(24) Saitō, H.; Tabeta, R.; Asakura, T.; Iwanaga, Y.; Shoji, A.; Ozaki, T.; Ando, I. *Macromolecules* **1984**, *17*, 1405–1412.

(25) Shoji, A.; Ozaki, T.; Saitō, H.; Tabeta, R.; Ando, I. *Macromolecules* **1984**, *17*, 1472–1479.

(26) Saitō, H.; Tabeta, R.; Shoji, A.; Ozaki, T.; Ando, I.; Miyata, T. *Biopolymers* **1984**, *23*, 2279–2297.

(27) Shoji, A.; Ozaki, T.; Saitō, H.; Tabeta, R.; Ando, I. *Makromol. Chem., Rapid Commun.* **1984**, *5*, 799–804.

(28) Yamanobe, T.; Ando. I.; Saitō, H.; Tabeta, R.; Shoji, A.; Ozaki, T. *Bull. Chem. Soc. Jpn.* **1985**, *58*, 23–29.

(29) Yamanobe, T.; Ando, I.; Saitō, H.; Tabeta, R.; Shoji, A.; Ozaki, T. *Chem. Phys.* **1985**, *99*, 259–264.

(30) Saitō, H.; Tabeta, R.; Shoji, A.; Ozaki, T.; Ando, I.; Asakura, T. In *Magnetic Resonance in Biology and Medicine*; Govil, G., Khetrapal, C. L., Saran, A., Eds.; Tata McGraw-Hill: New Delhi, 1985; pp 195–215.

(31) Ando, S.; Yamanobe, T.; Ando, I.; Shoji, A.; Ozaki, T.; Tabeta, R.; Saitō, H. *J. Am. Chem. Soc.* **1985**, *107*, 7648–7652.

(32) Müller, D.; Kricheldorf, H. R. *Polym. Bull.* **1981**, *6*, 101–108.

(33) Kricheldorf, H. R.; Mutter, M.; Mazer, F.; Müller, D.; Forster, D. *Biopolymers* **1983**, *22*, 1357–1372.

(34) Kricheldorf, H. R.; Müller, D. *Macromolecules* **1983**, *16*, 615–623.

(35) Kricheldorf, H. R.; Müller, D.; Ziegler, K. *Polym. Bull.* **1983**, *9*, 284–291.

(36) Ozaki, T.; Shoji, A.; Furukawa, M. *Makromol. Chem.* **1982**, *183*, 771–780.

(37) Ozaki, T.; Shoji, A. *Makromol. Chem., Rapid Commun.* **1982**, *3*, 157–160.

(38) Shoji, A.; Kawai, T. *Kobunshi Kagaku* **1971**, *28*, 805–809.

(39) Arnott, S.; Wonacott, A. J. *J. Mol. Biol.* **1966**, *21*, 371–383.

(40) Arnott, S.; Dover, S. D.; Elliott, A. *J. Mol. Biol.* **1967**, *30*, 201–208.

(41) Arnott, S.; Dover, S. D. *J. Mol. Biol.* **1967**, *30*, 209–212.

(42) Pines, A.; Gibby, M. G.; Waugh, J. S. *J. Chem. Phys.* **1973**, *59*, 569–590.

Comparison of Multicomponent Gas Chromatography Measurements of Vapor–Liquid Equilibrium with Static Measurements Using a Polymer/Two Solvent Ternary System

Thomas K. Tsotsis,* Craig Turchi, and Charles J. Glover

Department of Chemical Engineering, Texas A&M University,
College Station, Texas 77843.

Received May 28, 1986

ABSTRACT: Perturbation gas–liquid chromatography (GLC) was used to determine the equilibrium properties of the ternary cyclohexane/polybutadiene (PBD)/benzene system at finite concentrations for temperatures of 319.30, 333.15, and 348.15 K. Calculations using the multicomponent chromatography theory of Glover and Lau[1] showed an opposite temperature dependence for GLC-based solvent/solvent parameters compared with binary vapor-liquid equilibrium based solvent/solvent parameters. This confirms the trend previously reported by Ruff et al.[2] for the same system as in the present work. Static sorption data were also collected at 302.35, 319.30, and 333.15 K. Binary data for the benzene/PBD and cyclohexane/PBD systems were also obtained by both methods at the same temperatures. Excellent agreement was found between the two sets of binary data, reinforcing the utility of the GLC method to obtain polymer/solvent vapor–liquid equilibria. A comparison of calculated equilibria compositions using GLC-based parameters and the multicomponent chromatography of Glover and Lau[1] gave reasonable agreement with the ternary static sorption data at 302.35 and 319.30 K; however, due to the difficulties involved in these experiments, no definitive conclusion may be drawn from the data as to the adequacy of the multicomponent chromatography theory of Glover and Lau.[1]

Introduction

Numerous measurements of binary systems have been made by both chromatographic and static methods. Although some studies have indicated that agreement between the two methods is not always achieved, it is generally accepted that, in principle, gas–liquid chromatography (GLC) can be used to obtain accurate binary vapor–liquid equilibrium (VLE) when proper precautions are taken with experimental technique. Recently, Glover and Lau[1] extended the theory of perturbation chromatography (also called elution-on-a-plateau or step-and-pulse chromatography) to multicomponent systems. This work examines the results of the theory to calculate ternary GLC-based parameters and discusses the experimental difficulties in obtaining static ternary data.

Development of Chromatographic Techniques for Binary Systems. The use of GLC for the measurement of equilibrium properties of polymer/solvent systems was established by Guillet and co-workers.[3–5] Early experimental work by Schreiber and co-workers[6–8] justified the use of the GLC technique for equilibrium measurements by showing good agreement between GLC and equilibrium sorption (static) data. This work also established guidelines for the useful application of the GLC method to polymer solution thermodynamics.

