Vapor-Liquid Equilibria from Perturbation Gas Chromatography

Part II: Application to the Polybutadiene/Benzene/Cyclohexane Ternary System

This work brings together recent gas chromatography experiments and theory involving multiple sorbing species at finite concentration, and theories for multicomponent polymer solutions by means of the parameter estimation procedure of Part I. Results quantitatively describe the wide variation in peak retention times that are caused by phase equilibrium and chromatographic interference, the best solution models doing so to within or near experimental error. The chromatographic method is capable of detecting differences and peculiarities in the various polymer solution models in both the accuracy of the calculated retention times and the sensitivities of the calculations to the model parameters. Perturbation chromatography offers some unique capabilities for multicomponent vapor-liquid equilibrium determinations.

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Introduction

The technique of perturbation chromatography (alternatively called elution on a plateau, step-and-pulse, or inverse chromatography) as practiced in a variety of applications for determining the equilibrium sorption of a species at either infinite dilution or finite concentration, is quite straightforward (Eq. 2 of Part I, Ruff et al., 1986). The elution time gives the concentration derivative of the sorption isotherm at the steady state concentration. At infinite dilution this gives Henry's constant directly, while at finite concentrations the sorption isotherm can be calculated from a number of determinations over a range of concentration.

However, the situation for multiple sorbing species at finite concentration is considerably more involved (Glover and Lau, 1983). The complications, and a methodology for implementing the theory to extract multiple sorption equilibria are discussed in Part I.

Experimentally, perturbation chromatography has an advantage over standard static methods for multicomponent systems in that it does not require separate analyses to determine constituent concentrations, and experimental accuracy is maintained at infinite dilution. All equilibrium information is contained within the column response times, but a more complicated data reduction procedure results. A number of measurements and empirical or theoretical equilibrium models for each species are required before any equilibria can be determined.

This research presents the first detailed application of the theory of Valentin and Guiochon (1976) and Glover and Lau (1983) to a ternary system with chromatographic interference. Additionally, it adds to the limited multicomponent polymer solution data in the literature and compares theoretical polymer solution models in their ability to describe the ternary vapor-liquid equilibrium, as manifested in chromatographic retention times.

Specifically, vapor-liquid equilibria have been determined for the benzene-polybutadiene-cyclohexane ternary system. Equilibrium isotherms for the polymer solutions were calculated using multicomponent forms of the Flory-Huggins, Flory equation-of-state, and Sanchez-Lacombe solution theories, each optimized by selecting the three binary interaction parameters at each temperature that best fit the 30 different experimental retention times. The dependence of the retention times on composition in the multicomponent environment is explained very

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well by the combined chromatographic and polymer solution theories. Some differences between models are observed, and they suggest that chromatographic data are quite sensitive to model differences.

The experimental demonstration of perturbation gas chromatography for determining multicomponent vapor-liquid equilibria opens a new technique for engineering practice, although care in experimental design must be exercised to obtain reasonable certainty in estimates of parameters that represent interactions between minor components.

Polymer solutions are natural candidates for gas chromatography studies. Polymers generally are sufficiently nonvolatile to be used as the primary stationary phase component, and solvents will be sorbing species in the gas phase. Considerable experimental work has been done previously on polymer systems using perturbation gas chromatography for both infinite dilution and finite concentration of solvent.

Since the pioneer work of Smidsrod and Guillet (1969) on polymer systems, many researchers have used the technique of perturbation gas chromatography to determine the equilibrium of an infinitely dilute solvent with a polymer. Patterson et al. (1971) introduced the infinite-dilution weight-fraction activity coefficient to describe the thermodynamic properties of polymer-solvent systems. This concept circumvented the need to know accurately the polymer molecular weight and defined an activity coefficient that remained bounded as polymer molecular weight became unbounded. Newman and Prausnitz (1973) considered the experimental effects of gas flow rate, solvent sample size, and the influences of the solid support on the retention time of an infinitely dilute solvent. Chang and Bonner (1975a) discussed the effect of polymer degradation. Tait and Abushihada (1977) used experimental determinations to discuss the advantages of infinite-dilution gas chromatography over static vapor pressure measurements.

The extension of perturbation gas chromatography to finite solvent concentrations first was proposed by Guillet (1970). Brockmeier et al. (1972a,b; 1973) extended the experimental method to determine the thermodynamic properties for various binary solvent-polymer systems over a range of solvent concentrations. Data for other binary systems have been reported by Chang and Bonner (1975b) and Lau et al. (1982). Bonner and Brockmeier (1977), and Dinçer et al. (1979) have applied perturbation chromatography to the study of ternary solvent-polymer-solvent systems. Bonner and Brockmeier reported data for the case in which one of the solvents was at infinite dilution. Dinçer et al., working with the title system, presented finite concentration data that were correlated by using data from the respective binary pair systems. The chromatographic theory and the data reduction technique used in those publications, however, differ substantially from that presented in this work. Most notably, interference between species is neglected in the chromatographic relationships and the interaction parameters for the isotherm model are evaluated via single point determinations from the binary pair systems. Dondi et al. (1977a,b) describe a data reduction method for the theory of Valentin and Guiochon that is a parameter estimation procedure, and then compare eight different isotherm models in their ability to describe the experimental data. Their study, however, was for a binary system (benzene sorption on graphitized carbon black) and hence did not test the interference aspect of multicomponent chromatography. Comprehensive reviews by Guillet (1973), Bonner (1975), Gray (1977), and Conder and Young (1979) summarized more experimental work on gas chromatographic determinations of properties of polymers.

Solution Models

The chromatographic data of Lau (1980) are reduced to equilibrium sorption isotherms by estimating the fit parameters for an appropriate solution model. Polymer solution theories provide physically realistic models that describe the highly nonlinear isotherm behavior with a small number of adjustable-fit parameters, one to account for each binary pair interaction. In addition, some of these theories can be used to generate phase equilibrium data at solution compositions not studied experimentally, and to predict other thermodynamic behavior such as mixture miscibility limits; i.e., binodals, spinodals, and critical solution temperatures. The classical lattice theory of Flory (1942, 1953) and Huggins (1942); the equation-of-state theory of Flory (1965) and its simplification by Bonner and Prausnitz (1973), and Bonner and Brockmeier (1977); and the lattice fluid theory of Sanchez and Lacombe (1978) are compared as suitable isotherm models. Multicomponent forms of the model equations, mixture rules, and equations of state are summarized in Tables 1 and 2.

