

Vapor-Liquid Equilibria for Benzene/Polybutadiene and Cyclohexane/Polybutadiene Systems at 333, 355, and 373 K Using Gas Chromatography

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Synopsis

A perturbation chromatography apparatus has been designed and constructed for determining the vapor-liquid equilibrium between a two-component (solvent/helium) vapor phase and a two-component (polymer/solvent) liquid phase. The apparatus performed very well, giving reproducible and reliable results that agree with independent, previously reported studies. All tests of the equipment indicated that it was successful in meeting the conditions of low column pressure drop, small perturbations, and slow flow rate that are required for perturbation chromatography. Binary polymer/solvent data were obtained for polybutadiene (PBD)/benzene or polybutadiene/cyclohexane systems at solvent partial pressures to 40 kPa and for *n*-hexane at infinite dilution, all at the three temperatures of 333.15, 355.00, and 373.15 K. The experimental data for each system can be represented within experimental error by the Flory-Huggins polymer solution theory using a single binary interaction parameter that is independent of temperature and concentration.

INTRODUCTION

Accurate phase equilibrium properties of polymer/solvent systems are important for an improved understanding of polymer solution behavior and for design applications in industrial processes such as polymer devolatilization.

Chromatography is an elegant, simple, and fairly rapid method for obtaining vapor-liquid or vapor-solid equilibrium. The technique uses the response of a chromatographic column to a known input to determine the desired equilibrium properties. The known input may be either a step change in concentration (frontal analysis or frontal analysis by characteristic point methods) or a pulse input (elution by characteristic point or elution on a plateau methods). These four methods have been discussed in rather complete detail by Conder and Purnell¹ for the case of a single vapor solvent at finite concentration including corrections for column pressure drop and gas-phase nonideality. The elution on a plateau method is also referred to as perturbation chromatography by Deans et al.,² who give a more general analysis for multicomponent systems by including any number of components at finite concentration and by allowing for chemical reactions in addition to mass transfer reactions. It is this last technique that was used for this work and is described in more detail in the next section.

Previous examples of applications of perturbation chromatography to polymer/solvent systems have been primarily at infinite dilution, although some limited data have been obtained at finite concentration. A review by Bonner³ summarizes much of this work. Extension to finite solvent concentrations have been reported by Brockmeier et al.,⁴⁻⁶ Chang and Bonner,^{7,8} and Dincer et al.⁹

This most recent work was also for polybutadiene/benzene/cyclohexane systems but was restricted to low solvent partial pressures in the flowing phase at one temperature (371 K).

The primary objectives of the work presented here were (1) to design an improved perturbation chromatography apparatus suitable for determining thermodynamic data for polymer/solvent binary mixtures, and (2) to obtain thermodynamic data for polybutadiene/benzene and polybutadiene/cyclohexane systems over a range of temperatures using this apparatus.

CHROMATOGRAPHIC RELATIONS

In the elution on a plateau method (perturbation chromatography), the chromatographic column initially operates at steady state, with the flowing carrier gas consisting of both an inert component (e.g., helium) and an interacting (sorbing) component (e.g., solvent vapor). A composition perturbation of this steady state created by injecting a trace amount of solvent upstream proceeds through the column at a constant velocity (for sufficiently low carrier gas flow rates) which is slower than the average carrier gas flow rate because of extra time spent in the stationary phase.