In contrast to the work of Schreiber et al.,[8] several authors have reported discrepancies between static and GLC results. Bonner[9] notes systematic differences between extrapolated finite concentration static and infinite dilution GLC measurements. Lichtenthaler, Newman, and Prausnitz[10a] followed by Lichtenthaler, Prausnitz, Su, Schreiber, and Patterson[10b] reported notable disagreement between static and GLC-based activity coefficients as well as between retention volumes. Chang and Bonner,[11a] in examining the effects of polymer degradation on GLC results, found only fair agreement with other workers. In another article, Chang and Bonner[11b] note good agreement of GLC measurements with static measurements except at low benzene concentrations. Sharma and Lakhanpal[12] obtained correct qualitative predictions based on Flory's equation of state theory, but did not obtain quantitative agreement between theory and experiment.

Ashworth, Laub, et al.[13] attribute differences between static and GLC activity coefficients and interaction pa-

---

* Address correspondence to this author at Mechanics and Materials Center, Department of Civil Engineering, Texas A&M University, College Station, TX 77843.

0024-9297/87/2220-2445$01.50/0

rameters to experimental error rather than fundamental principle. Tait and Abushihada[14] performed comparative studies between static and GLC results for a wide range of solvents and obtained good agreement.

Open Tubular Columns. For systems which yield good agreement between static and GLC results, it has been shown that better agreement can be obtained by using coated capillary columns instead of packed columns.[10c] Lichtenthaler, Liu, and Prausnitz[10c] reported coated-column retention volumes and interaction parameters which differed by as much as 20% from packed column values.

The advantage of the coated columns was to provide an increase in film thickness and thus results that are more representative of conditions in the bulk material. However, Braun and Guillet[15] warn against the use of very thick films because retention volume measurements may become highly flow-rate dependent due to increased mass-transfer effects, thus distorting equilibrium calculations. Indeed, Lichtenthaler, Liu, and Prausnitz[10c] reported a flow-rate dependence for some systems while noting that for other systems GLC data appear to be insensitive to film thickness.

In addition to providing more accurate results, coated columns may be more precise than packed columns. Pawlisch[16] notes that there is less peak broadening with a coated column than with a packed column. Less peak broadening allows for more precise determination of retention times.

Analysis of Multicomponent Systems by Chromatography. Glover and Lau[1] provide a theoretical basis for interpreting perturbation gas chromatographic data for multicomponent systems. Their method provided a result which relates the retention times of each eluted peak of a multicomponent system to all of the isotherm partial derivatives for all of the sorbing species. In order to use this theory, a highly implicit nonlinear parameter estimation procedure was developed by Ruff, et al.[17] and applied to the data of Lau[18] for the PBD/cyclohexane and PBD/benzene systems as well as the ternary system cyclohexane/PBD/benzene. Data obtained by this technique for a ternary system which has poorer mixing characteristics also have been reported.[19]

In these cases, where independent binary data are available, agreement with the GLC work is very good. However, no data for the ternary systems have been available for comparison. Consequently, the primary objective of this work was to obtain independent static data on the ternary cyclohexane/PBD/benzene system for comparison with the GLC data. A second objective was to improve the accuracy and precision of our technique. This would allow more definite conclusions to be made concerning trends in the dependence of polymer solution theory binary interaction parameters on temperature and on the use of solvent/solvent parameters obtained from independent solvent/solvent VLE.

Experimental Methods

For the experiments described here, a *cis,trans*-polybutadiene (PBD) of molecular weight 213 000 manufactured by Scientific Polymer Products, Inc., and standard reagent quality benzene and cyclohexane were used.

Static Measurement: Description and Procedure. Equilibrium sorption data were obtained by measuring the number of moles of solvent (benzene, cyclohexane, or a mixture of both) sorbed by a known mass of polybutadiene at 302.35, 319.30, and 333.15 K at various pressures. A Micromeritics AccuSorb 2100 was used to evacuate the system and measure pressures. An external heater maintained the desired constant temperature in the insulated polymer sample tube. The apparatus schematic for the AccuSorb system and the solvent/breaker tubes are shown in Figures 1 and 2.

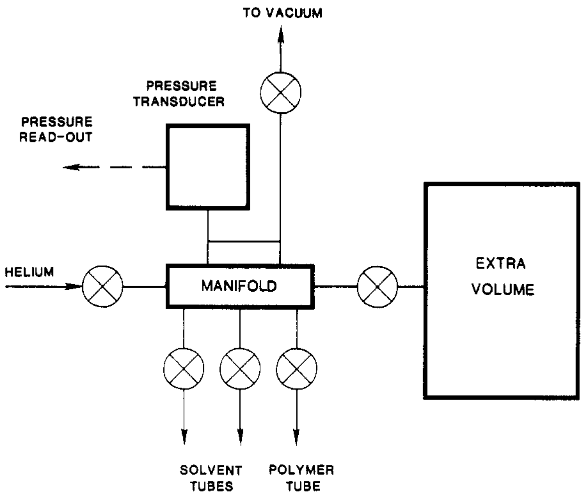

Figure 1. Schematic of AccuSorb system.

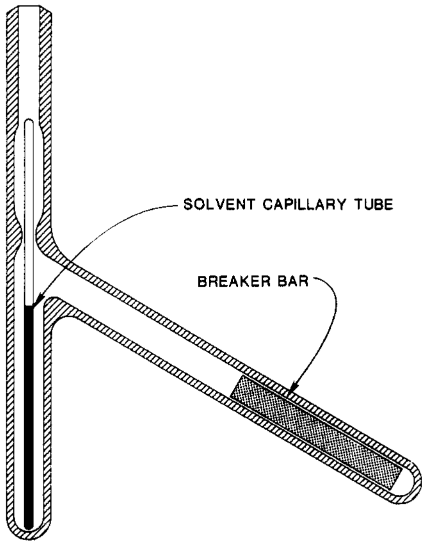

Figure 2. Solvent/breaker tube.

The procedure for use of the AccuSorb configuration shown in Figure 1 is as follows: 50-μL pipets filled with solvent were sealed, weighed, and placed in a tube connected to the AccuSorb. A tube coated with polymer was also connected to the AccuSorb. The system was then evacuated and brought to the temperature desired. This generally required between 4 and 6 h.

A direct-current voltage source was used to move the breaker bar in the solvent/breaker tube shown in Figure 2 to break the sealed capillary tube containing either benzene or cyclohexane. After breaking the tube, the solvent was allowed to enter either the system manifold or the manifold and extra volume combined. The solvent/breaker tube was then shut off from the system and the pressure allowed to reach equilibrium. This equilibrium together with known manifold temperature and volume gave a precise measurement of the total number of moles of solvent admitted to the system.

