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Gas Chromatographic Determination of Thermodynamic Properties of Polymer Solutions at High Pressure

The gas chromatographic (GC) method for thermodynamic measurements of polymer-solvent systems at finite concentration has been improved to extend its operating range from atmospheric pressure to over 70 atm and over 240°C. This paper describes the design and operation of the equipment and the mathematical treatment of the GC data, and presents experimental results for *n*-hexane and isooctane in high density polyethylene. These results include the solubility isotherms, activity coefficients, and polymer-solvent interaction parameters. The activity coefficients covering a range from 4 to 70 atm for *n*-hexane in the polymer solution were correlated successfully as a function of composition using a two-parameter segment interaction equation.

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SCOPE

There is a scarcity of solubility isotherms and other thermodynamic data for polymer-solvent systems at the elevated temperatures and pressures often encountered in commercial processing. One especially important area for which there is little data available is that of devolatilization of monomer or solvent remaining in a high temperature melt. This study reports the details of apparatus design and operation for a gas chromatographic method to acquire these data rapidly with sufficient accuracy for design purposes. The method, employing the elution of a solvent peak on a constant plateau of solvent concentration in the carrier gas, uses gas chromatographic equipment that is readily available and relatively easy to adapt to operation at high pressure. The flexibility of the apparatus permits measurements to be obtained for practically any thermally stable solvent that can be vaporized with any film-forming polymer.

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CONCLUSIONS AND SIGNIFICANCE

Solubility isotherms were obtained with an estimated error of 5% for *n*-hexane and isooctane in high density polyethylene at selected temperatures ranging from 137° to 237°C and selected total pressures ranging from 4 to 70 atm. Activity coefficients and interaction parameters at the limit of infinite dilution are within 20% of the values measured by gas chromatography at low pressure in other studies. At finite concentration and pressures above 4 atm, the interaction parameters are concentration dependent in contrast to values reported for similar systems at low pressure. This may be a direct pressure effect and/or an effect caused by the presence of a carrier gas. The chromatographic technique at finite concentration provides a new method that is much more rapid than conventional static methods for determining thermodynamic parameters for polymer-solvent systems, usually requiring one normal workday per isotherm. The results are accurate enough to apply to process design and, with some refinements, to the evaluation of solution theories. Furthermore, a two-parameter model correlates the hexane results over the full range with less than 2% deviation.

Workers in a number of laboratories have been successful in adapting gas chromatography (GC) to the measurement of activity coefficients in polymer-solvent systems at infinite dilution (Smidsrød and Guillet, 1969; Hammers and de Ligny, 1971; Patterson et al., 1971; Covitz and King, 1972; Summers et al.,1972). Newman and Prausnitz (1972, 1973a, 1973b) have also reported chromatographic measurements on a large variety of amorphous polymer systems using both polar and nonpolar solvents. In their most recent study (1973b) Newman and Prausnitz present experimental data for 91 binary polymer-solvent systems in the temperature range 50° to 200°C, in addition to derivations of the equations necessary to interpret the chromatographic data.

We have extended the GC technique to include a wide range of composition, using the method of elution on a plateau of solvent in the carrier gas, adapted from the work of Conder and Purnell (1968a, 1968b, 1969). Our earlier work at low pressure included some amorphous polymer-solvent systems (Brockmeier et al., 1972a, 1972b) and some semicrystalline systems (Brockmeier et al., 1973). Our extended technique permits the measurement of solubility isotherms in addition to activity coefficients and interaction parameters as a function of solvent fraction in the polymer. In this work, we have extended the GC measurements from atmospheric pressure to 70 atm and 237°C, using both hexane and isooctane with high density polyethylene (HDPE).

EXPERIMENT

Preparation of Carrier Gas

Figure 1 shows the apparatus used for preparing the carrier gas and controlling its flow through the GC columns. It is basically the same design as that used for our low pressure work described by Brockmeier et al., 1972b. The important changes include the replacement of all glass and copper tubing with 316 stainless steel tubing, 0.64 cm (1/4-in.) O.D. in most cases. The pressures at the inlets and outlets of the columns are indicated on a Heise gauge with a 16-in. dial graduated from 0 to 102 atm (1500 lb./sq. in. gauge in one lb./sq. in. increments). Mercury-filled lines with suitable valving connect the gauge to the desired points.