The Flory-Huggins theory was chosen because it represents the first qualitatively correct attempt to model polymer solution thermodynamics, and for its simplicity. This classical theory performs remarkably well despite its simplifications and is still widely applied today. Both volume fraction and segment fraction forms were used.

Three equation-of-state theories were used. The Flory (1965) theory, developed from the work of Prigogine (1957), represents the first serious improvement to the description of polymer solution thermodynamics through theoretical considerations; it has been applied extensively in the literature. Bonner and Prausnitz worked with a simplified Flory theory that avoided the use of segment-surface ratios and site fractions. Bonner and Brockmeier (1977) extended the theory to ternary systems. Finally, the recent theory of Sanchez and Lacombe (1978) was chosen for its enriched predictive capabilities based on a generalization of the original Flory-Huggins model.

Data

Chromatographic data

The chromatographic data used for isotherm calculations were those reported by Lau (1980). These data were obtained for the benzene-polybutadiene (PBD)-cyclohexane system at 333, 355, and 373 K. A complete description of the experimental apparatus, materials, and procedure used to obtain these data was published by Lau et al. (1982). The data of 355 K are presented in Table 3. Two of the experimental net retention times in this table differ from those reported by Lau (1980) as the result of a careful review of the original chromatograms.

For each temperature there are fifteen steady state compositions at which response times were determined. The first composition is infinite dilution in both solvents. The next eight are two sets of four compositions, each of which is infinite dilution in one of the solvents with the other maintained at various finite concentrations. The last six compositions have both solvents at finite concentrations.

At each composition the two retention times depend upon spe-

Table 1. Polymer Solution Model Equations

Model	Solution Activity ($\hat{a}_i^s$)
Flory-Huggins (VOL)*	$\Phi_i \exp\left[\sum_j\left(1-\frac{r_i}{r_j}\right)\Phi_j-\sum_{j=1}^{n-1}\sum_{k=j+1}^{n}\Phi_j\Phi_k\chi_{jk}\frac{r_i}{r_j}+\sum_j\Phi_j\chi_{ij}\right]$
Flory-Huggins (SEG)**	$\Psi_i \exp\left[\sum_j\left(1-\frac{r_i}{r_j}\right)\Psi_j-\sum_{j=1}^{n-1}\sum_{k=j+1}^{n}\Psi_j\Psi_k\chi_{jk}\frac{r_i}{r_j}+\sum_j\Psi_j\chi_{ij}\right]$
Flory EOS***	$\Psi_i \exp\left(\sum_j\left(1-\frac{r_i}{r_j}\right)\Psi_j+\frac{M_i v_{isp}^*}{RT}\left\{p_i^*\left[3\tilde{T}_i\ln\frac{\tilde{v}_i^{1/3}-1}{\tilde{v}^{1/3}-1}+\tilde{\rho}_i-\tilde{\rho}+\tilde{p}_i(\tilde{v}-\tilde{v}_i)\right]\right.\right.$ $\left.\left.-\tilde{\rho}\sum_{j=1}^{n-1}\sum_{k=j+1}^{n}\theta_j\frac{s_i}{s_j}X_{jk}\theta_k+\tilde{\rho}\sum_j\theta_jX_{ij}\right\}\right)$
Simplified Flory†	$\Psi_i \exp\left(\sum_j\left(1-\frac{r_i}{r_j}\right)\Psi_j+\frac{M_i v_{isp}^*}{RT}\left\{p_i^*\left[3\tilde{T}_i\ln\frac{\tilde{v}_i^{1/3}-1}{\tilde{v}^{1/3}-1}+\tilde{\rho}_i+\tilde{p}_i(\tilde{v}-\tilde{v}_i)\right]\right.\right.$ $\left.\left.+\tilde{\rho}\sum_j\sum_k\Psi_j\Psi_kp_{jk}^*-2\tilde{\rho}\sum_j\Psi_jp_{ji}^*\right\}\right)$
Sanchez-Lacombe‡	$\Psi_i \exp\left[\sum_j\left(1-\frac{r_i}{r_j}\right)\Psi_j+\frac{M_i v_{isp}^*}{RT}\left(p_i^*\{\tilde{\rho}_i-\tilde{\rho}+\tilde{p}_i(\tilde{v}-\tilde{v}_i)+\tilde{T}_i[(\tilde{v}-1)\ln(1-\tilde{\rho})\right.\right.$ $\left.\left.-(\tilde{v}_i-1)\ln(1-\tilde{\rho}_i)]\}-\frac{\tilde{\rho}}{2}\sum_j\sum_k\Psi_j\Psi_k\Delta p_{jk}^*+\tilde{\rho}\sum_j\Psi_j\Delta p_{ji}^*\right)+\ln\frac{\tilde{\rho}}{\tilde{\rho}_i}\right]$

*VOL = volume fraction model. $\chi_{ij}=\chi_{ji}(r_i/r_j)$; $r_i/r_j=M_iv_{isp}/M_jv_{jsp}$

**SEG = segment fraction model. $\chi_{ij}=\chi_{ji}(r_i/r_j)$; $r_i/r_j=M_iv_{isp}^*/M_jv_{jsp}^*$

***$X_{ij}=(s_i/s_j)X_{ji}$; $r_i/r_j=M_iv_{isp}^*/M_jv_{jsp}^*$; $\theta_j=\Psi_j/[\Sigma_k\Psi_k(s_k/s_j)]$

†$p_{ij}^*=p_{ji}^*$; $p_{ii}^*=p_i^*$, the pure-component value.