For ternary runs, the extra volume valve is closed. The pressure of solvent remaining in the manifold is proportional to the number of moles removed from the system when the manifold is subsequently evacuated. The capillary containing the second solvent is then broken as described above, allowing the solvent to expand into the manifold. The second solvent/breaker tube is then shut off from the system and the pressure allowed to equilibrate. This pressure gives the number of moles of the second solvent in the system.

The gas phase to be equilibrated with the polymer is either pure cyclohexane or benzene, or it is a mixture created by allowing the first solvent in the extra volume to mix with the second solvent in the manifold. When the pressure of the pure or mixed solvent

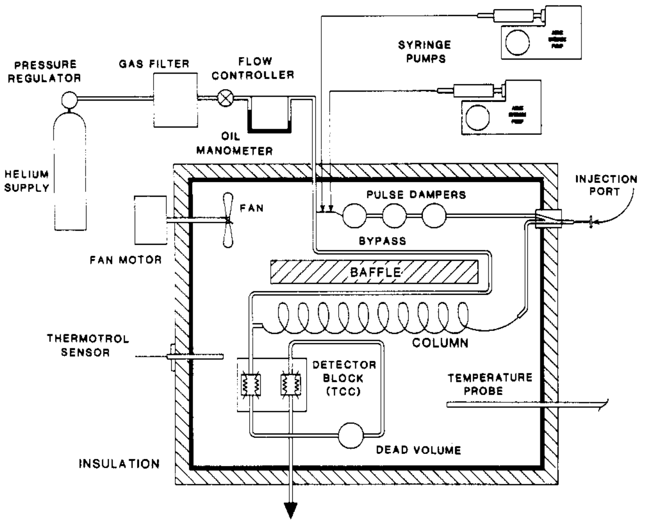

Figure 3. Schematic of chromatographic apparatus.

Table I
Column Parameters[a]

	column 1	column 2
polymer mass, g	0.12964	0.08821
mass percent error (precision)	0.065	0.170
polymer film thickness, cm	4.97×10^{-4}	3.38×10^{-4}

[a] Length = 7.264 m = 23 ft, 10 in.; i.d. = 0.10795 cm = 0.0425 in.; coating solvent, chloroform.

equilibrates, the experiment is ready to begin.

To perform the measurements, the sample tube coated with polymer is exposed to the system (pure or mixed solvent) and the pressure measured until it reaches an equilibrium value. The amount of solvent sorbed is determined by comparing final pressures and volumes to initial pressures and volumes under the assumption of the ideal gas law.

The polymer sample tube was coated by filling a clean tube with PBD dissolved in chloroform and driving off the solvent to form a thin layer of polymer on the inside of the tube. Capillary tubes were prepared by sealing one end of each 50-μL pipet, filling them with the desired amount of solvent, placing them in an ice bath to keep down vapors, and then sealing the open end of each pipet.

Gas Chromatograph: Description. The apparatus used in GLC measurements was a modification of that designed and built by Joffrion,[20] shown in Figure 3. Column temperature was controlled by a Totco 1083 Thermotrol temperature controller to better than ±0.1 °C. Flow of helium carrier gas was regulated by an Analabs HAC-187 flow controller and measured with a calibrated oil manometer (sp gr 0.826). Pressure drop through the system was measured by an oil manometer and atmospheric pressure by a Thermodynamics Research Center (TRC) standardized pressure transducer. Solvents were injected through a rubber septum with a 10-μL Precision Sampling Co. syringe for cyclohexane and a 10-μL Hamilton Co. syringe for benzene. For finite concentrations of solvent in the vapor phase of the chromatographic system, Sage Instrument syring pumps and Glenco 10-mL gas-tight syringes were used to pump solvent through polyethylene tubing into the column flow stream.

The column was prepared as described by Ettre.[21] Type 321 stainless steel, i.d. 0.0425 in., 23 ft 10 in. long, with a wall thickness of 0.010 in. was used. The column parameters are shown in Table I. Before coating the column, it was cleaned with several solvent washings. The dynamic method of coating was used; Figure 4 shows the schematic of the apparatus used to coat the column. The coating solution was made by dissolving between 4 and 5 g of PBD in 50 mL of chloroform. This solution was placed in a reservoir and pushed through the column with helium at a pressure of about 10 psig. Flow was controlled by an Analabs HAC-187 flow controller to prevent too rapid a flow rate. Continued helium flow and heating dry the polymer which adheres to the inner wall of the column. The amount of polymer in the column is determined by the difference in weight between the cleaned uncoated column and the dried coated column. Weights were accurate to within ±0.2 mg, indicating an accuracy of ±0.15% for the polymer weight. The average film thickness is calculated from the volume of the polymer and the inside surface area of the column.

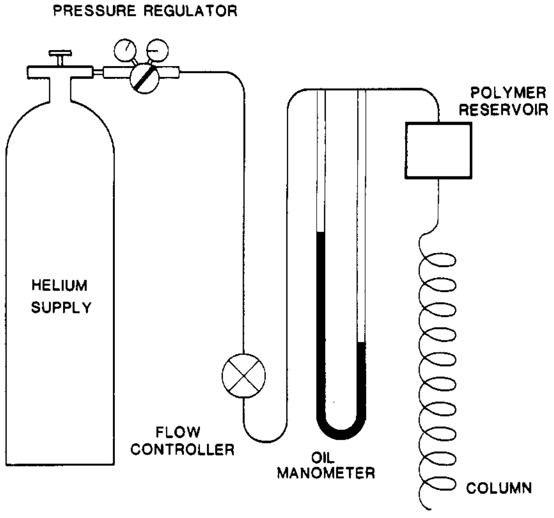

Figure 4. Schematic of coating apparatus.

A Gow-Mac 10-077 thermal conductivity cell (TCC) of 350-μL internal volume was used to determine retention times by sending voltages to a Hewlett-Packard 3421A data acquisition/control unit and the voltages were integrated by a Hewlett-Packard 9816 microcomputer. Retention times calculated were based on the peak centers of the collected voltage data. Due to the use of a wall-coated column, these peaks were sharp and symmetric.