Nitrogen (Baker, prepurified) is obtained from a standard cylinder through two regulators—a single-stage (340 atm outlet) and a two-stage (200 atm outlet)—connected in series. There are actually two of the latter regulators placed in parallel to permit operation to be switched from pure nitrogen carrier (line A) to nitrogen mixed with solvent (line B). The carrier gases are split and one stream is passed through the reference column while the other is passed through the sample column. Carrier flow rates are controlled by setting the desired column pressure on the appropriate regulator and adjusting the precision high temperature needle valve on each column outlet to achieve the desired flow, measured with a bubble-type flow meter.

For a mixed carrier gas, nitrogen is directed through line B, where it enters a 300-ml cylinder that contains the solvent (analytical reagent grade). The nitrogen bubbles through the solvent, which is either at its bubble point temperature at the system pressure or slightly below its critical point (whichever is lower), and becomes saturated. The mixed vapor leaves through a reflux condenser that reduces the high saturation level to any desired value set by its coolant temperature and the prevailing pressure. The temperature of the glycerol coolant is regulated by a Haake Model 1273 constant-temperature circulator. 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 and maintained well above the dew point of the most concentrated carrier mixture. Type J thermocouples are used to monitor coolant temperatures and selected skin temperatures at several points in the saturator section.

Preparation of GC Columns

Both columns used for this work were prepared using acid washed Chromosorb W, 80/100 mesh. The HDPE (Amoco Chemicals 680 B4 of 13 melt index) was coated on the support by slowly cooling and then evaporating a dilute solution in mixed xylenes. For the 1% column, 0.5 g of polymer was added to 300 g of xylene which was refluxing under nitrogen in a one-liter flask equipped with a magnetic stirrer. After the polymer dissolved completely, the flask was cooled enough to break the reflux and 49.5 g of Chromosorb was added slowly with stirring. The resultant slurry was cooled to ambient temperature and spread out on a tray to dry overnight. The last traces of solvent were removed at 170°C under vacuum. With this technique, only a negligible amount of polymer was lost. The 3% column packing was prepared in the same way, except that 1.5 g of polymer and 48.5 g of support were used. The columns were filled by a vibration technique, using 3 m of 0.64-cm stainless steel tubing for each. A typical finished column contained about 16 g of support, of which 0.1749 g and 0.4867 g are HDPE for the 1% and the 3% columns, respectively.

One generally expects that such light loadings may lead to problems in GC work. Such problems, especially adsorption on

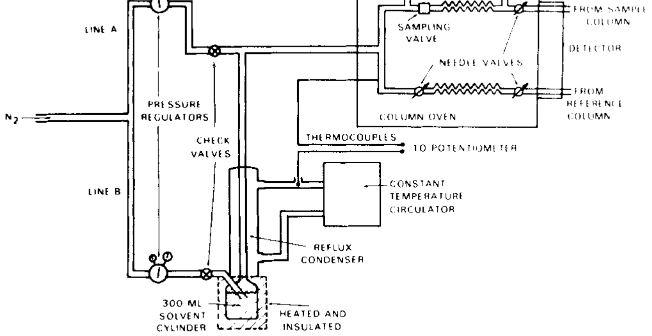

Fig. 1. Schematic diagram of high pressure GC apparatus.

the support, were negligible in our systems and have been discussed elsewhere (Brockmeier et al., 1972b, 1973). Experiments showed that even at high pressures and temperatures, our results were not affected more than a percent or two by adsorption. Our early work emphasized the necessity for very thin coatings in finite concentration work to eliminate any diffusion limitation in the sorption.

Collection of GC Data

The GC data were obtained from a Bendix instrument, Model 2110, equipped with a dual thermal conductivity detector and a 1-mV recorder. After the system had come to a steady state at a preset solvent concentration plateau in the carrier, an additional small amount of solvent was injected with a Valco gas sampling valve, Model VSV-6-HTX. The retention time was recorded for this small peak on top of the relatively large plateau. Using the same valve, a sample of helium was injected and the retention time for this nonsorbed material was recorded. The primary GC data consisted of the difference between these two times. Where there was sufficient peak separation (> 20 s), both helium and solvent were injected simultaneously. A sample size of 60 μl of gas was satisfactory for runs at pressures from 3 to 11 atm, while 360 μl of gas were injected while the columns were operated at 70 atm. The pressure in the sample loop was held between 0.7 and 1.4 atm. Note from Figure 1 that the detector was always operated at ambient pressure. Gas velocity through the detector was kept low by diverting most of the flow through a separate vent for runs at 70 atm (not shown in figure). The carrier flow rates measured at atmospheric pressure were typically 0.9 ml/s at 3 atm and 14 ml/s at 70 atm.