This extra time spent in the column will be directly proportional to the slope of the solvent sorption isotherm evaluated at the unperturbed steady-state column conditions. At constant total gas-phase concentration,¹⁰

$$t_{\text{peak}} - t_{\text{inert}} = \frac{Vm_3(1 - ay_1)}{Q} \left(\frac{\partial X_1}{\partial y_1} \right)_{T,P} \quad (1)$$

where t_{peak} and t_{inert} are the elution times for the solvent peak and an inert (e.g., air) species peak; Q is the gas-phase volumetric flow rate at column conditions of temperature and pressure; m_3 is the mass of polymer in the column; V is the gas-phase molar volume at column conditions; and X_1 is solvent (component 1) sorption (mass of solvent/mass of polymer), a function of gas phase solvent mole fraction y_1 as well as of temperature and pressure. The factor a corrects for gas-phase deviations from ideality and is given by

$$a = 1 + \frac{2y_1PB_{22}(1 - y_1)}{RT}$$

where B_{22} is the helium second virial coefficient, T is the temperature, P is the pressure, and R is the gas constant. This factor is very close to unity at our test conditions. Note that in these equations subscript 1 refers to solvent (in either phase), subscript 3 refers to polymer, and subscript 2 refers to helium in the gas phase. The helium mole fraction does not appear explicitly in any of the equations that are given since it can be expressed in terms of the solvent mole fraction ($y_2 = 1 - y_1$).

Historically, the product $Q(t_{\text{peak}} - t_{\text{inert}})$ has been called the retention volume (or more properly the net retention volume), the extra volume of gas phase in addition to the column void volume required to elute the composition perturbation from the column. Furthermore, this volume, expressed per mass of polymer and converted to a reference temperature of 0°C, has been termed the specific retention volume and is then treated as the fundamental property obtained from chromatography experiments. As such, other subsequent equations

(for infinite dilution activity coefficients, for example) have been written in terms of this retention volume. This terminology has the advantage of emphasizing the experimental measurements required, i.e., the peak elution times and the volumetric flow rate. It has the disadvantages, however, first, of employing a reference temperature which may have nothing to do with the actual experimental conditions and which must be reincorporated in its later use to obtain thermodynamic properties; and second, of failing to convey any appropriate fundamental physical meaning. Consequently, we have found such terminology to be cumbersome and awkward when the objective is to determine thermodynamic properties.

For perturbation chromatography at constant pressure, we prefer to write

$$\left(\frac{\partial X_1}{\partial y_1}\right)_{T,P} = \frac{N}{m_3} \left(\frac{t_{\text{peak}} - t_{\text{inert}}}{1 - ay_1}\right) \quad (2)$$

where $N = Q/V$ is the gas-phase total molar flow rate, which is independent of temperature at constant total concentration; and where $(\partial X_1/\partial y_1)_{T,P}$ has a clear thermodynamic meaning as the partial derivative of the sorption isotherm at the unperturbed steady-state conditions. At infinite dilution ($y_1 = 0$), for example, the inverse of this derivative is proportional to the Henry's law constant for sorption of the solvent. Perturbations at several steady-state compositions yield the corresponding sorption isotherm slopes, which in turn can be integrated graphically or numerically to give actual sorption values, since

$$X_1(y_1) = \int_0^{y_1} \left(\frac{\partial X_1}{\partial y_1}\right)_{T,P} dy_1 \quad (3)$$

The composition X then can be converted to weight fraction w :

$$w_1 = \frac{X_1}{1 + X_1} \quad (4)$$

to give y_1 vs. w_1 or p_1 vs. w_1 equilibrium isotherms, where p_1 is the partial pressure of solvent 1.

Several assumptions which must be met experimentally in order to obtain accurate thermodynamic data are made in these equations. First is that pressure drop (ΔP) along the length of the column be suitably small. Conder and Purnell¹ state that $y_1(\Delta P/P)$ should be of the order of the measurement errors for the relative retention time $(t_{\text{peak}} - t_{\text{inert}})/t_{\text{inert}}$ for the peak. This frequently is about 1%. Second is that as the perturbation proceeds down the column, local equilibrium is achieved instantaneously at all points within the column. Experimentally, the flow rate through the column must be sufficiently slow that mass transfer is fast compared to the flow rate. Third is that the slope of the sorption isotherm is constant over the range of composition changes accompanying the perturbation or, equivalently, that the isotherm can be approximated as linear near the steady-state operating conditions. Experimentally, then, perturbations must be kept as small as possible.