‡$\Delta p_{ij}^*=p_i^*+p_j^*-2p_{ij}^*$; $\Delta p_{ii}^*=0$; $r_i/r_j=M_iv_{isp}^*/M_jv_{jsp}^*$; Sanchez and Lacombe define a dimensionless parameter, $X_{ij}=\Delta p_{ij}^*/p_i^*\tilde{T}_i$

Summations are from 1 to n unless otherwise indicated.

cies interactions in solution and hence on solution theory binary interaction parameters. For the first composition, both solvents, being at infinite dilution, interact with only the polymer. Consequently, both retention times depend upon only one binary interaction parameter, the appropriate polymer-solvent parameter. For the next eight compositions, one of the solvents (the one that is at finite concentration) interacts only with the polymer, producing a retention time that depends upon only that one binary interaction parameter. The other solvent (the one at infinite dilution), however, interacts with both the polymer and the other solvent and consequently its retention time depends upon both polymer-solvent parameters and the solvent-solvent binary

Table 2. Mixture Rules and Equations of State for Polymer Solution Models

Model	Mixture Rules	Equation-of-State
Flory-Huggins (VOL, SEG)	None	None
Flory	$p^*=\sum_i\Psi_ip_i^*-\sum_{i=1}^{n-1}\sum_{j=i+1}^{n}\Psi_iX_{ij}\theta_j$ $T^*=p^*\Big/\left(\sum_i\Psi_ip_i^*/T_i^*\right)$	$\frac{\tilde{p}\tilde{v}}{\tilde{T}}=\frac{\tilde{v}^{1/3}}{\tilde{v}^{1/3}-1}-\frac{1}{\tilde{v}\tilde{T}}$
Simplified Flory	$p^*=\sum_i\sum_j\Psi_i\Psi_jp_{ij}^*$ $T^*=p^*\Big/\left(\sum_i\Psi_ip_i^*/T_i^*\right)$	(Same as Flory)
Sanchez-Lacombe	$p^*=\sum_i\Psi_ip_i^*-\sum_{j=1}^{n-1}\sum_{k=j+1}^{n}\Psi_j\Psi_k\Delta p_{jk}^*$ $T^*=p^*\sum_i\frac{\Psi_i^oT_i^*}{p_i^*}$ where $\Psi_i^o=\frac{\Psi_iP_i^*}{T_i^*}\sum_j\frac{\Psi_j^oT_j^*}{p_j^*}$ and $\frac{1}{r}=\sum_j\frac{\Psi_jp_j^*}{r_j^oT_j^*}\sum_k\frac{\Psi_k^oT_k^*}{p_k^*}$	$\tilde{\rho}^2+\tilde{p}+\tilde{T}\left[\ln(1-\tilde{\rho})+\left(1-\frac{1}{r}\right)\tilde{\rho}\right]=0$

Table 3. Experimental Data at 355 K

Data Point	Vapor-Phase Mole Fraction		Vapor Flow Rate µmol/s	Net Retention Time, s		Avg. Col. Pressure kPa
	Benzene	Cyclohex		Peak A	Peak B	
1	0.0000	0.0000	4.65	173(B)*	145(C)*	102.3
2	0.0959	0.0000	4.96	164(B)	148	101.7
3	0.2000	0.0000	4.96	163(B)	152	101.8
4	0.2959	0.0000	4.96	167(B)	159	101.9
5	0.4000	0.0000	5.54	156(B)	164	101.1
6	0.0000	0.0790	4.96	162	139(C)	101.7
7	0.0000	0.1646	4.96	167	144(C)	102.0
8	0.0000	0.2436	4.96	177	149(C)	101.2
9	0.0000	0.3680	4.96	190	150(C)	101.4
10	0.0959	0.0790	4.96	145	168	101.5
11	0.0959	0.1646	4.96	144	179	101.4
12	0.0959	0.2436	4.96	153	195	101.6
13	0.2000	0.0790	4.96	152	185	102.2
14	0.2000	0.1646	4.96	151	196	101.8
15	0.2959	0.0790	4.96	156	186	101.6

*(B) Benzene peak; (C) Cyclohexane peak.
Mass of PBD in column = 0.2283 g.

parameter. For the last six compositions, both retention times depend upon all three interaction parameters. Retention times that depend upon only one of the polymer-solvent binary interaction parameters and not the other and not upon solvent-solvent interactions are indicated with the appropriate solvent, B (benzene) or C (cyclohexane) in the tables.

At each of the fifteen compositions, peaks with the retention times shown may be produced by a variety of composition perturbations, and the observed effluent peak compositions vary accordingly. The characteristic times, however, are always the same. Figure 1 shows column responses to perturbations with three different species for compositions 1 and 8 at 355 K (Table 3). With all species at infinite dilution, each perturbation with a pure component produces a single response peak at a time that is characteristic of its own equilibrium with the polymer, Figure 1a. With cyclohexane at finite concentration, Figure 1b, a perturbation with cyclohexane again produces a single positive peak. A perturbation with either *n*-hexane or benzene, however, produces peaks for each of these components and also a second peak at the cyclohexane characteristic time. These secondary responses are the result of induced cyclohexane perturbations created by injecting another species at constant pressure into the finite-concentration cyclohexane carrier stream. At compositions 10 through 15, injecting either benzene or cyclohexane produces an induced peak and injecting *n*-hexane produces two induced peaks. These experimental observations are in complete accord with the multicomponent chromatographic theory.