DATA REDUCTION

The treatment of the GC data is basically the same as that reported by Conder and Purnell (1969) and by Brockmeier et al. (1972b) using the method of elution on a plateau. One important point of departure from this previous approach is the use of the Redlich-Kwong equation of state instead of the virial equation. This change was necessary for accurate calculations at pressures above several atmospheres. Another significant change is the inclusion of corrections for liquid and vapor phase nonidealities in the equation for the activity coefficient Ω_1.

One of the features of this GC technique is that the carrier gas contains a predetermined concentration level, or plateau, of the chosen solvent during the course of an experiment. The mole fraction of solvent coming from the saturator is determined by solving a dew point calculation using two equations of the form:

$$y_i = K_i x_i \qquad (1)$$

Two factors complicate the simpler case that applied in our low pressure GC work: The Poynting correction affects the vapor pressure of solvent and there is appreciable solubility of nitrogen carrier gas in the solvent. The values of K_i were interpolated from measurements reported by Poston and McKetta (1966) for hexane and nitrogen as a function of T and P. The values for the isooctane-nitrogen system were calculated using the correlation of Chao and Seader (1961), with NGPA coefficients for nitrogen.

The solvent concentration in the gas at the column outlet is

$$c = \frac{P_o y_1}{Z_m RT} \qquad (2)$$

where Z_m, the mixture compressibility factor, is estimated with the Redlich and Kwong (1949) equation of state. This concentration is the basis for evaluating the solubility isotherm. The GC apparatus measures the difference ΔV between the retention volumes of the solvent and a nonsorbed gas such as helium, as computed from the difference in retention times:

$$\Delta V = (t_R - t_M) \cdot \frac{T}{T_F} \cdot \frac{Z_m P_F}{P_o} \cdot F_W \cdot V_F \qquad (3)$$

where the subscript F refers to conditions in the flow meter. The factor F_W (usually 0.97) corrects the flows for the amount of water vapor added in bubbling through the flow meter.

Solubility Isotherms

Before integrating the ΔV data to obtain a solubility, ΔV must be corrected for the sorption effect in the substrate (Conder and Purnell, 1969). We use the following value for the plateau concentration of solvent:

$$\psi = Z_m (B_2^1 / B_3^2) \cdot J_3^2 \cdot y_1 \qquad (4)$$

Conder and Purnell describe this procedure and define the J_3^2 and B_n^m factors. The J_3^2 factor compensates for gas compressibility that occurs because a small pressure gradient is required for flow through the column. The value of ΔV corrected for sorption varies in the following way with the plateau level:

$$\Delta V_c = \frac{\Delta V}{1 - \psi} \qquad (5)$$

The solubility isotherm we use is defined as the g-mol of solvent sorbed per gram of dry polymer at a mean column pressure P

$$q(P) = \frac{J_3^2}{m_2} \int_0^c \Delta V_c \, dc \qquad (6)$$

where m_2 is the mass of polymer in the GC column. The weight fraction of sorbed solvent follows directly from Equation (6)

$$w_1 = \frac{q(P) \cdot M_1}{1 + q(P) \cdot M_1} \qquad (7)$$

Activity Coefficients

Given the solvent solubility and the densities of the solvent and polymer as a function of T and P, we have calculated some system thermodynamic properties in the following way. Patterson et al. (1971) have defined a form of activity coefficient Ω_1 that is particularly advantageous for polymer systems because it requires no knowledge of the MWD of the polymer or its average molecular weight. We use the same coefficient in the following form:

$$\Omega_1 \equiv \frac{f_1}{f_1^0 w_1} = \frac{a_1}{w_1} \qquad (8)$$

where Ω_1 is computed at the system pressure and temperature, and the solvent activity is defined in terms of fugacities. The vapor fugacity at mean column pressure is

$$f_1 = \Phi_1 y_1 P \qquad (9)$$

The standard liquid fugacity is calculated from

$$f_1^0 = \Phi_1^s P_1^s \exp\left(\frac{-P_1^s V_1}{RT}\right) \qquad (10)$$

where the reference pressure is zero. The fugacity coefficients of the saturated solvent in Equation (10) and of the mixed vapor in Equation (9) are estimated from the classical Redlich-Kwong equation using appropriate composition values. For the special case of operation at infinite dilution, Equation (8) is inconvenient because w_1 approaches zero. At these conditions, Ω_1 is determined by this relationship:

$$\Omega_1^{\infty} = \frac{RTm_2}{M_1 \Delta V J_3^2} \cdot \frac{\Phi_1}{f_1^0} \qquad (11)$$

which is derived from Equations (2) to (8) in the limit as $y_1 \rightarrow 0$.