A bypass column was used to increase TCC sensitivity by decreasing the solvent vapor phase concentration at the TCC by diluting it with helium. Also, the bypass served to reduce the flow rate through the column to increase peak separation.

Gas Chromatograph: Procedure. The system was brought to steady state by turning on the heater, circulating fans, Thermotrol sensor, injection port heater, and thermal conductivity cell after selecting the desired helium flow rate. For finite concentration runs, the syringe pumps were also started. Generally, 4 h were needed to reach steady state. The injection port heater was generally operated at 10–15% of the maximum current and the TCC at 115 mA.

Before beginning a run, the thermal conductivity cell must be zeroed. After zeroing, the data collection program is loaded on to the microcomputer and the data acquisition unit activated. The program is started immediately after injecting the desired pertubation sample (air or air and a solvent) into the column. Peaks are also recorded with an Omniscribe chart recorder.

After the data are collected, the data collection program is additionally used to convert the stored voltage data to retention time data. These data are used in a data-reduction program to optimize selection of solution theory interaction parameters and to calculate VLE isotherms. Solution theories used were (1) the Flory–Huggins theory[22,23] in both the volume and segment fraction forms, (2) the Flory–Prigogine equation of state model[24,25] with $s_B/s_{PBD} = s_C/s_{PBD} = 0.96$ and $s_B/s_C = 1.00$ and a simplified "Corresponding States" version of Bonner and Brockmeier,[26] and (3) the lattice fluid model of Sânchez and Lacombe[27a,b] with $1/r = 0$ and $1/r \neq 0$. The multicomponent forms of the equations used in this work are given by Ruff et al.[2]

Results and Discussion

Gas Chromatograph. Results obtained from two coated open tubular chromatographic columns are presented. The first column was used to collect finite-concentration binary as well as infinite-dilution ternary data (one solvent at infinite dilution) and the second column was used to collect finite-concentration ternary (both solvents at finite concentration in the flowing phase) data at 310.30, 333.15, and 348.15 K. In addition, the first

Table II
Estimated Interaction Parameters and Associated 90% Confidence Limits

model and temp, K	interaction parameters[a] (confidence intervals) CH-PBD	BZ-PBD	BZ-CH
Flory–Huggins segment			
302.35[b]	0.461 (±0.005)	0.452 (±0.005)	
319.30	0.464 (±0.008)	0.460 (±0.008)	−0.082 (±0.034)
333.15	0.461 (±0.007)	0.462 (±0.013)	0.304 (±0.184)
348.15	0.461 (±0.031)	0.461 (±0.017)	0.623 (±0.192)
Flory–Huggins volume			
302.35	0.232 (±0.005)	0.196 (±0.008)	
319.30	0.242 (±0.011)	0.207 (±0.010)	0.033 (±0.056)
333.15	0.218 (±0.020)	0.197 (±0.009)	0.281 (±0.142)
348.15	0.188 (±0.051)	0.175 (±0.032)	0.579 (±0.163)
Flory–Prigogine equation of state			
302.35	16.4 (±0.1)	19.4 (±0.3)	
319.30	17.5 (±0.2)	20.6 (±0.4)	−4.3 (±1.2)
333.15	18.5 (±0.2)	22.4 (±0.8)	12.4 (±7.7)
348.15	19.8 (±1.3)	23.7 (±0.8)	27.2 (±8.3)
corresponding states			
302.35	577.1 (±0.1)	606.6 (±0.2)	
319.30	576.4 (±0.1)	605.9 (±0.2)	532.1 (±0.7)
333.15	575.9 (±0.1)	605.0 (±0.3)	524.4 (±3.9)
348.15	575.3 (±0.7)	604.4 (±0.5)	516.8 (±4.1)
lattice fluid ($1/r \neq 0$)			
302.35	5.1 (±0.1)	6.0 (±0.3)	
319.30	5.6 (±0.2)	7.0 (±0.3)	0.1 (±1.6)
333.15	5.4 (±0.4)	7.3 (±0.3)	8.5 (±3.6)
348.15	5.2 (±1.4)	7.2 (±1.1)	19.7 (±4.9)
lattice fluid ($1/r = 0$)			
302.35	5.2 (±0.1)	6.0 (±0.3)	
319.30	5.2 (±0.1)	6.4 (±0.3)	−1.8 (±1.0)
333.15	5.0 (±0.2)	6.8 (±0.4)	8.7 (±2.7)
348.15	4.9 (±1.0)	6.7 (±0.8)	17.3 (±4.6)

[a] Parameters in (MJ/m^3) except for Flory–Huggins (both volume and segment) models which are dimensionless. [b] Values at 302.35 K are taken at infinite dilution.

column was used to collect infinite-dilution binary data at 302.35 K.

Infinite-dilution ternary data were obtained from column 1 by perturbing the column with a small sample of cyclohexane for finite benzene in the flowing phase or benzene for finite cyclohexane in the flowing phase. No finite-concentration ternary data could be obtained from the first column as it failed after the completion of the binary infinite-dilution and finite-concentration runs.

The data collected by using the second column were reduced to obtain solvent/solvent parameters by using the binary polymer/solvent parameters obtained from the first column as fixed parameters in the optimization procedure of Ruff et al.[17] The polymer/solvent parameters were checked against the first column by performing infinite-dilution runs at all three temperatures. This check yielded virtually identical polymer/solvent parameters for both columns at infinite dilution. Solvent/solvent parameters also exhibited very good agreement between the two columns. These two points justify the use of the polymer/solvent parameters from column 1 in the calculations of column 2.

Open Tubular Column. The use of an open tubular coated column met the objectives of (1) improved self-consistency of the data at all concentrations, (2) a small pressure drop of about 300 kPa, approximately one-tenth that of the packed column used by Lau[18] (3) very well-known polymer mass, 0.1 g ± 0.2 mg much better than for a packed column, and (4) improved peak symmetry; other than for the air peak and peaks that interfered, all peaks were quite symmetric.

The use of a coated open tubular column allowed for small perturbations. At infinite dilution, and at low finite concentrations, only trace vapor injections were required. Even at the highest concentrations used in the column, for the binary as well as for the ternary case, injections no larger than 0.2–0.4 μL of liquid were needed.

