gions from nuclei which are randomly positioned in space and time.

A plot of $[r(K)/K^2]$ *vs.* K^2 should be linear with a slope of $-2M_K$ and an intercept at $K^2 = 0$ of $2M_K K_c^2$ (see eq 10). Figure 4 shows that experiment confirms this prediction. The scatter in the points is due to unavoidable variations in the twelve different 1% agarose solutions which were used to collect the data.

The least-squares fit shown in Figure 4 yields $M_K = 4.62 \times 10^{-20}$ cm^4/sec and $K_c^2 = 8.08 \times 10^8$ cm^{-2}. Van Aartsen *et al.*[11-13] have confirmed the occurrence of spinodal decomposition during a liquid-liquid phase separation in a polymer system. They show that K_c is an increasing function of $T_s - T$ where T_s is the spinodal temperature for a given concentration and T the quenching temperature. If we associate the locations of the maxima in the Rayleigh ratios in Figure 1 with the magnitudes of $K_m = K_c/(2)^{1/2}$ we are thus able to account for the observed temperature shift in terms of the spinodal mechanism. We can then also conclude that the absence of a maximum in the upper curve in Figure 1 is the result of quenching to a temperature above T_s. This conclusion is supported by the absence of an exponential growth region in Figure 2b.

The increased broadening of the maxima in Figure 1 at lower quenching temperatures is most likely a result of spinodal decomposition occurring while the sample is cooling down to the final quench temperature. Since the wave number of the fastest growing Fourier component of the fluctuations increases with decreasing temperature, the resultant maxima will be broadened at lower quench temperatures.

Finally we note that, while we have confirmed the occurrence of spinodal decomposition in the agarose system by observing its initial stages, it is the entire mechanism that is responsible for the final structure observed in Figure 1. Studies of the later stages of spinodal decomposition[14] indicate that a coarsening reaction sets in resulting in an increase in the spacing between regions of high concentration. And indeed, we find that the maxima in Figure 1 do occur at lower K values than the K_m values obtained from the exponential growth during the initial stages.

We have seen that in order for spinodal decomposition to occur, the stage of phase separation proceeding by nucleation and growth must be bypassed. This is possible if the rate of material diffusion is slow relative to the rate at which the quenching temperature is established in a sample. This condition is likely to prevail in polymer systems where the viscosity is high. Our study of the agarose system may thus be viewed as an example of the significant control which the mechanism of spinodal decomposition can exert over the final morphology of polymer systems.

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Thermodynamic Interactions in Polymer Systems by Gas-Liquid Chromatography. IV. Interactions between Components in a Mixed Stationary Phase

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ABSTRACT: The glc method of determining specific retention times of a vapor-phase probe in a polymeric stationary phase is used to measure the thermodynamic interaction between the components (2,3) in a binary stationary phase. The Flory-Huggins interaction parameter χ_{23} may be obtained. An application of the more recent Prigogine-Flory theory is made to the ternary probe-stationary-phase system, leading to the X_{23} parameter. A variety of probes, mainly aliphatic hydrocarbons, are used with pure *n*-tetracosane (*n*-$\mathrm{C_{24}}$), di-*n*-octyl phthalate (DOP), and poly(dimethylsiloxane) (PDMS) stationary phases. Binary stationary phases are represented by *n*-$\mathrm{C_2}$DDOP and *n*-$\mathrm{C_{24}}$-PDMS. Self-consistent χ and X parameters are obtained for interactions between the probes and the pure stationary phases, and also those within the binary stationary phases.

The application of gas-liquid chromatography (glc) to the determination of thermodynamic interactions in systems with a polymeric component in the stationary phase has been the subject of several recent publications.[3-5] In our earlier work, we have obtained specific retention volumes (V_g^0) for hydrocarbon gas-phase components (probes) at high dilution in the polymer. This led to the evaluation of thermodynamic interaction parameters (χ, χ^*) at the limit of the concentration range. The work of Brockmeier and coworkers[6] has extended the capability of the glc approach to finite concentration of the volatile phase, so that useful thermodynamic information may now be obtained over a broad range of polymer-probe concentrations. To date, limits of accuracy of thermodynamic data obtained from the glc results have not been established unequivocally.[7] It is clear, however, that glc is a most rapid and convenient method to obtain thermodynamic data for polymer systems. In the work being presented here, we have extended the glc method, using probes to measure the interaction between two nonvolatile

Table I
Forms of Glc Eq 1 for Binary Stationary Phases

Left-Hand Side Contains	Right-Hand Side Contains
$(a_1/N_{1,\text{liq}})^\infty$	W_{liq}
$\gamma_x^\infty = (a_1/x_{1,\text{liq}})^\infty$	$x_2M_2 + x_3M_3$
$\gamma_w^\infty = (a_1/w_{1,\text{liq}})^\infty$	M_1
$\gamma_\varphi^\infty = (a_1/\varphi_{1,\text{liq}})^\infty$	$V_1/(w_2v_{2,\text{sp}} + w_3v_{3,\text{sp}})$

and nonassociated liquids in a binary stationary phase. (Littlewood and Willmott,[8] for instance, have considered the case of associated liquids.) A measure of the interaction of two polymers may be obtained from phase separation in the mixed-polymer system. The interaction is also accessible through the osmotic pressure of a dilute solution of the two polymers. However, the glc approach may well represent the most convenient and generally applicable route to interaction data for such systems.

