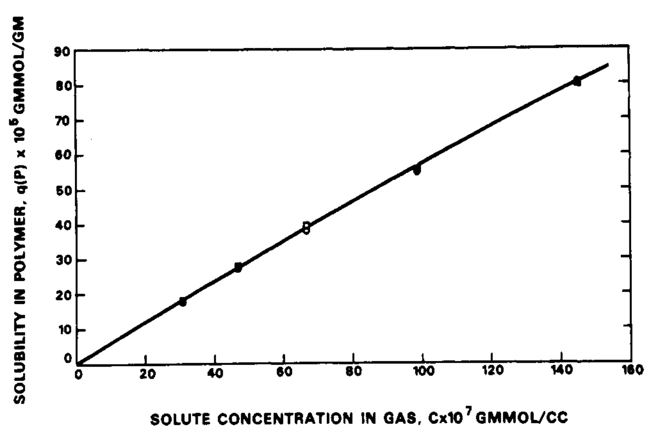

Figure 9. Distribution isotherm in atactic polypropylene at 80° and 1.3 atm total pressure.

Atactic Polypropylene. Data for the atactic polypropylene in *n*-hexane at 80°, obtained in columns no. 5 and 6, were somewhat similar to those for the other amorphous polymer systems, which yielded Ω values of from 4 to 5 at infinite dilution. However, as shown in Figure 9, the solubility isotherm has a slight Langmuir curvature, rather than the upward curvature typical of the other polymers. Data points from the separate gc columns are in close agreement (about 3% discrepancy).

Figure 10 shows values of χ calculated from the separate column solubility data. Although the scale of the ordinate gives the appearance of high scatter, the values fall within ± 0.02. The increase in χ as the concentration of *n*-hexane increases leads to a negative value for the $\psi^{(1)}$ coefficient of eq 15, in contrast to the results obtained for the other polymer systems.

Figure 11 shows the Ω curve calculated from the following parameters: $r = 0.791$, $\psi^{(0)} = 0.18$, $\psi^{(1)} = -3.5$. The χ values rise rapidly enough to cause Ω to increase slightly at low w_1. However, this trend must reverse so that Ω ap-

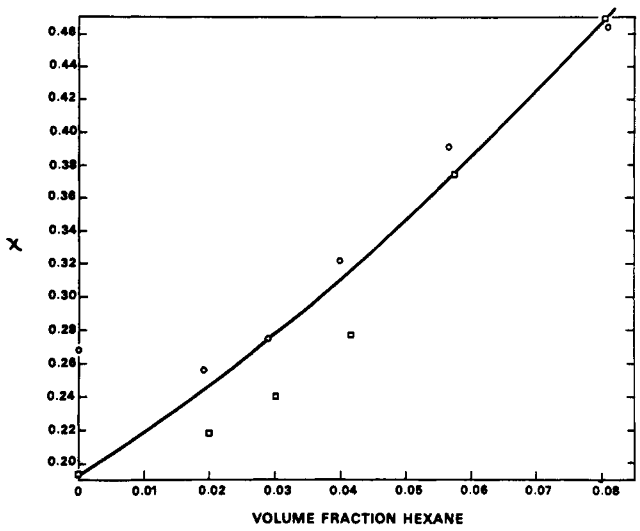

Figure 10. Interaction parameters in atactic polypropylene.

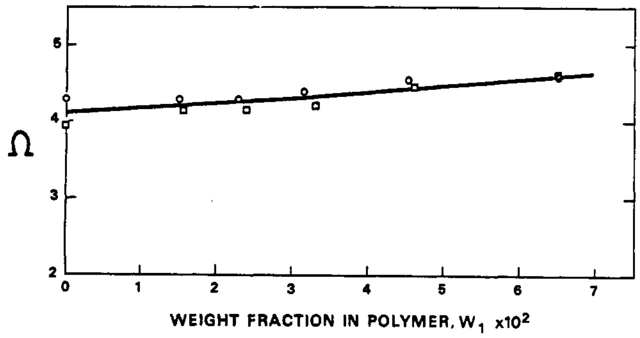

Figure 11. Equilibrium ratios in atactic polypropylene.

proaches unity unless the solubility limit is reached first. Note that this kind of polymer–solvent system gives a special case in which Ω is nearly constant over a moderate range of composition, *i.e.*, up to about 30 vol % solvent.