Parameter Estimates. The open tubular column's improved performance led to improved parameter estimates over those of Ruff et al.[2] Table II contains the parameters and their 90% confidence intervals and Table III contains the statistical error in model predictions of retention times using the optimized parameter values relative to the experimentally determined retention times. In all cases, and for all the solution models, the calculated values agreed better than similar data for a packed column. The weighted residuals of retention times for the coated column were 1–2% compared to 1–4% for the packed column of Lau.[18] In addition, Lau[18] reported approximately a 3% variation in retention time measurements. In this study, most retention times were reproducible to within 1% with very few worse than 3%. This indicates more reliable (or at least more precise) retention time measurements are obtained from an open tubular column than for a packed column.

Solvent/Solvent Parameters. The previous results obtained by Ruff et al.[2] using the data of Lau[18] of increasing solvent/solvent parameter with temperature were confirmed. This trend is, however, in disagreement with the trend of the binary benzene/cyclohexane parameter predicted from benzene/cyclohexane vapor–liquid equilibria data as noted by Ruff et al.[2] This is significant as a basic tenet of all the solution theories is than binary parameters may be used to predict multicomponent behavior.

In the measurements taken in this work, even at the highest concentrations of solvent in the vapor phase, the segment fraction of solvent in the stationary phase was never greater than 30%. Additionally, since the system is quite dilute in solvent, polymer/solvent interactions are

Table III
Average Weighted Residuals[a] of Retention Time Estimates × 10^2

model and temp, K	CH-PBD	BZ-PBD	BZ-CH[b]
Flory–Huggins segment			
302.35[c]	0.53	0.85	
319.30	1.19	2.01	0.95 (4.26)
333.15	0.88	1.51	1.90 (2.65)
348.15	2.08	1.87	1.30 (1.27)
Flory–Huggins volume			
302.35	0.53	0.86	
319.30	2.67	2.48	1.64 (4.31)
333.15	2.99	1.93	2.13 (3.05)
348.15	2.79	3.78	1.26 (2.43)
Flory–Prigogine equation of state			
302.35	0.54	0.86	
319.30	1.27	2.13	0.85 (4.33)
333.15	0.59	1.72	1.89 (2.71)
348.15	1.98	1.77	1.31 (1.18)
corresponding states			
302.35	0.54	0.86	
319.30	1.19	1.92	0.95 (4.31)
333.15	0.85	1.31	1.91 (2.70)
348.15	2.09	2.02	1.27 (1.34)
lattice fluid ($1/r \neq 0$)			
302.35	0.54	0.86	
319.30	1.78	2.17	1.46 (4.39)
333.15	1.82	1.36	6.04 (3.02)
348.15	2.36	3.19	1.18 (2.02)
lattice fluid ($1/r = 0$)			
302.35	0.54	0.86	
319.30	1.09	1.86	1.05 (4.31)
333.15	0.59	1.08	1.94 (2.85)
348.15	2.03	2.20	1.23 (2.05)

[a] Weighted residuals are calculated from $[(1/n)\sum_{i=1}^{n}[(t_{\text{calcd}} - t_{\text{exptl}})/t_{\text{exptl}}]_i^2]^{1/2}$. [b] Numbers in parentheses are infinite dilution ternary values from column 1; numbers not in parentheses are from column 2. [c] Values at 302.35 K are taken at infinite dilution.

much more important than solvent/solvent interactions. Therefore, the models are relatively insensitive to the solvent/solvent parameter in the concentration range of this experiment.

It is also seen that the 90% confidence intervals of the solvent/solvent parameter are large enough that the trend of increasing solvent/solvent parameter with temperature may be more due to experimental conditions that some thermodynamic effect. At higher temperatures these intervals become even larger for the GLC results, making definitive conclusions as to the behavior of the solvent/solvent parameter with temperature more difficult.

Despite this, it appears that the trends observed for the solvent/solvent parameter in this work and in the work of Ruff et al.[2] based on the data of Lau[18] are real and that both results are in direct contradiction with the trend of binary VLE solvent/solvent parameters. The reasons for this are unclear, but do seem to give an indication that the presence of the polymer phase has a significant effect on the interaction of the two solvent species.

These effects, whether due to the physical restrictions of the polymer lattice or to changes in the chemical potential of the system, are not yet understood. In addition, the multicomponent chromatography model assumes that binary polymer/solvent parameters may be used in the ternary calculations. Small changes in these parameters may in fact occur in the ternary case. However, if these changes were to be taken into account, the calculational parameter estimation procedure becomes unreasonably difficult with the additional possibility of nonunique solutions.

Therefore, it is advantageous to hold the solvent/polymer parameter fixed in the estimation procedure of the solvent/solvent parameter from GLC data. In addition, since in the present system benzene and cyclohexane are similar species, it is expected that the physical constraints of the polymer lattice should affect either species equivalently. Thus, any change in the interaction of the two solvents from their binary VLE behavior is likely due to changes in the chemical potential due to the presence of the polymer.

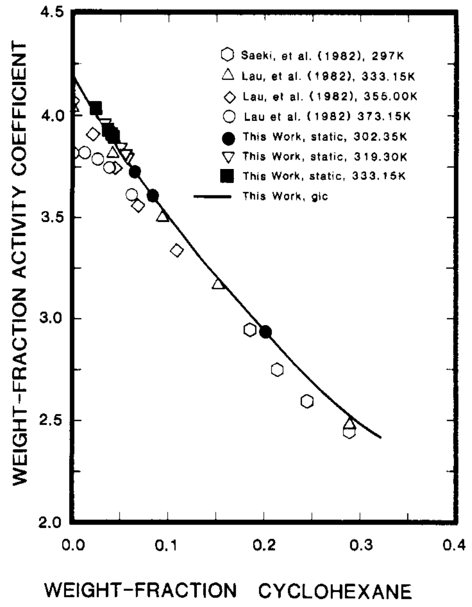

Figure 5. Weight-fraction activity coefficients vs. weight fraction for cyclohexane. Data from Saeki, Holste, and Bonner,[28] Lau et al.,[2] and this work.