Thermodynamic Interactions

It is very useful in testing polymer solution theories to compute from the isotherm the polymer-solvent interaction parameter as a function of composition. Specifically, if the interaction χ is defined in terms of the Flory-Huggins equation,

$$\ln \frac{f_1}{f_1^0} = \ln \phi_1 + \phi_2 + \chi\phi_2^2 \qquad (12)$$

the value of Ω_1^{∞} can be used to determine χ^{∞} (Patterson et al., 1971). We have adapted this procedure to finite concentrations and use two assumptions: The degree of polymerization is high enough (> 100) to neglect its effect in Equation (12), and component volumes are additive. The equation for χ takes this form (Brockmeier et al., 1972b)

$$\chi = [\ln (\Omega_1/(\phi_2/r + \phi_1) - \phi_2]\phi_2^{-2} \qquad (13)$$

where r is the ratio of the specific volume of the polymer to that of the solvent. In the limit of infinite dilution ($\phi_2 = 1$):

$$\chi^{\infty} = \ln (r\Omega_1) - 1 \qquad (14)$$

The results from our GC experiments can also be used to estimate the composition at which the polymer becomes saturated with solvent and a second liquid phase appears. For those systems such as ours in which the second liquid to appear is very low in polymer, the solvent activity of the second phase (and thus the system) is practically unity. For this situation, the reference pressure for the saturated liquid fugacity must be the system pressure:

$$f_1^0 = \Phi_1^s P_1^s \exp\left[\frac{(P - P_1^s)V_1}{RT}\right] \qquad (15)$$

RESULTS

n-Hexane—HDPE System at Infinite Dilution

Several sets of experiments were conducted at infinite dilution with both the 1% and 3% HDPE columns, at 3.3 atm and 70 atm, with carrier gas flow rates covering a range of more than a factor of two, and using different sample sizes. Our operating conditions were well within the range in which variations in flow rate and sample size had no noticeable effect on retention volume. The solvent elution peaks were always of Gaussian shape, though somewhat broader than the helium peaks. Baseline noise was noticeable with nitrogen as the carrier gas, whereas no noise was noticed when helium was tested as a carrier gas late in the studies. Figure 2 shows how the specific retention volume of hexane in the amorphous fraction of polymer decreased as the column operating temperature was raised. (The amorphous fraction at low temperature was 30%.) This curve is very similar to curves reported for low density polyethylene and polypropylene by Guillet and Stein (1970) and nearly identical to a curve for decane in HDPE reported by Gray and Guillet (1971). The crystalline melting point of our polymer, determined from the maximum on the molten branch of the curve, was 125°C.

Figure 3 shows the hexane Ω_1 and χ values computed at low pressure by taking data points from the smooth curve in Figure 2 in order to eliminate a little scatter in the higher-temperature data. We conclude that both of these thermodynamic parameters reach a significant maximum slightly below the melting point of a semicrystalline polymer.

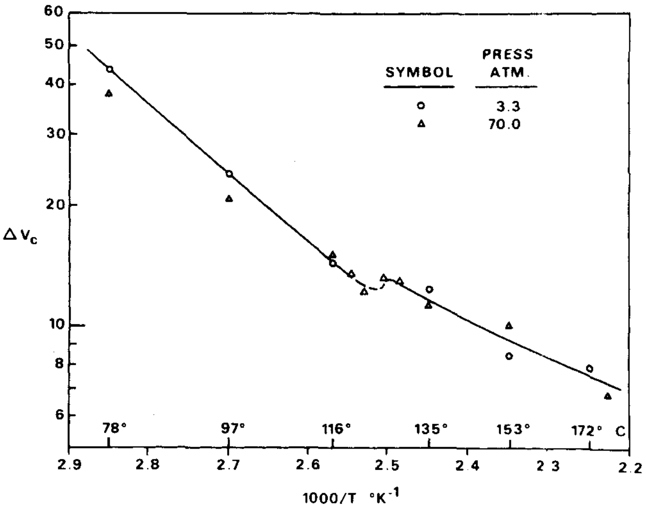

Fig. 2. Hexane retention volume in high density polyethylene.