THERMODYNAMIC RELATIONS

From the sorption isotherm (y_1 vs. w_1 , for example), the weight-fraction activity coefficient for solvent Ω_1 may be obtained using standard thermodynamic

relationships¹¹:

$$\Omega_1 = \frac{\hat{f}_1^v}{w_1 f_1^0} = \frac{y_1 P / Z_{\text{mix}} \exp[2(y_1 B_{11} + y_2 B_{12})/V]}{w_1 P_1^s \exp\left[\frac{B_{11} P_1^s}{RT}\right]} \quad (5)$$

where \hat{f}_1^v and f_1^0 are the vapor and saturated liquid fugacities, respectively; P_1^s is the pure solvent vapor pressure; and B_{11} and B_{12} are the pure solvent second virial coefficient and the solvent helium interaction second virial coefficient, respectively. An average column pressure is used in this equation and is given by¹²

$$P = \frac{2}{3} P_0 \frac{[(P_i/P_0)^3 - 1]}{[(P_i/P_0)^2 - 1]}$$

where P_i and P_0 are the pressures at the column inlet and outlet, respectively. For the small pressure drops required by the chromatographic theory, this average pressure is very close to the arithmetic average. The gas-phase compressibility factor Z_{mix} is given by

$$Z_{\text{mix}} = \frac{PV}{RT} = 1 + \frac{PB_{\text{mix}}}{RT}$$

where B_{mix} is the second virial coefficient for the steady-state carrier gas mixture. Values of solvent vapor pressure were calculated from the Antoine equation, and the Antoine constants for benzene and cyclohexane were obtained from Reid et al.¹³ Values of the second virial coefficients were calculated using the corresponding states correlation of Pitzer extended for mixtures as given in Smith and Van Ness.¹⁴ Note that at the experimental conditions of this work, the exponential terms are close to unity. At infinite dilution, eq. 5 becomes

$$\Omega_1^\infty = \frac{P \exp(2B_{12}/V)}{Z_2 P_1^s (\partial X_1 / \partial y_1)^\infty \exp(B_{11} P_1^s / RT)} \quad (6)$$

where Ω_1^∞ is the infinite dilution value of the weight fraction activity coefficient and $(\partial X_1 / \partial y_1)^\infty$ is the slope of the sorption isotherm at infinite dilution and is determined from a solvent perturbation at infinite dilution ($y_1 = 0$) according to eq. (2).

EXPERIMENTAL

Apparatus

A schematic diagram of the chromatographic apparatus designed for this work is shown in Figure 1. The capillary tube and oil manometer measured helium volumetric flow rate. This allowed rapid and accurate helium flow rate adjustments to the desired value and in addition gave an easily observed indication of flow rate stability.

An oven housed the column and the thermal conductivity detector. A baffle and electric fan provided internal circulation for an isothermal environment inside the oven. Temperature was controlled to within 0.05 K.

A solvent injection system provided the required solvent for the steady-state carrier gas composition. A syringe pump was used for the continuous injection