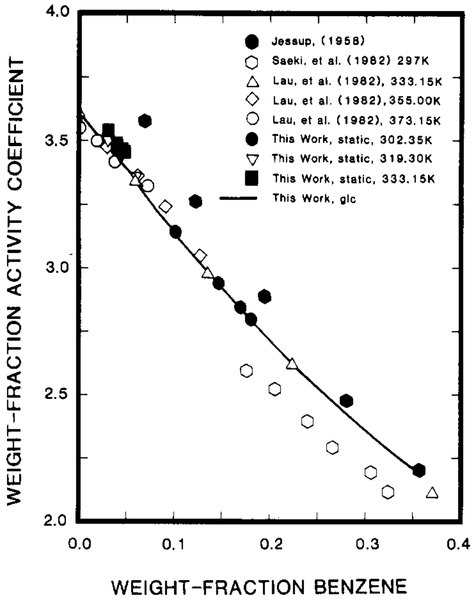

Figure 6. Weight-fraction activity coefficients vs. weight fraction for benzene. Data from Saeki, Holste, and Bonner,[28] Lau et al.,[2] Jessup,[30] and this work.

Static Data. Equilibrium sorption data were obtained in order to confirm the solution theory predictions of equilibrium from chromatographic data. The static data have been converted to weight-fraction activity coefficients and are plotted in Figure 5 for the benzene/PBD data and in Figure 6 for the cyclohexane/PBD data. Comparisons with previous work are also shown in the figures with the solid curve representing the chromatographic work of this paper calculated using the Flory–Huggins segment fraction model. Differences between the several sets of data may be due to differences in the microstructure of the PBD

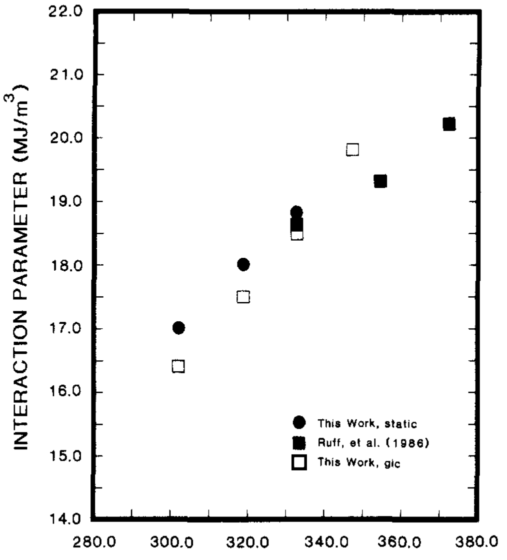

Figure 7. Interaction parameter vs. temperature using the Flory–Prigogine equation of state model for the cyclohexane/PBD interaction parameter using data from Ruff et al.[2] and this work.

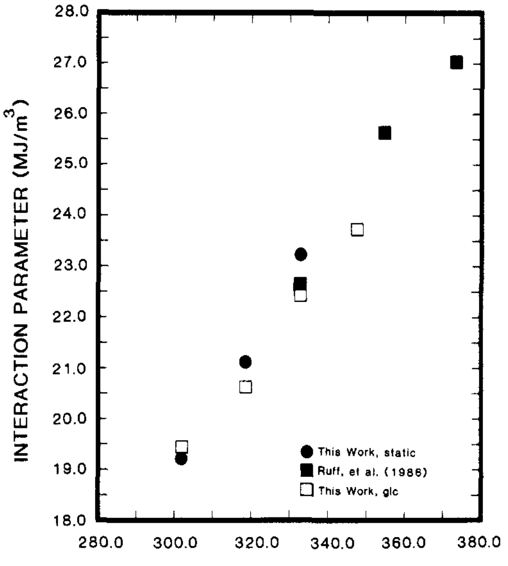

Figure 8. Interaction parameter vs. temperature using the Flory–Prigogine equation of state model for the benzene/PBD interaction parameter using data from Ruff et al.[2] and this work.

used in the different studies. Indeed, Saeki, Holste, and Bonner[28] report significant differences in behavior between random *cis,trans*-PBD and *cis*-PBD.

This work, along with the work of Ashworth, Laub, et al.,[13] contradicts the conclusions reached by Lichtenthaler, Newman, and Prausnitz[10a] and Lichtenthaler et al.[10b] who reported notable discrepancies between static and GLC-based activity coefficients. This contradiction confirms the conclusion of Ashworth, Laub, et al.[13] that discrepancies between equilibrium sorption activity coefficients and interaction parameters from GLC results are primarily due to experimental artifact and not to a failure of the chromatographic theory.

Comparison of Binary Static and GLC Results. The static values of the interaction parameters were calculated by optimizing to a parameter which best matched the experimental sorption values over all the data at each experimental pressure and temperature. Polymer/solvent interaction parameters calculated by using the Flory–Huggins segment fraction model for the static data showed excellent agreement with parameters calculated from GLC data. This agreement reinforces the conclusion made earlier that GLC and static results are compatible. Figures 7–9 show comparisons between the GLC and static parameters of this study, as well as the GLC parameters of Ruff et al.[2] for the Flory–Prigogine equation of state models. It is seen in these figures that the results are consistent with the results of Ruff et al.[2] Also, the static parameters as well as the parameters of Ruff et al.[2] lie within the 90% confidence intervals of the GLC-determined parameters of this work.

Since the two sets of data agree so well as is seen in Figures 5 and 6, it can be stated that the GLC technique is a valid and accurate method of determining polymer/solvent VLE. The GLC measurements, though, can be performed much more rapidly. This is highly advantageous, especially when several polymers are to be examined and/or many solvents used.