Also in agreement with the theory is an initial shortening of the retention time-molar flow rate product (proportional to the retention volume) followed by a lengthening as concentration is increased from infinite dilution for a binary system. For sorption of a single species from a binary vapor phase this product, and hence the retention volume, is proportional to the product of the isotherm composition derivative and the mole fraction of the nonsorbing vapor-phase species. This mole fraction factor has been termed the sorption effect. Consequently, for polymer-solvent systems where the solvent sorption increases essentially exponentially with increasing concentration, the isotherm and vapor phase concentration work in opposite directions to effect changes in the retention time. As the vapor phase concentration of the sorbing species increases, the concentration of the nonsorbing species decreases (linearly) whereas the isotherm derivative increases essentially exponentially. As the concentration builds from infinite dilution in a series of experiments, then, the retention volume at first decreases but ultimately increases as

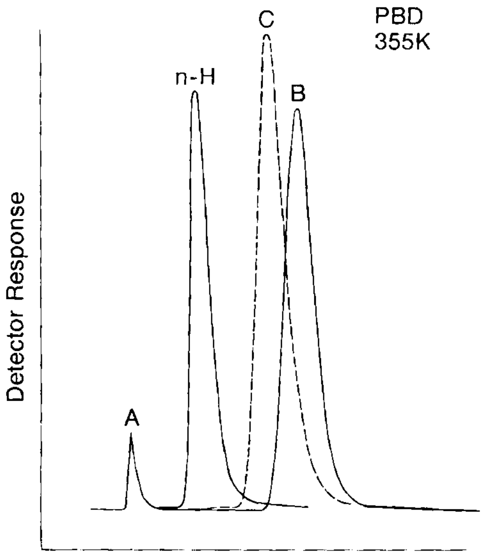

Figure 1a. Column response to perturbation using a helium carrier gas, 355 K.

A. Air
B. Benzene
C. Cyclohexane
n-H. *n*-Hexane

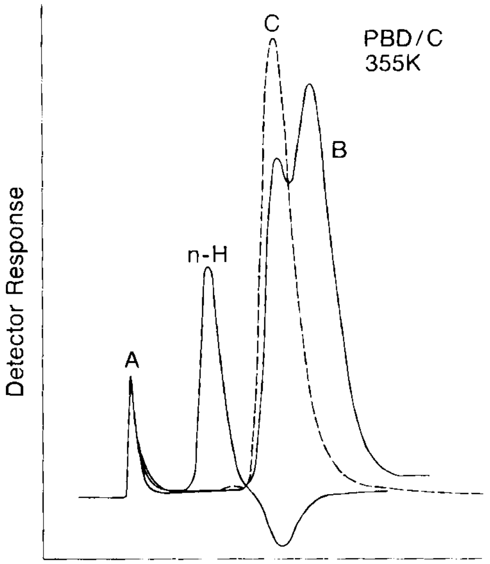

Figure 1b. Column response to perturbation using a helium-cyclohexane mixture carrier gas, 355 K.

A. Air
B. Benzene
C. Cyclohexane
n-H. *n*-Hexane

the isotherm derivative dominates the behavior. This phenomenon is suggested by the experimental data in Table 3 and is more obvious when the data at all three temperatures are reviewed.

Physical properties of the pure components

The Rackett equation (Smith and Van Ness, 1975), a generalized correlation requiring only critical constants, was used to estimate solvent densities at the three temperatures. Solvent vapor pressures were estimated using the Antoine equation. The experimentally reported density of 0.94 g/mL at 298 K for polybutadiene (PBD) was used for all models at all temperatures. The solvent critical properties, Antoine constants, and acentric factors were taken from Reid et al. (1977).

Characteristic parameters

Three characteristic equation-of-state parameters are required for each pure component for the Flory, simplified Flory, and lattice fluid models: characteristic specific volume, pressure, and temperature. These parameters are identical for the Flory and simplified Flory models since both obey the same equation of state. The Flory-Huggins segment fraction model requires only values of the characteristic specific volume. In accordance with literature, the characteristic volumes used for this lattice model were from the Flory equation-of-state theory.

The characteristic parameters of the solvents were obtained from Bonner and Prausnitz (1973) for the Flory model and from Sanchez and Lacombe (1976) for the lattice fluid model. The characteristic parameters of PBD were estimated from the data of Barlow (1978) using the procedure outlined by Bonner and Prausnitz (1973). This computational procedure need only be modified to reflect the Flory or lattice fluid equation of state. The resulting characteristic parameters are assumed to be independent of temperature and pressure over the range for which they are evaluated. Note, however, that their procedure cannot be applied to a low molecular weight solvent for the lattice fluid model because a corresponding-states principle is not satisfied. The characteristic equation-of-state parameters are compiled in Table 4.

Segment-surface ratios

Both the Flory and lattice fluid models allow for molecular contact dissimilarities between components. The latter implicitly accounts for surface area effects through the mixing rules (Sanchez and Lacombe, 1978), while the Flory theory introduces the correction explicitly through the segment-surface ratios s_i/s_j (Flory, 1965). Note that this extra computational degree of freedom was eliminated in the simplified Flory theory by Bonner and Prausnitz (1973), where equal contact areas for all segments in the mixture were assumed.

Therefore, the segment-surface ratios for the Flory model represent additional parameters that must be estimated. These ratios can be estimated from crystallographic or other geometric considerations (Eichinger and Flory, 1968; Pouchly and Patterson, 1976), or via the group contribution format of Bondi (1968). A third possible method considered here is from gas chromatographic data as an additional adjustable-fit parameter. The results are given in Table 5.

Table 4. Pure-Component Characteristic Parameters

Model and Component	v_{sp}^* cm^3/g	p^* MJ/m^3	T^* K
Flory EOS and Simplified Flory			
Benzene*	0.890	576	4780
Cyclohexane*	1.02	513	5060
Polybutadiene**	1.051	689	5170
Sanchez-Lacombe Lattice Fluid			
Benzene†	1.006	444	523
Cyclohexane†	1.109	383	497
Polybutadiene**	0.964	441	598

*Bonner and Prausnitz (1973)
**Estimated from PVT data of Barlow (1978)
†Sanchez and Lacombe (1976)

Table 5. Segment-Surface Ratios for Flory Theory

Method	s_B/s_{PBD}	s_C/s_{PBD}	s_B/s_C†
Geometric considerations*	0.99	0.93	1.06
Group contribution format**	0.96	0.96	1.01
Gas chromatography***	0.96	0.94	1.02

†$s_B/s_C = (s_B/s_{PBD})/(s_C/s_{PBD})$
*Delmas and De Saint-Romain (1974)
**Bondi (1968)
***This work

Results and Discussion

The data reduction methodology presented in Part I was used to obtain estimates of the binary interaction parameters. We assumed that the standard deviation of the error in determining the retention time was approximately proportional to the retention time and hence each residual was weighted by dividing by the experimental time.