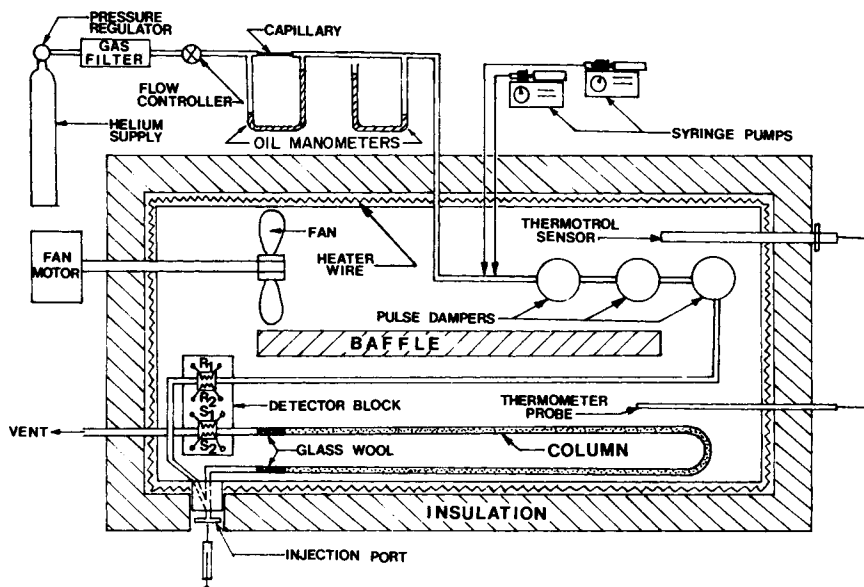


Fig. 1. Schematic of the apparatus.

of benzene or cyclohexane. A glass syringe, Teflon tubing, and a 25-cm-long stainless steel needle conducted liquid solvent through the oven wall for vaporization into the carrier gas flow stream. All syringe surfaces exposed to the solvents were inert, composed of either glass or Teflon. All connections were threaded or soldered to prevent leaks. Three pulse dampers in series smoothed solvent composition fluctuations in the helium/solvent carrier gas.

Flow stream concentration perturbations were detected with a standard-design thermal conductivity detector. The column carrier gas itself, upstream of the perturbation injection port, served as the reference side of the detector so as to provide a highly stable baseline and consequently high sensitivity to perturbations.

The column pressure drop was measured with an oil manometer. The column outlet pressure, assumed equal to atmospheric, was measured with a mercury barometer with a precision of 0.001 in. mercury.

Materials and Procedure

The column used in this work was stainless steel tubing (1.22 m long; 2.1 mm inside diameter) packed with polybutadiene-coated Fluoropak-80. The polybutadiene (PBD) used in this study was a random cis-trans sample obtained from Firestone Tire and Rubber Company and had a structural composition of 34.3% cis-1,4 addition, 54.3% trans-1,4 addition, 11.4% vinyl-1,2 addition, with 4.5% unresolved. The polymer density was 0.94 g/mL; and the number-, weight-, z -, and viscosity-average molecular weights were 6.52×10^4 , 2.13×10^5 , 5.43×10^5 , and 1.93×10^5 , respectively. The organic solvents, including cyclohexane, *n*-hexane, benzene, and chloroform, were reagent-grade products of better than 99% purity, obtained from Fisher Scientific Company.

Approximately 0.5 g of polybutadiene was weighed accurately and dissolved

in 50 mL chloroform. Fluoropak-80, approximately eight times the mass of polymer, was weighed and added to the mixture after complete dissolution of the polymer. The mixture then was stirred constantly until all the liquid chloroform was evaporated. The coated substrate was further dried in an oven at 333 K to constant weight and then packed and weighed into the tubing. A vibrator was used to increase the uniformity of the packing. The ends of the column were loosely plugged with glass wool to prevent loss of column contents.

Experiments were performed at 333, 355, and 373 K. At each temperature, a series of experiments were made with the solvent syringe pump set at different flow rates to provide different steady-state carrier gas compositions. The helium flow rate was adjusted so that the gas-phase total molar flow rate was the same for all experiments (2.97×10^{-4} mol/min, which corresponds to about 6.5 mL/min at room conditions). The system was then allowed to equilibrate to steady state, at which time solvent perturbations were introduced.

Several experimental checks were made to assure that the chromatographic conditions met those required by the assumptions of the theory mentioned above.

In general, the sample perturbation used was the smallest that would give a sufficiently large peak to obtain an accurately measured retention time. The smallest such sample injections were at infinite dilution conditions and were 10 microliters air saturated with the solvent vapor. The largest injections were at the highest finite concentration experiments and were 0.5 microliter liquid solvent. At all experimental conditions a range of perturbation sizes was used. In no case was a peak time dependence on sample size observed.