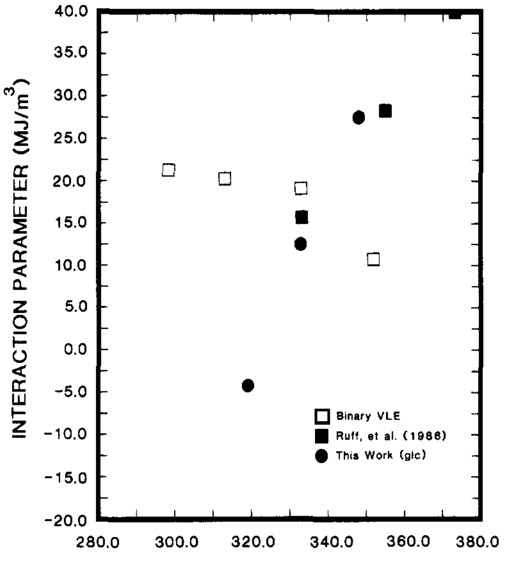

Figure 9. Interaction parameter vs. temperature using the Flory–Prigogine equation of state model for the benzene/cyclohexane interaction parameter using data from Ruff et al.[2] and this work.

Ternary Results. Ternary total sorption data were collected in the same manner as the binary sorption data as is described in the experimental section at 302.35 and 319.30 K. The final vapor-phase composition could not be determined experimentally in this study because samples of sufficient size for analysis could not to be collected from the apparatus, consequently the individual sorption of each component could not be determined.

In order to analyze these data, an iterative procedure to balance the calculated values of the total moles of each solvent in the vapor and stationary phases with their initial values at the experimental pressures and temperatures is used. These results are presented in Tables IV and V.

Agreement between the calculated values obtained by using the GLC-determined interaction parameters and experimental static values of total sorption was found to be about the same as if the system were considered to be a combination of two binary systems. However, no clear trend is apparent in the data to indicate that the multicomponent chromatography of Glover and Lau[1] is confirmed.

Several problems exist with the apparatus used in this work to obtain the ternary data. The result of these problems is the inability to obtain final equilibrium vapor-phase compositions. Due to this, the assumption of

Table IV
Calculated and Experimental Static Ternary Equilibrium Sorption Data at 302.35 K

	experimental			calculated			
solvent	init mol $\times 10^6$	equilib pressure, atm	(mol sorbed)/(g of polymer) $\times 10^4$	partl pressure, atm	(mol sorbed)/(g of polymer) $\times 10^{4\,a}$	$\times 10^{4\,b}$	mol $\times 10^6$
CH[c]	116.27			0.0357	9.23	9.11	116.84
BZ	26.43			0.0079	2.32	2.24	26.63
total		0.0447	12.03		11.55	11.35	
CH[c]	103.22			0.0348	8.09	7.98	103.62
BZ	26.52			0.0080	2.34	2.25	26.90
total		0.0446	11.02		10.42	10.23	
CH[c]	143.11			0.0163	5.05	4.59	143.37
BZ	532.47			0.0581	21.29	20.60	532.34
total		0.0773	24.44		26.43	25.19	
CH[c]	148.11			0.0167	5.29	4.78	147.67
BZ	554.02			0.0601	22.47	21.69	553.56
total		0.0808	26.42		27.76	26.47	
CH[d]	499.19			0.0587	17.04	16.46	499.74
BZ	136.33			0.0153	5.51	5.10	136.59
total		0.0766	20.85		22.55	21.56	
CH[e]	205.00			0.0227	5.16	5.05	205.67
BZ	140.59			0.0146	4.14	4.04	140.54
total		0.0385	9.82		9.30	9.09	
CH[e]	125.69			0.0140	3.05	2.99	125.59
BZ	148.92			0.0157	4.28	4.22	149.38
total		0.0306	7.15		7.33	7.21	

[a] Calculated by using the GC value of interaction parameter and Flory–Huggins segment fraction model. [c] Calculated by using the binary VLE value of interaction parameter and Flory–Huggins segment fraction model. [c] Polymer mass = 64.70 mg. [d] Polymer mass = 59.31 mg. [e] Polymer mass = 99.92 mg.

Table V
Calculated and Experimental Static Ternary Equilibrium Sorption Data at 319.15 K

	experimental			calculated			
solvent	init mol $\times 10^6$	equilib pressure, atm	(mol sorbed)/(g of polymer) $\times 10^4$	partl pressure, atm	(mol sorbed)/(g of polymer) $\times 10^{4\,a}$	$\times 10^{4\,b}$	mol $\times 10^6$
CH[d]	128.03			0.0174	1.76	1.75	128.60
BZ	118.40			0.0157	1.97	1.96	118.34
total		0.0339	3.88		3.73	3.71	
CH[d]	14.42			0.0071	0.69	0.68	14.53
BZ	15.06			0.0069	0.83	0.83	15.11
total		0.0144	1.52		1.52	1.51	
CH[d]	27.09			0.0132	1.30	1.30	27.18
BZ	22.16			0.0102	1.26	1.25	22.48
total		0.0236	2.55		2.56	2.55	
CH[c]	22.14			0.0104	1.02	1.02	21.96
BZ	26.57			0.0119	1.47	1.46	27.22
total		0.0224	2.58		2.48	2.47	
CH[e]	230.86			0.0295	3.09	3.06	231.18
BZ	143.91			0.0178	2.31	2.29	143.98
total		0.0479	5.47		5.40	5.35	
CH[e]	153.59			0.0196	2.05	2.02	153.56
BZ	207.20			0.0256	3.31	3.29	206.97
total		0.0458	5.47		5.36	5.31	

[a] Calculated by using the GC value of interaction parameter and Flory–Huggins segment fraction model. [b] Calculated by using the binary VLE value of interaction parameter and Flory–Huggins segment fraction model. [c] Polymer mass = 64.70 mg. [d] Polymer mass = 59.31 mg. [e] Polymer mass = 99.92 mg.

complete mixng of the two gas phases and the use of total pressures and sorptions to determine equilibrium compositions cannot be corroborated.

An apparatus dedicated to this type of experiment would eliminate these problems as well as allow for wider ranges of compositions to be examined more easily. In addition, provisions could be made to easily collect samples of the equilibrium phase so as to pinpoint its composition.

Conclusions on Ternary Static Results. Due to the above difficulties, no definitive conclusion is possible as to the trend of the solvent/solvent parameter from the static ternary data. Thus, gas–liquid chromatography may be superior in determining the solvent/solvent parameter. The primary reason for this is that VLE predictions from the chromatograph are based on the partial derivatives of the isotherms. These derivatives, in the form of the retention times, are relatively sensitive to the solvent/solvent parameter, providing improved estimates of the parameters from experimental GLC data. In contrast, total and component sorption from static experiments are relatively insensitive to the solvent/solvent parameter making conclusions as to its behavior difficult.