The parameter values for each of the solution models and each temperature are given in Table 6. Confidence intervals for

Table 6. Estimated Interaction Parameters for Models

Model and Temp.	Interaction Parameters*		
	B-PBD	C-PBD	B-C
Flory-Huggins (VOL)			
333 K	0.23 (±0.05)	0.24 (±0.05)	0.29 (±0.06)
355 K	0.18 (±0.03)	0.15 (±0.02)	0.41 (±0.08)
373 K	0.13 (±0.04)	0.10 (±0.04)	0.49 (±0.16)
Flory-Huggins (SEG)			
333 K	0.46 (±0.06)	0.46 (±0.01)	0.30 (±0.05)
355 K	0.47 (±0.02)	0.43 (±0.02)	0.48 (±0.10)
373 K	0.46 (±0.03)	0.42 (±0.04)	0.61 (±0.20)
Flory EOS			
333 K	22.7 (±0.4)	18.6 (±0.5)	16 (±3)
355 K	25.6 (±0.9)	19.3 (±0.7)	28 (±6)
373 K	27.0 (±1.8)	20.2 (±2.1)	40 (±13)
Simplified Flory			
333 K	621.0 (±0.2)	591.0 (±0.3)	537 (±1)
355 K	619.7 (±0.5)	590.9 (±0.4)	530 (±3)
373 K	618.9 (±0.9)	590.6 (±1.0)	526 (±6)
Sanchez-Lacombe			
333 K	8.6 (±1.5)	5.9 (±1.0)	12 (±2)
355 K	7.8 (±1.2)	4.1 (±0.4)	18 (±4)
373 K	7.1 (±1.6)	3.2 (±1.5)	24 (±8)

*Parameters in MJ/m^3 except for FHVOL and FHSEG, which are dimensionless.

Numbers in parentheses are 90% confidence intervals.

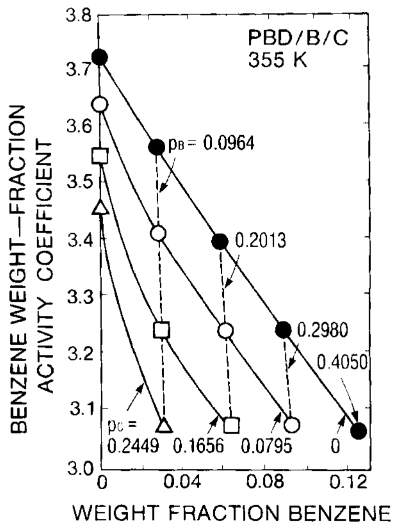

Figure 2. Benzene weight fraction activity coefficients at 355 K for fixed partial pressures of solvents.

——— Cyclohexane
– – – – Benzene

the estimated parameters, also shown in Table 6, were calculated by using an approximating linear expansion for each isotherm model (Draper and Smith, 1981, Ch. 10).

Calculated weight fraction isotherms for the two binary polymer-solvent systems are as previously reported (Lau et al., 1982). Weight fraction activity coefficients for benzene in the ternary system at 355 K are given in Figure 2, where curves are shown for values of the partial pressures of the solvents fixed at the actual experimental conditions. Results at the other temperatures and for cyclohexane appear in Ruff (1984). Adding either solvent to the solution enhances the sorption of the other, resulting in a reduced activity coefficient.

While the thermodynamic equilibrium results themselves are of value, our primary interest in this work was the demonstration of the chromatographic technique to evaluate ternary sorption, and comparisons of several solution models available for multicomponent polymer systems. Further discussion of the results focuses on these objectives.

Retention times

For the five model versions considered (two Flory-Huggins, two Flory equation-of-state, and one Sanchez-Lacombe lattice fluid), the agreement of the calculated net retention time with the experimental time (as a fraction of the experimental time) for each experimental condition at 355 K is shown in Table 7. Similar results were obtained at 333 and 373 K. As discussed above, data points 1–9 in this table represent compositions that maintain one solvent at infinite dilution and the other at various finite concentrations. From these compositions, two sets of net retention times, associated with the asterisked residuals in Table 7 and indicated by (B) or (C) in Table 3 were used to estimate the two solvent-polymer interaction parameters. These parameters were assumed to be independent of composition, an unnecessary constraint as far as the parameter estimation procedure is concerned, but one that worked very well for this system. The second response peak at each of these nine compositions arises from perturbing with the solvent that is maintained at infinite dilution. These times, in combination with data points 10–15—which are results for both solvents at finite concentration—involve solvent-solvent binary interactions and were used to estimate the solvent-solvent interaction parameter (also assumed independent of composition). An average residual value, reported as the root mean square for each binary parameter, is listed at the bottom of the table.

Table 7. Retention Time Residuals for Models, 355 K

			Weighted Residuals†									
Data Point No.	Exp. Net Ret. Time s		Flory-Huggins (VOL)		Flory-Huggins (SEG)		Flory EOS		Simplified Flory		Sanchez-Lacombe	
1	173*	145*	−0.05*	−0.01*	−0.03*	0.01*	−0.02*	0.01*	−0.03*	0.01*	−0.04*	0.00*
2	164*	148	−0.03*	−0.04	−0.02*	−0.03	−0.02*	−0.02	−0.02*	−0.03	−0.03*	−0.03
3	163*	152	0.01*	−0.00	0.01*	0.01	0.01*	0.01	0.01*	0.01	0.01*	0.01
4	167*	159	0.03*	0.03	0.02	0.03	0.02*	0.04	0.02*	0.03	0.03*	0.03
5	156*	164	0.03*	−0.04	−0.00*	−0.04	−0.00*	−0.04	−0.00*	−0.04	0.02*	−0.04
6	162	139*	−0.01	−0.01*	0.01	0.00*	0.01	0.01*	0.01	0.00*	−0.01	0.00*
7	167	144*	0.01	−0.01*	0.02	−0.01*	0.03	−0.01*	0.02	−0.01*	0.01	−0.01*
8	177	149*	−0.01	−0.02*	0.00	−0.03*	0.00	−0.03*	0.00	−0.03*	−0.01	−0.03*
9	190	150*	0.01	0.04*	0.02	0.02*	0.02	0.01*	0.01	0.02*	0.01	0.03*
10	145	168	−0.01	−0.00	−0.00	0.01	0.00	0.01	−0.00	0.01	0.00	0.00
11	144	179	0.02	−0.01	0.02	−0.00	0.02	−0.00	0.02	−0.00	0.02	−0.01
12	153	195	−0.01	−0.03	−0.02	−0.02	−0.03	−0.02	−0.02	−0.02	−0.02	−0.03
13	152	185	0.00	−0.03	−0.00	−0.02	−0.00	−0.02	−0.00	−0.02	0.00	−0.02
14	151	196	0.02	−0.02	0.01	−0.02	0.01	−0.02	0.01	−0.02	0.01	−0.01
15	156	186	−0.01	0.03	−0.00	0.03	−0.00	0.03	−0.00	0.03	0.01	0.03
			Root Mean Square of Weighted Residuals for Each Interaction Pair.									
Benzene-polybutadiene			0.0324		0.0180		0.0173		0.0192		0.0275	
Cyclohexane-polybutadiene			0.0223		0.0159		0.0159		0.0159		0.0171	
Benzene-cyclohexane			0.0207		0.0196		0.0197		0.0199		0.0192	