To check for instantaneous equilibrium, the flow rate was halved at several representative compositions and the experiment was repeated. In no instance were the results dependent on flow rate.

The column pressure drops ranged between 2 and 3 kPa, so that $y(\Delta P/P)$ was a maximum of about 1.2%, an acceptable approximation to zero pressure drop.

As an additional check on column preparation procedures and overall repeatability, data were obtained on two different packed columns. The two columns reproduced peak times, adjusted for the mass of polymer, and activity coefficients to within 1%.

RESULTS

Perturbation chromatography data were obtained for polybutadiene/benzene and polybutadiene/cyclohexane systems. Column response data (peak times) were converted to solvent weight fractions in the polymer phase and weight fraction activity coefficient using eqs. (2) through (5). Additionally, *n*-hexane results at infinite dilution (for which the column carrier gas contains no *n*-hexane) were obtained.

Results for the polybutadiene/benzene system are shown in Figures 2 and 3. Figure 2 shows the vapor-phase benzene partial pressure vs. liquid-phase benzene weight fraction at the three temperatures. Note that the three partial pressure isotherms also must pass through the corresponding pure solvent vapor pressure at each temperature when solvent weight fraction is unity. These are 52.0, 106.6, and 179.5 kPa at 333.15, 355.0, and 373.15 K, respectively. Benzene weight

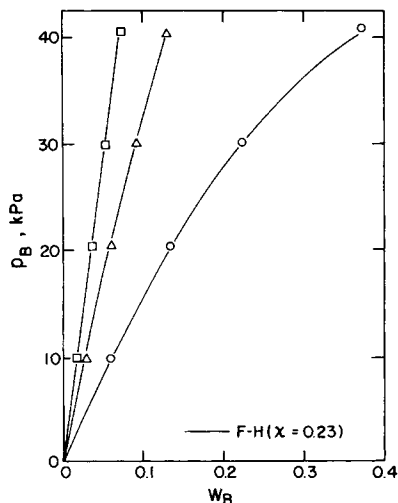


Fig. 2. Partial pressure of benzene as function of its weight fraction in binary PBD/benzene solution: (O) 333.15 K; (Δ) 355.00 K; (\square) 373.15 K.

fraction activity coefficients show an essentially linear decrease with weight fraction but show no dependence on temperature over the range studied.

Activity coefficients for polybutadiene/benzene systems determined by Jessup¹⁵ and Saeki and Holste¹⁶ also are shown in Figure 3. Both of these sets of data were obtained at lower temperatures (300 and 297 K, respectively) using static measurement methods. The Saeki and Holste data were on the same random *cis-trans* polybutadiene material used in this work. Jessup did not indicate the composition of his polymer, but Saeki and Holste showed that there was little difference between *r*-polybutadiene and *cis* polybutadiene samples. These independent results are entirely consistent with the chromatographic data.

Polybutadiene/cyclohexane data are given in Figures 4 and 5. Cyclohexane pure solvent vapor pressures are 51.7, 104.4, and 174.1 kPa at the three tem-

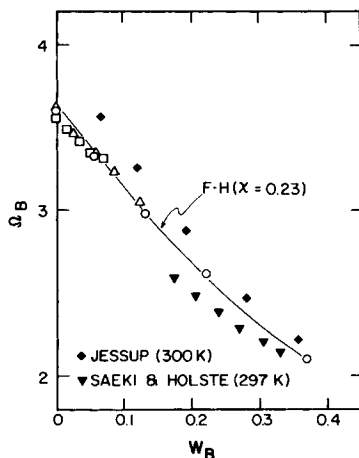
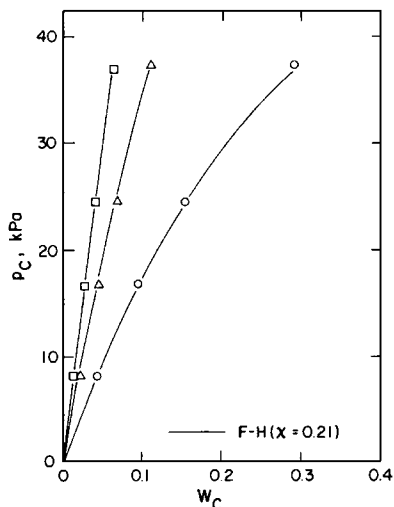