The two sets of data in Figure 11 (circles and squares) demonstrate a typical degree of scatter inherent in the Ω values: ±0.2 absolute or ±5% relative error. We believe that the rising χ value and the other results indicate that this sample of atactic polypropylene has a significant degree of order, in contrast to the other amorphous systems.

Conclusion

Comparison of our χ and Ω values with those measured by others using static methods or using gc at infinite dilution indicates that our method of elution on a plateau gives reliable values over a range of compositions. Furthermore, our method is one of the best available for studies in the range of 0–5 or 10% solvent in a polymer. The solubility isotherm calculated from the data permits easy estimation of thermodynamic properties for an analogous system in a corresponding state (at the same solvent vapor pressure). The ability to acquire thermodynamic data (especially χ) over a range of solution compositions permits an exacting test of the various solution theories. With some minor refinements in accuracy this method can be used to investigate small changes in molecular order as reflected in χ for solutions approaching pure polymer.

Our experience with this apparatus indicates that it can also be used to make similar measurements using semicrystalline polymers. These results will be reported in part II of this two-part series.

Acknowledgments. The authors thank Amoco Chemicals Corporation for permission to publish these results, R. F. Abbott for helpful discussions concerning the methods, and one of the reviewers for drawing their attention to an article by J. E. Guillet that points out the feasibility of this gc technique.[20]

Nomenclature

a	Dimensionless correction factor
a_1	Solvent activity over the stationary phase, $P\psi/P_1^0$
A	B.E.T. surface area of gc solid support, cm²/g
A_1, A_2, A_3	Coefficients in simplified van Deemter equation
b_n^m	Flow rate correction factor for sorption
B_{22}	Second virial coefficient of pure solvent vapor at column temperature
c	Solvent concentration, (g mol)/cm³ in mobile phase
D_1	Solvent diffusivity in polymer phase, cm²/sec
$F(y)$	Total volumetric flow rate, measured at outlet pressure and flowmeter temperature, through a zone of composition y, cm³/sec
H	Column height equivalent to a theoretical plate, cm
J_n^m	Gas compressibility correction for Δp through column
j	Approaches the gas compressibility factor, J_3^2, as $y_0 \rightarrow 0$
k	Solvent mass distribution coefficient, grams of solute in stationary phase/gram of solvent in mobile phase
M_1	Molecular weight of solvent, g/(g mol)
p	Total pressure, atm
P_2	Solvent partial pressure, atm
P	Mean total pressure defined as $P_0J_3^4$
P_1^0	Vapor pressure of solvent at oven temperature, atm
q	Moles of solvent per unit mass of polymer in stationary phase, (g mol)/g
r	Ratio of specific volumes, polymer to solvent
R	Gas constant, (cm³ atm)/(g mol °K)
t	Time at which a zone of concentration C passes a detector, sec
T	Column temperature, °K
T_F	Flowmeter temperature, °K
u	Linear gas velocity through gc column, cm/sec
v	Specific volume, cm³/g
V_M	Gas hold-up (measured with helium), cm³
V_R	Retention volume, cm³
V_2	Mass of polymer in stationary phase
w_1	Weight fraction of solvent sorbed in polymer
y_0	Mole fraction solute in gas phase at pressure p_0 in zone of concentration c
ψ	Corrected gas-phase mole fraction of solvent
δ	Average coating thickness, Å
χ	Polymer–solvent interaction parameter defined in eq 14
ω	Weight fraction polymer coating on support
Ω	Vapor–polymer equilibrium ratio, a_1/w_1
ϕ	Volume fraction in polymer solution
$\psi^{(0)}$	Limiting value of Maron interaction parameter at $\phi_1 = 0$
$\psi^{(1)}$	Coefficient of second term of Maron interaction parameter

Subscripts

1	Refers to solvent
2	Refers to polymer
i	Refers to inlet
o	Refers to outlet

(20) J. E. Guillet, *J. Macromol. Sci. Chem.*, **4**, 1669 (1970).