†Weighted residual = $(t_{calc} - t_{exp})/t_{exp}$

*Residuals for binary compositions, not used for ternary optimization

Considering the wide range of experimental retention times and the variation of composition, all five of the solution theories did quite well at reproducing the experimental retention times at all three temperatures. The worst multiple correlation coefficient was 0.98 for each parameter of the Flory-Huggins volume fraction model at the lowest temperature. The agreement for all but this volume fraction model and the lattice fluid model is especially good, generally producing agreement with retention times that approaches the experimental error of about 3%. One retention time at 333 K is not described well by any model, having a residual of about 10%. Most likely this point is not reliable, considering the uniformly good agreement otherwise. The excellent agreement between experiment and theory provides strong support first for the correctness of the multicomponent perturbation chromatographic theory and its experimental implementation, and second, for the applicability of the solution models for ternary VLE calculations, at least for this system.

Isotherms

Even though the models all do quite well in an absolute sense, there are some readily discernible differences between them. Most notably, the Flory-Huggins volume fraction model and the Sanchez-Lacombe model do a poorer job of reproducing the experimental retention times, as noted above. These differences are somewhat less noticeable when the isotherms rather than the retention times are compared, either as dry-basis (moles of sorbed solvent per mass of dry polymer) or weight fraction values. Calculations show that the sensitivity of these values to the model parameters is somewhat less than the sensitivity of the retention times, apparently due to the fact that the times are related to the isotherm derivatives rather than to the isotherms directly. This suggests that the chromatographic technique offers some inherent advantages for model discrimination and accurate parameter estimation over static methods, even for binary measurements at finite concentrations, other factors being equal.

Observations on the parameters

The confidence intervals for the parameters shown in Table 6 in general depend upon both the quality of the fit and the sensitivity of the model to the parameter. The effects of these two factors are not equal for the two kinds of parameters, however. The polymer-solvent parameter estimates are determined with reasonable certainty and show some fairly mild deterioration with increasing temperature. In this case, the sensitivity of the model to the parameters, even at infinite dilution in solvent, is quite good since the concentration of one of the species, the polymer, is high. Furthermore, deterioration with temperature is primarily the result of somewhat poorer fits rather than decreasing sensitivity. The solvent-solvent parameter, however, generally is determined with somewhat less certainty than the polymer-solvent parameters and exhibits a much more significant deterioration with temperature. In this case, both effects are primarily the result of the extremely low sensitivity of the models to this parameter when the concentrations of both solvent species are low. Solvent-solvent parameter confidence intervals can be improved by using higher solvent partial pressures.

These parameter confidence intervals serve as additional criteria for comparing the various models for VLE calculations, apart from the criterion of residual comparisons. For example, comparing the Flory EOS model with the simplified version, which is simply a different form of the same equation with all segment-surface ratios equal to unity, we see that the parameter for the latter case must be known much more precisely (as a percent of the value of the parameter) than for the former. This we consider to be a disadvantage of this model and we would choose to simplify the Flory equation, if that is desirable, by setting the segment-surface ratios to unity without changing the form of the equation. The lattice fluid model of Sanchez and Lacombe, although not as good at modeling the data compared to the Flory model, has a somewhat larger range of the parameter (as a percentage). That is, there is more room for error in choosing the Sanchez-Lacombe parameter. This we view as an advantage. The Flory-Huggins segment fraction model is clearly superior to the volume fraction model in its ability to model the retention times with no significant effects on the parameter sensitivity.

The sensitivity of a model to the parameters is determined by the extent to which the model is truly predictive. The larger the fraction of the activity coefficient that is calculated by the terms not directly dependent upon the parameters, the less sensitive the model is to the parameters. For instance, both the Flory-Huggins segment fraction model and the Flory EOS model calculate the same segment fractions and hence the same combinatorial contribution to the activity. However, the Flory model calculates some of the noncombinatorial part of the activity from the pure-component properties, which are known, and from the mixture average properties, which are not strongly dependent upon the parameters. Hence, the contributions of the parameters are smaller and the sensitivity of the model to the parameters is smaller. The Sanchez-Lacombe model accounts for an even larger fraction of the activity coefficient with combinatorial contributions.

Temperature trends in the parameters are noted in the values of the optimum parameters, but they must be considered in light of the parameter ranges discussed above. The mild trends in the polymer-solvent parameters seen in some cases may be real, as well as those in the solvent-solvent parameters. However, the solvent-solvent parameter trend obtained from this work is actually opposite that determined from independent benzene-cyclohexane VLE data, Table 8, although the actual values are not unreasonable, especially at the lower temperature considering the insensitivities of the gas chromatography estimates. The values of the benzene-cyclohexane parameter determined from the binary VLE could be used *a priori* to obtain very reasonable estimates of the ternary VLE. More precise experiments are

Table 8. Estimated Benzene-Cyclohexane Interaction Parameters from Binary Solvent VLE Data

	Temperature, K		
Model†	333*	343**	355***
F-H(VOL)	0.377	0.334	0.192
F-H(SEG)	0.378	0.335	0.196
Flory EOS	19.8	18.1	10.6
Simp. Flory	535	536	539
S-L	15.9	14.7	8.7

†Parameters in MJ/m^3 except for Flory-Huggins (VOL) and Flory-Huggins (SEG), which are dimensionless.
*Boublik (1963)
**Scatchard et al. (1939)
***Harrison and Berg (1946)

required to evaluate further the dependence of the parameters on temperature.