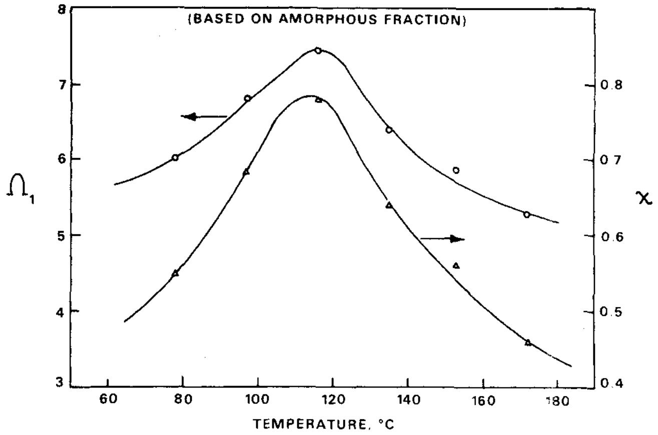

Fig. 3. Hexane activity coefficients and interaction parameters in HDPE at 3.3 atm.

n-Hexane—HDPE System at Finite Concentration

Using *n*-hexane and HDPE GC studies were conducted with finite concentrations at selected pressures from 4.4 to 70 atm and temperatures from 137° to 157°C. The integration of ΔV_c with Equation (6) yields the hexane solubility isotherms shown in Figure 4. The relative positions of the isotherms and their upward curvature are as expected for sorption of a nonpolar solvent in an amorphous polymer where Van der Waals forces predominate. At the highest concentration shown, $c = 4.8 \times 10^{-4}$ gmol/cm^3, there is 22.6 mol % hexane in the carrier gas at 70 atm. The highest plateau level was 47% hexane, corresponding to the last data point on the 137° isotherm. There is a wider separation between the 137° and 143° isotherms than between the 143° and 157° isotherms because solvent nonidealities increased as the pressure was raised from 11 to 70 atm. Furthermore, it is estimated that at 70 atm nitrogen carrier gas dissolved in the polymer solution to the extent of 5%. The presence of this third component may affect the hexane solubility.

The sorption isotherms are shown on more conventional coordinates in Figure 5, with weight percent hexane as a function of the activity evaluated at the system pressure. It is important for processing to estimate the conditions

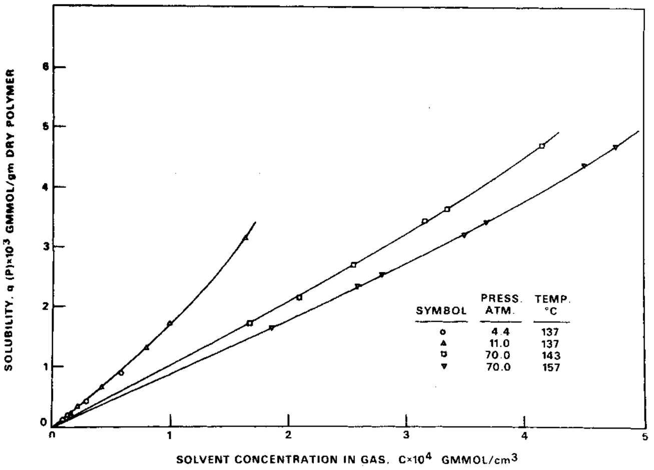

Fig. 4. Hexane solubility isotherms in HDPE.

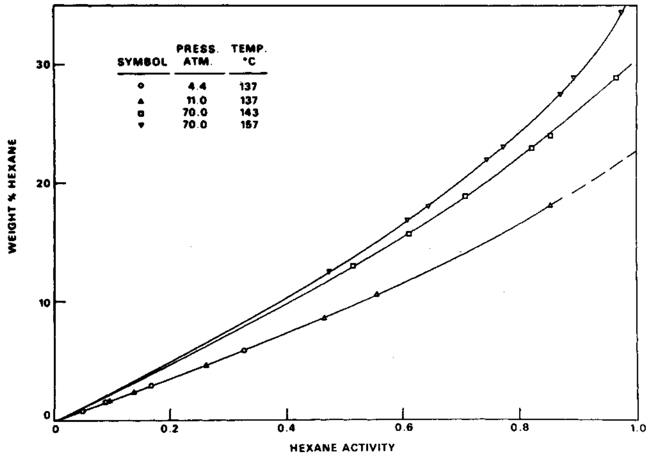

Fig. 5. Hexane activity in HDPE solutions.