It should be possible to calculate static solvent/solvent interaction parameters by using a larger volume apparatus so that more moles would be present at equilibrium and hence larger samples could be condensed out. Also, a higher manifold temperature would allow for higher solvent vapor pressures and therefore higher weight fractions of solvent in the solid phase. It should also be possible to analyze the gas-phase composition directly (without having to condense it) in a gas chromatograph.

More significantly, experiments with less ideal systems exhibiting strong enhanced sorption effects should be more sensitive to the solvent/solvent parameter and thus more conclusively demonstrate the agreement between static and GLC-based ternary VLE. Furthermore, such a system would provide a conclusive test of the multicomponent chromatography theory.

Conclusions

The principal conclusions of this work are the following: Results comparing static and GLC results showed good agreement for the binary cases. The temperature trend of GLC-based solvent/solvent parameters seen in previous work[2] was confirmed and was found to be opposite the behavior predicted by binary solvent/solvent VLE. The primary objective of confirming the multicomponent theory was not met, but the results are encouraging, suggesting that a modified apparatus may yield conclusive results. The results obtained by use of an open tubular column proved to be more precise than those from a packed column. For the system measured in this study, infinite-dilution measurements may be used quite accurately to predict finite-concentration behavior. The Flory–Huggins segment fraction model and the Flory–Prigogine equation of state model gave the best fits of the chromatography data, and the Flory–Huggins volume fraction model and the lattice fluid model with $1/r \neq 0$ gave the poorest fits.

Registry No. PBD, 9003-17-2; C_6H_6, 71-43-2; cyclohexane, 110-82-7.

References and Notes

(1) Glover, C. J.; Lau, W. R. *AIChE J.* **1983**, *29*, 73.
(2) Ruff, W. A.; Glover, C. J.; Watson, A. T.; Lau, W. W. R.; Holste, J. C. *AIChE J.* **1986**, *32*, 1954.
(3) Smisrød, O.; Guillet, J. E. *Macromolecules* **1969**, *2*, 272.
(4) Gray, D. G.; Guillet, J. E. *Macromolecules* **1970**, *4*, 129.
(5) Guillet, J. E.; Stein, A. N. *Macromolecules* **1970**, *3*, 102.
(6) Summers, W. R.; Tewari, Y. B.; Schreiber, H. P. *Macromolecules* **1972**, *5*, 12.
(7) Tewari, Y. B.; Schreiber, H. P. *Macromolecules* **1972**, *5*, 329.
(8) Schreiber, H. P.; Tewari, Y. B.; Patterson, D. *J. Polym. Sci., Polym. Phys. Ed.* **1973**, *11*, 15.
(9) Bonner, D. C. *J. Macromol. Sci.—Rev. Macromol. Chem.* **1975**, *C13*, 2.
(10) (a) Lichtenthaler, R. N.; Newman, R. D.; Prausnitz, J. M. *Macromolecules* **1973**, *6*, 650. (b) Lichtenthaler, R. N.; Prausnitz, J. M.; Su, C. S.: Schreiber, H. P.; Patterson, D. *Macromolecules* **1974**, *6*, 577. (c) Lichtenthaler, R. N.; Liu, D. D.; Prausnitz, J. M. *Macromolecules* **1974**, *7*, 565.
(11) (a) Chang, Y. H.; Bonner, D. C. *J. App. Polym. Sci. Polym. Phys. Ed.*, **1975**, *19*, 2439. (b) Chang, Y. H.; Bonner, D. C. *J. Appl. Polym. Sci., Polym. Phys. Ed.* **1975**, *19*, 2457.
(12) Sharma, S. C.; Lakhanpal, M. L. *J. Polym. Sci., Polym. Phys. Ed.*, **1983**, *21*, 353.
(13) Ashworth, A. J.; Chien, C. F.; Furio, D. L.; Hooker, D. M.; Kopečni, M. M.; Laub, R. J.; Price, G. J. *Macromolecules* **1984**, *17*, 1090.
(14) Tait, P. J. T.; Abushihada, A. M. *Polymer* **1977**, *18*, 810.
(15) Braun, J. M.; Guillet, J. E. *Macromolecules* **1975**, *8*, 557.
(16) Pawlisch, C. A. Ph. D. Dissertation, University of Massachussets, Amherst, MA, 1985.
(17) Ruff, W. A.; Glover, C. J.; Watson, A. T. *AIChE J.* **1986**, *32*, 1948.
(18) Lau, W. W. R. Master's Thesis, Texas A&M University, College Station, TX, 1980.
(19) Joffrion, L. L.; Glover, C. J. *Macromolecules* **1986**, *19*, 1710.
(20) Joffrion, L. L. Master's Thesis, Texas A&M University, College Station, TX, 1984.
(21) Ettre, L. S. *Open Tubular Columns in Gas Chromatography*; Plenum: New York, 1963.
(22) Flory, P. J. *J. Chem. Phys.* **1942**, *10*, 51.
(23) Huggins, M. L. *Ann. N. Y. Acad. Sci.* **1942**, *43*, 1.
(24) Flory, P. J. *J. Am. Chem. Soc.* **1965**, *87*, 1833.
(25) Prigogine, I., *The Molecular Theory of Solutions*; North-Holland: Amsterdam, 1957.
(26) Bonner, D. C.; Brockmeier, N. F. *Ind. Eng. Chem. Process Des. Dev.* **1977**, *16*, 80.
(27) (a) Sânchez, I. C.; Lacombe, R. H. *J. Phys. Chem.* **1976**, *80*, 2352. (b) Sânchez, I. C.; Lacombe, R. H. *Macromolecules* **1978**, *11*, 1145.
(28) Saeki, S.; Holste, J. C.; Bonner, D. C. *J. Polym. Sci., Polym. Phys. Ed.* **1982**, *20*, 793.
(29) Lau, W. R.; Glover, C. J. Holste, J. C. *J. Appl. Polym. Sci.* **1982**, *27*, 3067.
(30) Jessup, R. S. *J. Res. Natl. Bur. Stand.* **1958**, *60*, 47.