Fig. 3. Benzene weight fraction activity coefficient vs. weight fraction in PBD/benzene solution: (O) 333.15 K; (Δ) 355.00 K; (\square) 373.15 K.



• Fig. 4. Partial pressure of cyclohexane as function of its weight fraction in binary PBD/Cyclohexane solution: (○) 333.15 K; (△) 355.00 K; (□) 373.15 K.

peratures. Again, the weight fraction activity coefficients show a linear decrease with solvent weight fraction and little dependence on temperature.

Activity coefficients for this system at 297 K obtained by Saeki and Holste¹⁶ also are given in Figure 5. These results also suggest little or no temperature dependence down to at least 300 K, again being completely consistent with the chromatographic results.

Figure 6 gives infinite dilution weight fraction activity coefficients vs. temperature for benzene, cyclohexane, and *n*-hexane. Cyclohexane and benzene show little temperature dependence, while *n*-hexane shows some decrease with increasing temperature.

Figures 7 and 8 show the infinite dilution weight fraction activity coefficients

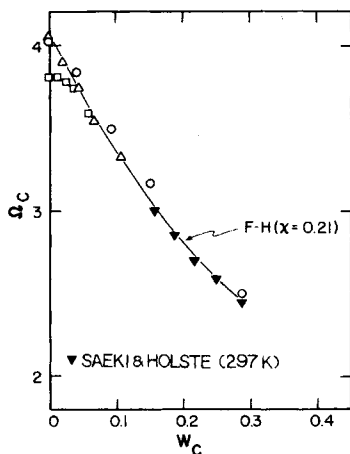


Fig. 5. Cyclohexane weight fraction activity coefficient vs. weight fraction in PBD/cyclohexane solution: (○) 333.15 K; (△) 355.00 K; (□) 373.15 K.

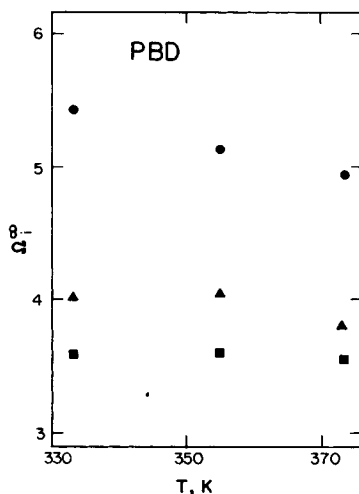


Fig. 6. Infinite dilution weight fraction activity coefficients vs. temperature: (●) $n\text{-C}_6$; (▲) $c\text{-C}_6$; (■) C_6H_6 .

for n -hexane and cyclohexane as the weight fraction of benzene increases, and for n -hexane and benzene as the weight fraction of cyclohexane increases. In both cases the activity coefficients show a marked decrease with increasing solvent composition in the polymer phase. Adding benzene or cyclohexane solvent to the polymer phase enhances the sorption (or decreases the volatility) of other solvent components which are at infinite dilution.

Attempts to go to higher solvent partial pressures resulted in apparent alterations to the column or to the loading of the polymer on the substrate, a result that is not too surprising in view of the very high solvent weight fractions that are present.