under which a homogeneous solution will separate into two phases—one polymer-rich and the other polymer-lean. At equilibrium the solvent activity must be equal in each phase, and this activity will be approximately unity if one phase is nearly pure solvent as is the case for our systems. Therefore, extrapolation of the data in Figure 5 to unit activity gives a reasonably accurate estimate of the saturation composition of the polymer-rich phase in the presence of a high partial pressure of nitrogen. As temperature and pressure are raised in this range, hexane becomes more miscible with HDPE. The effect of pressure is qualitatively the same as Zeman and Patterson (1972) report for polystyrene in methyl acetate. However, the temperature effect is opposed to that observed by Orwoll and Flory (1967) for hexane in HDPE.

Activity coefficients for hexane were calculated from Equation (8) and are shown for four sets of conditions in Figure 6. It is interesting to note that although three sets of data at widely different pressures were brought to coincidence by evaluating Ω_1 in this manner, two sets of data at 70 atm that differ by 14°C were not. The Ω_1 values at 143° are consistently higher than those at 157°C, a result that agrees with Ω_1^∞ curve in Figure 3. The solid curves through the data were generated using the two-parameter segment interaction equation of Heil and Prausnitz (1966). Their equation for solvent activity provides an excellent correlation for our data. Because it is somewhat complex, the interested reader is referred to their publication for details of the equation. Attempts to model these data with the Maron equation were not successful (Maron and Nakajima, 1959).

The adjustable parameters in the segment interaction equation represent molecular interaction energies. The value g_{12} represents the energy between a 1 − 2 pair where 1 stands for a solvent molecule and 2 stands for a polymer segment. These energies were assumed to be independent of polymer MW and only weak functions of temperature. If we neglect any interaction with the *nitrogen* carrier gas, the two adjustable parameters take the form of $(g_{12} - g_{11})$ and $(g_{12} - g_{22})$. The pair parameters used to generate the solid curves in Figure 6 are tabulated in Table 1.

The curve for the systems at 137° was omitted because it nearly coincided with the one at 157°C. In applying these results to process design, we have used the Heil-Prausnitz equation to calculate the equilibrium vapor pressure of hexane over its solutions with HDPE, as a function of temperature and composition. Figure 6 demonstrates that the quality of fit between our data and this equation is good enough to permit cautious extrapolation somewhat beyond the limits of the data.

These values are truly unique in determining the shape of the Ω_1 curves, as evidenced by a large number of trials both negative and positive. As $(g_{12} - g_{22})$ becomes algebraically larger relative to $(g_{12} - g_{11})$, the Ω_1 curve tends to bow upward. This behavior is typical for a polymer-solvent system having partial miscibility.

Figure 7 shows why it has been necessary to resort to a two-parameter equation to model the behavior of hexane activity for our system. The Flory-Huggins χ deter-

TABLE 1. PAIR PARAMETERS FOR HEXANE ACTIVITY COEFFICIENTS

Pressure, atm	Temp, °C	$(g_{12} - g_{11})$ kJ/gmol	$(g_{12} - g_{22})$ kJ/gmol
4.4	137	−2.60	5.32
11.0	137	−2.60	5.32
70.0	143	−2.70	6.28
70.0	157	−2.89	5.86

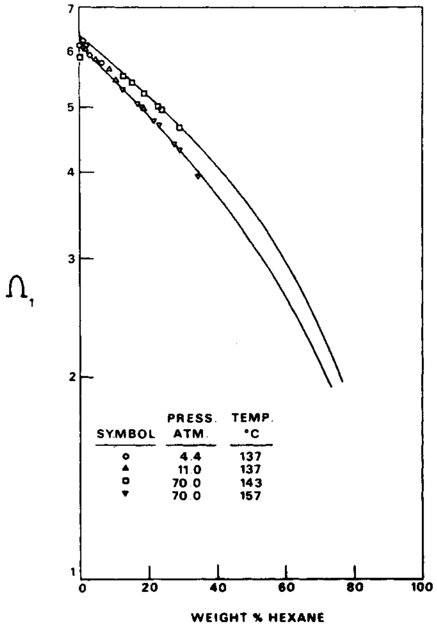

Fig. 6. Composition dependence of hexane activity coefficients in HDPE solutions.