Effect of segment-surface ratio

The ternary equations for the Flory EOS model contain three segment-surface ratios, s_i/s_j, which must be estimated. These ratios, which quantify the molecular surface area to volume ratio of component i to that of component j, reflect the relative number of contact sites available for interaction between the components. The results of three alternative methods, i.e., geometric considerations, Bondi's (1968) correlations, and gas chromatography, all agree to within about 3% for the polymer-solvent ratios and 5% for the benzene to cyclohexane ratio, Table 5.

Each solvent-polymer ratio determined in this work was evaluated as that ratio which produced the minimum in the fit standard deviation. Then, the optimal solvent-solvent ratio was calculated as the ratio of the two solvent-polymer ratios. Note that ternary data were not used for these determinations.

For increasing temperature, the predicted isotherms became less sensitive to the solvent-polymer segment-surface ratio, as indicated by a broadening range of ratios which resulted in the same minimum in standard deviation. At the lowest temperature of 333 K, however, the effects of the ratio were more pronounced and it is the values at this temperature that are reported.

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Notation

$\hat{a}_i^s$ = activity of component i in stationary-phase solution
g = dry base sorption, moles sorbed per mass of dry polymer
M = molecular mass
n = total number of components in stationary phase
p = absolute pressure
$\tilde{p}$ = reduced pressure, $\tilde{p} = p/p^*$; $\tilde{p}_i^*$ for component i in a mixture
p^* = characteristic pressure; $\tilde{p}_i^*$ for component i in a mixture
p_{ij}^* = binary interaction parameter for simplified Flory model
Δp_{ij}^* = binary interaction parameter for lattice fluid model
R = universal gas constant
r = mixture average segments per molecule
r_i = number of segments per molecule for component i in mixture, Flory and Sanchez-Lacombe models, or for pure component i, Flory model
r_i° = number of segments per molecule for pure component i, lattice fluid model
s = number of intermolecular contact sites per segment, Flory model
T = absolute temperature
$\tilde{T}$ = reduced temperature, $\tilde{T} = T/T^*$; $\tilde{T}_i = T/T_i^*$ for component i in a mixture
T^* = characteristic temperature; T_i^* for component i in a mixture
t_r = net retention time of peak
v_{sp} = specific volume
$\tilde{v}$ = reduced volume, $\tilde{v} = v/v^*$; $\tilde{v}_i^* = v_i/v_i^* = v_{isp}/v_{isp}^*$ for component i
v^* = characteristic close-packed volume per segment
v_{sp}^* = characteristic close-packed volume per unit mass
w_i = stationary phase weight fraction
X_{ij} = binary interaction parameter for Flory model

Greek letters

θ_i = site fraction, Flory model
$\tilde{\rho}$ = reduced density, $\tilde{\rho} = 1/\tilde{v}$; $\tilde{\rho}_i = 1/\tilde{v}_i$ for component i
Φ_i = volume fraction
χ_{ij} = binary interaction parameter for Flory-Huggins models
Ψ_i = segment fraction

Subscripts

$i, j, \ldots$ = species $i, j, \ldots$
sp = per unit mass
B = benzene
C = cyclohexane
PBD = polybutadiene
calc = calculated using a solution model
exp = experimental

Literature cited

Barlow, J. W., "Measurement of the PVT Behavior of cis-1,4-Polybutadiene," *Polym. Eng. Sci.*, **18**, 238 (1978).

Bondi, A. A., *Physical Properties of Molecular Crystals, Liquids, and Glasses*, Wiley, New York (1968).

Bonner, D. C., "Vapor-Liquid Equilibria in Concentrated Polymer Solutions," *J. Macromol. Sci. Chem.*, **C13**, 263 (1975).

Bonner, D. C., and N. F. Brockmeier, "Infinite-Dilution Activity Coefficients of Ethylene in Solvent–High-density Polyethylene Mixtures," *Ind. Eng. Chem. Process Des. Dev.*, **16**, 180 (1977).

Bonner, D. C., and J. M. Prausnitz, "Vapor-Liquid Equilibrium Calculations for Concentrated Polymer Solutions," *AIChE J.*, **19**, 943 (1973).

Boublik, T., "An Estimate of Limiting Values of Relative Volatility from Help of Theorem of Corresponding States. II: Binary Systems of Tetrachloromethane, Benzene, and Cyclohexane," *Coll. Czech. Chem. Comm.*, **28**, 1771 (1963).

Brockmeier, N. F., R. W. McCoy, and J. A. Meyer, "Gas Chromatographic Determination of Thermodynamic Properties of Polymer Solutions," *Macromol.*, **5**, 130 (1972a).

———, "Gas Chromatographic Determination of Thermodynamic Properties of Polymer Solutions. I: Amorphous Polymer Systems," *Macromol.*, **5**, 464 (1972b).

———, "Gas Chromatographic Determination of Thermodynamic Properties of Polymer Solutions. II: Semicrystalline Polymer Systems," *Macromol.*, **6**, 176 (1973).

Chang, Y. H., and D. C. Bonner, "Sorption of Solutes by Poly(ethylene Oxide). I: Infinite-Dilution Studies," *J. Appl. Polym. Sci.*, **19**, 2439 (1975a).

———, "Sorption of Solutes by Poly(ethylene Oxide). II: Benzene at Finite Concentrations," *J. Appl. Polym. Sci.*, **19**, 2457 (1975b).

Conder, J. R., and C. L. Young, *Physicochemical Measurement by Gas Chromatography*, Wiley, New York (1979).