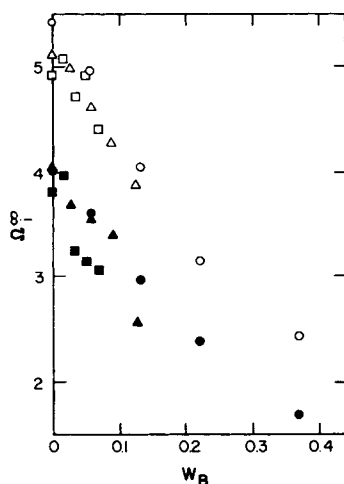


Fig. 7. n -Hexane and cyclohexane infinite dilution weight fraction activity coefficients in binary PBD/benzene solutions. $n\text{-C}_6$: (○) 333.15 K; (△) 355.00 K; (□) 373.15 K. $c\text{-C}_6$: (●) 333.15 K; (▲) 355.00 K; (■) 373.15 K.

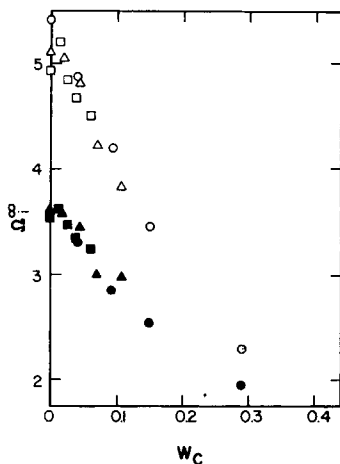


Fig. 8. *n*-Hexane and benzene infinite dilution weight fraction activity coefficients in binary PBD/cyclohexane solutions. *n*-C₆: (○) 333.15 K; (△) 355.00 K; (□) 373.15 K. *c*-C₆: (●) 333.15 K; (▲) 355.00 K; (■) 373.15 K.

POLYMER SOLUTION THEORY CALCULATIONS

Flory-Huggins interaction parameters have been calculated for both benzene and cyclohexane solvents at all three temperatures using the equation¹⁷

$$\ln(\Omega_1 w_1) = \ln(1 - \Phi_3) + \left(1 - \frac{1}{x_{13}}\right)\Phi_3 + \chi_{13}\Phi_3^2 \quad (7)$$

where Φ_3 is the polymer volume fraction, x_{13} is the ratio of polymer molar volume to solvent molar volume, and χ_{13} is the Flory-Huggins polymer/solvent interaction parameter. At infinite dilution, the F-H interaction parameter χ_{13}^∞ can be calculated from Ω_1^∞ and the polymer and solvent densities (ρ_1 and ρ_3 respectively) using

$$\chi_{13}^\infty = \ln \frac{\Omega_1^\infty \rho_1}{\rho_3} - 1$$

In making the calculations, weight fractions were converted to volume fractions by assuming ideal solution behavior, and $1/x_{13}$ was taken to be approximately zero. The values of the interaction parameter for both benzene and cyclohexane at all temperatures were relatively constant. For cyclohexane, χ_{13} varied from 0.15 to 0.25, with an average of 0.21; while for benzene, χ_{13} varied from 0.20 to 0.25, with an average value of 0.23. There was a general trend for the interaction parameter to increase with increasing solvent weight fraction.

Using these average values for benzene and cyclohexane, weight fraction activity coefficients and solvent partial pressures were calculated and are shown as the solid lines in Figures 2 through 5. The agreement with the experimental results allows the generation of vapor pressure data over a range of temperatures for design applications, since eqs. (7) and (5) can be used to calculate solvent partial pressure as a function of solvent weight fraction.

The values of the interaction parameter at infinite dilution for *n*-hexane were 0.34, 0.28, and 0.24 at the three temperatures of 333.15, 355.00, and 373.15 K,

respectively. Using these values, eqs. (7) and (5) should allow reasonable extrapolation of *n*-hexane equilibrium with polybutadiene to moderate finite concentrations. For this system, it is probably best to use the value specific for each temperature since the temperature dependence is greater than for either benzene or cyclohexane.

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