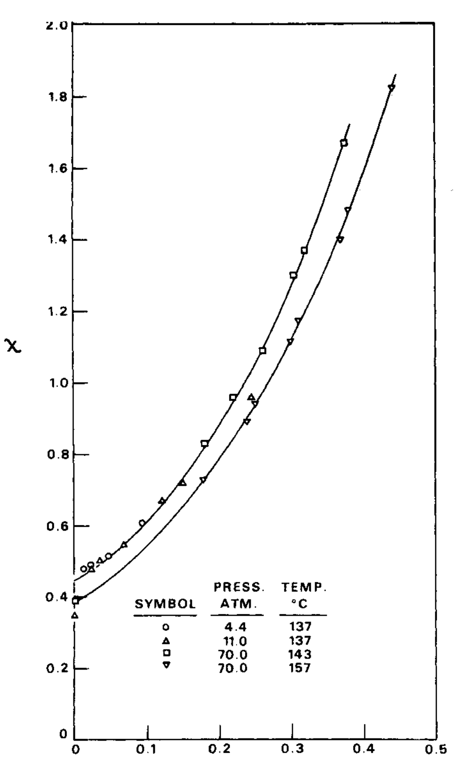

Fig. 7. Flory-Huggins interaction parameters for hexane in HDPE.

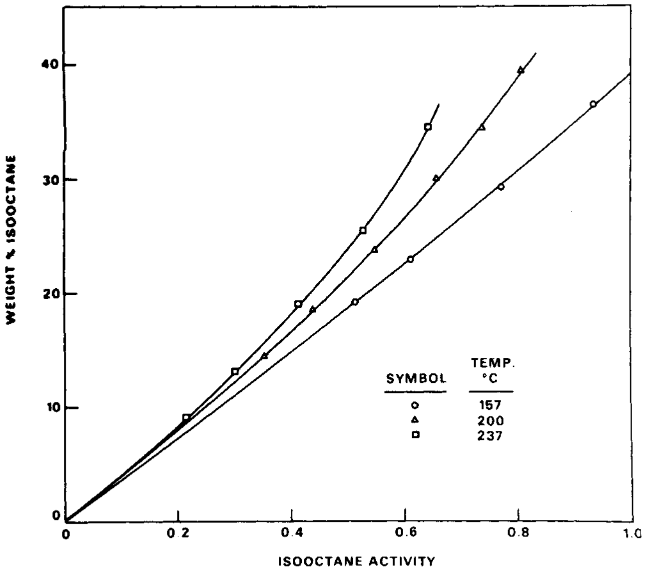

Fig. 8. Isooctane activity in HDPE at 70 atm total pressure.

mined from Equation (13) increases markedly with the addition of hexane to the polymer at these conditions. As in Figure 6, all of the data fall nearly on one of two closely adjacent curves that rise from about 0.4 to 1.8 as hexane is sorbed.

Isooctane-HDPE System

Measurements of isooctane retention times in HDPE were carried out at 70 atm and three temperatures: 157°, 200°, and 237°C. Figure 8 depicts the sorption isotherms for this system. The higher solubilities of isooctane compared with hexane are in line with expectations. Note that at constant solvent activity the sorption increases as the temperature is raised, as noted with hexane. Extrapolation of the isotherms to unit activity gives a reasonable estimate of the saturation composition of isooctane in HDPE.

Figure 9 shows the activity coefficients for isooctane at the three temperatures. All three curves had about the same Ω_1^∞ value of 4.00 ± 0.08, a value considerably less than for hexane. None of these curves through the data could be correlated either by the segment interaction equation or by the Maron equation. The extreme upward bowing of the curves prevented a matching with only two parameters in the equation.