Delmas, G., and P. De Saint-Romain, "Upper and Lower Critical Solution Temperatures in Polybutadiene-Alkane Systems. The Effect of the Surface-to-Volume Ratio of the Polymer," *Eur. Polymer J.*, **10**, 1133 (1974).

Dinçer, S., D. C. Bonner, and R. A. Elefritz, "Vapor-Liquid Equilibria in the Benzene-Polybutadiene-Cyclohexane System," *Ind. Eng. Chem. Fund.*, **18**, 54 (1979).

Dondi, F., M.-F. Gonnord, and G. Guichon, "Chromatographic Determination of Gas-Solid Adsorption Isotherms by the Step-and-Pulse Method. I: Apparatus and Data Processing," *J. Colloid Interf. Sci.*, **62**, 303 (1977a).

———, "Chromatographic Determination of Gas-Solid Adsorption Isotherms by the Step-and-Pulse Method. II: Choice of a Model for the Adsorption Isotherm of Benzene and Cyclohexane on Graphitized Carbon Black," *J. Colloid Interf. Sci.*, **62**, 316 (1977b).

Draper, N. R., and H. Smith, *Applied Regression Analysis*, 2nd ed., Wiley, New York (1981).

Eichinger, B. E., and P. J. Flory, "Thermodynamics of Polymer Solutions. 1: Natural Rubber and Benzene," *Trans. Faraday. Soc.*, **64**, 2035 (1968).

Flory, P. J., "Thermodynamics of High Polymer Solutions," *J. Chem. Phys.*, **10**, 51 (1942).

———, *Principles of Polymer Chemistry*, Cornell U. Press, Ithaca, NY (1953).

———, "Statistical Thermodynamics of Liquid Mixtures," *J. Am. Chem. Soc.*, **87**, 1833 (1965).

Glover, C. J., and W. R. Lau, "Determination of Multicomponent Sorption Equilibria Using Perturbation Gas Chromatography," *AIChE J.*, **29**, 73 (1983).

Gray, D. G., "Gas Chromatographic Measurements of Polymer Structure and Interactions," *Prog. Polym. Sci.*, **5**, 1 (1977).

Guillet, J. E., "Molecular Probes in the Study of Polymer Structure," *J. Macromol. Sci. Chem.*, **A4**, 1669 (1970).

———, *Advances in Analytical Chemistry and Instrumentation,* Wiley, New York **11**, Ch. 5 (1973).

Harrison, J. M., and L. Berg, "Vapor-Liquid Equilibria of Binary Hydrocarbon Systems," *Ind. Eng. Chem.*, **38**, 117 (1946).

Huggins, M. L., "Thermodynamic Properties of Solutions of Long-Chain Compounds," *Ann. NY Acad. Sci.*, **43**, 1 (1942).

Lau, W. W. R., "Determination of Phase Equilibria for Binary Polybutadiene/Benzene and Polybutadiene/Cyclohexane/Polybutadiene Systems at 333, 355, and 373 K," M. S. Thesis, Texas A&M Univ. College Station, TX (1980).

Lau, W. R., C. J. Glover, and J. C. Holste, "Vapor-Liquid Equilibria for Benzene/Polybutadiene and Cyclohexane/Polybutadiene Systems at 333, 355, and 373K Using Gas Chromatography," *J. Appl. Polym. Sci.*, **27**, 3067 (1982).

Newman, R. D., and J. M. Prausnitz, "Thermodynamics of Concentrated Polymer Solutions Containing Polyethylene, Polyisobutylene, and Copolymers of Ethylene with Vinyl Acetate Propylene," *AIChE J.*, **19**, 704 (1973).

Patterson, D., Y. Tewari, H. P. Schreiber, and J. E. Guillet, "Application of Gas-Liquid Chromatography to the Thermodynamics of Polymer Solutions," *Macromol.*, **4**, 356 (1971).

Pouchly, J., and D. Patterson, "Polymers in Mixed Solvents," *Macromol.*, **9**, 574 (1976).

Prigogine, I., *The Molecular Theory of Solutions*, North-Holland, Amsterdam (1957).

Reid, R. C., J. M. Prausnitz, and T. K. Sherwood, *The Properties of Gases and Liquids*, McGraw-Hill, New York (1977).

Ruff, W. A., "Reduction of Perturbation Gas Chromatographic Data to Equilibrium Sorption Isotherms with Application to the Ternary Benzene/Polybutadiene/Cyclohexane System," M. S. Thesis, Texas A&M Univ., College Station, TX (1984).

Ruff, W. A., C. J. Glover, and A. T. Watson, "Vapor-Liquid Equilibria from Perturbation Gas Chromatography. I: Multicomponent Parameter Estimation," *AIChE J.*, **32**, 1948 (Dec., 1986).

Sanchez, I. C., and R. H. Lacombe, "An Elementary Molecular Theory of Classical Fluids. Pure Fluids," *J. Phys. Chem.*, **80**, 2352 (1976).

———, "Statistical Thermodynamics of Polymer Solutions," *Macromol.*, **11**, 1145 (1978).

Scatchard, G., S. E. Wood, and J. M. Mochel, "Vapor-Liquid Equilibrium. III: Benzene-Cyclohexane Mixtures," *J. Phys. Chem.*, **43**, 119 (1939).

Smidsrod, O., and J. E. Guillet, "Study of Polymer-Solute Interactions by Gas Chromatography," *Macromol.*, **2**, 272 (1969).

Smith, J. M., and H. C. Van Ness, *Introduction to Chemical Engineering Thermodynamics*, 3rd ed., McGraw-Hill, New York (1975).

Tait, P. J. T., and A. M. Abushihada, "Comparative Studies on the Use of Gas Chromatographic and Vapor Pressure Techniques for the Determination of the Interaction Energy Parameter," *Polymer*, **18**, 810 (1977).

Valentin, P., and G. Guiochon, "Determination of Gas-Liquid and Gas-Solid Equilibrium Isotherms by Chromatography. I: Theory of the Step-and-Pulse Method," *J. Chromat. Sci.*, **14**, 56 (1976).

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