Figure 10 shows how the Flory-Huggins χ changes with the addition of isooctane. The pronounced composition

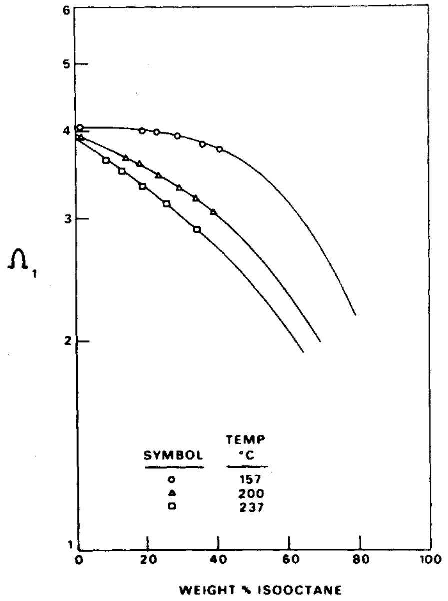

Fig. 9. Composition dependence of isooctane activity coefficients in HDPE solutions at 70 atm total pressure.

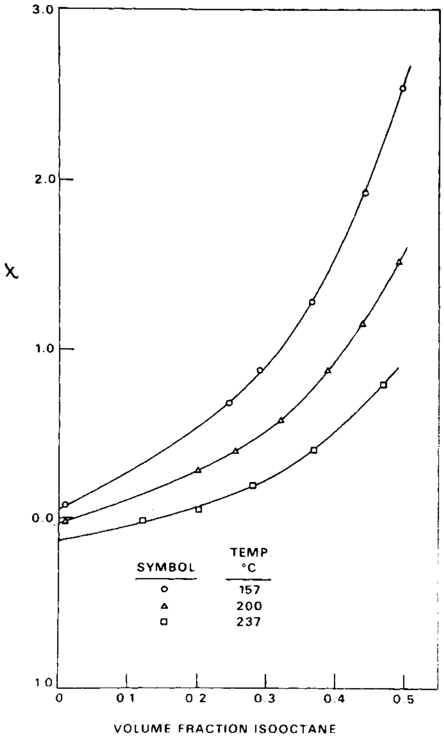

Fig. 10. Interaction parameters for isooctane in HDPE at 70 atm pressure.

dependence of χ is similar to the behavior of hexane in HDPE shown in Figure 7. As expected, χ for isooctane is significantly less at infinite dilution than the hexane χ at the same point. The value of χ at 157°C rises from about zero to over 2.5 at $\phi_1 = 0.5$. This unexpectedly large change determined at 70 atm is in direct contrast to the nearly constant χ values reported for similar polymer-solvent systems at lower pressures (Van der Waals and Hermans, 1950; Newman and Prausnitz, 1973a). The change in χ may be the effect of pressure and/or the effect of nitrogen on the solution.

ACKNOWLEDGMENT

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NOTATION

a_1 = solvent activity in polymer solution
B_n^m = flow rate correction factor for sorption
c = solvent concentration in carrier gas, gmol/cm^3
f_1 = solvent fugacity in carrier gas, atm
f_1^0 = pure liquid fugacity of solvent, atm
g_{12} = interchange energy between solvent and polymer segment, kJ/gmol
F_W = correction to flow meter reading required by water vapor saturation
J_n^m = correction for pressure drop across column
K_1 = conventional vapor-liquid equilibrium ratio, y_1/x_1
m_2 = mass of polymer in stationary phase, g
M_1 = solvent molecular weight
MWD = molecular weight distribution
P = mean total pressure defined as $P_oJ_3^4$, atm
P_F = atmospheric pressure, atm
P_i = absolute column inlet pressure, atm
P_o = absolute column outlet pressure, atm
P_1^s = saturation vapor pressure of pure solvent, atm
q = solvent sorbed per unit mass of polymer, gmol/g
r = ratio of the polymer specific volume to that of the solvent
R = gas constant
t = time at which a zone of concentration c passes a detector, s
T = column temperature, °K
V_F = total flow rate measured at outlet, cm^3/s
ΔV_c = retention volume corrected for sorption at finite concentration, cm^3/g
V_1 = molar volume of solvent, cm^3/gmol
w_1 = weight fraction solvent in polymer
x_1 = liquid mole fraction of solvent in saturator
y_1 = gas mole fraction of solvent
Z_m = mixture compressibility factor

Greek Letters

χ = Flory-Huggins interaction parameter
Ω_1 = weight fraction activity coefficient
ψ = solvent mole fraction in mobile phase used to correct for sorption
ϕ = volume fraction
Φ = fugacity coefficient

Subscripts

F = flow meter
i = inlet
M = helium peak time
o = outlet
R = solvent peak time
1 = solvent
2 = polymer

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