It is well known that the interaction between the components of a binary system affects their overall affinity for another component. Usually, as in the cosolvency phenomenon, the binary system is composed of two low molecular weight solvents. Their affinity for a polymeric component present in low concentration may be measured through the polymer solubility, intrinsic viscosity or heat of solution. In the present case, it is the gas-phase probe which is dissolved at low concentration in a mixture of high molecular weight substances in the stationary phase, and it is their interaction which affects the affinity of the stationary phase for the probe. Our ultimate interest in studying the mixed columns is to generate data for systems with both basic and applied interest. The present data are for tetracosane (n-C_{24}), poly(dimethylsiloxane) (PDMS), and di-*n*-octyl phthalate (DOP) as stationary-phase constituents with various aliphatic and aromatic hydrocarbon probes. This choice was based on the availability of thermodynamic interaction data for probes with n-C_{24} and PDMS. Results will soon be reported for a system of practical interest, poly(vinyl chloride)–DOP.

Glc Equations for a Mixed Stationary Phase (2–3) and Probe (1)

The basic glc equation for the partition of molecules of 1 between the gas and liquid (stationary) phases is[9]

$$N_{1,\text{gas}}/N_{1,\text{liq}} = V_{\text{N}}^\circ/V_{\text{liq}}$$

Here V_N^0 is the net retention volume at zero pressure, the N_1 are numbers of molecules and V_{liq} is the volume of the liquid phase which may contain any number of components. Bringing in the activity, a_1, of component 1 and the specific retention volume V_g^0 corrected to 0°, one has at high dilution of component 1

$$\ln\left[\left(\frac{a_1}{N_{1,\text{liq}}}\right)^\infty\right] = \ln\left[\frac{(273.2R/P_1^\circ V_g^\circ)}{W_{\text{liq}}}\right] - \frac{P_1^\circ}{RT}(B_{11} - V_1) \tag{1}$$

Here W_{liq} is the weight of the liquid phase and the other symbols have their usual significance. However, eq 2 is often modified to replace the fundamental ratio $(a_1/N_{1,\text{liq}})^\infty$ by the activity coefficient $\gamma_x^\infty = (a_1/x_{1,\text{liq}})^\infty$. Then, for a liquid phase containing a single component, W_{liq} is replaced in eq 1 by the molecular weight M_2. For a binary 2–3 liquid phase, M_2 becomes $x_2M_2 + x_3M_3$, as indicated in Table I. If either 2 or 3 is a polymer, the relevant M becomes the number-average molecular weight, which may be difficult to evaluate precisely. Furthermore, as M_2 or M_3 tends to infinity, $\ln \gamma_x^\infty$ tends to $-\infty$. This shows that the mole fraction is an unsuitable concentration variable for polymer systems, as noted in our discussion of single component systems.[3a] Other concentration variables than x have been suggested in order to define activity coefficients, *e.g.*, the weight fraction w or volume fraction φ. The relevant changes in eq 1 are listed in Table I. In the case of γ_φ^∞, v_{sp} is the specific volume of component 2 or 3 and is still defined unambiguously.

Thermodynamic Equations for a Mixed Stationary Phase

Theory of Flory-Huggins Type. The Flory-Huggins theory of polymer solution thermodynamics, as applied to three components by Tompa[10] and Scott[11] gives an expression for the chemical potential of the probe (1) in the mixed stationary phase (2–3) in terms of volume fractions, φ (see eq 7.22 of ref 10 and eq 9 of ref 11). At infinite dilution of 1, $\varphi_1 \rightarrow 0$, and introducing a_1, we have

$$\ln (a_1/\varphi_1)^\infty = [1 - (r_1/r_2)]\varphi_2 + [1 - (r_1/r_3)]\varphi_3 +$$

combinatorial term

$$[\chi_{12}\varphi_2 + \chi_{13}\varphi_3 - r_1(\chi_{23}/r_2)\varphi_2\varphi_3] = \chi_{1(23)} \tag{2}$$

noncombinatorial term

Here the r_i are numbers of segments in the components, and in the case of polydispersity are to be construed as number-average quantities, with $r_i = V_i/v$, V_i and v being the molar volumes of respectively the component i and a segment chosen of equal volume for all components. The χ_{ij} are the traditional Flory interaction parameters defined by

$$(\chi_{ij})_{\text{Flory}} = r_i z \Delta w_{ij}/kT \tag{3}$$

with Δw_{ij} being the interchange free energy for a pair of segments. In this definition, χ_{ij} is normalized to a unit of size equal to r_i segments, *i.e.*, a molecule of component i. Consequently, $(\chi_{ij})_{\text{Flory}} \neq (\chi_{ji})_{\text{Flory}}$. On the other hand, the χ_{ij} used by Tompa is normalized to a single segment of components i or j, so that it is symmetrical and

$$(\chi_{ij})_{\text{Tompa}} = z\Delta w_{ij}/kT = (\chi_{ij})_{\text{Flory}}/r_i \tag{4a}$$

The Tompa quantity and w_{ij} both have the disadvantage of depending on the essentially arbitrary choice of what volume (v) of component constitutes a segment. Some workers[12] have normalized the interaction to unit volume of a component, introducing the ratios

$$\alpha_{ij} \equiv (\chi_{ij})_{\text{Flory}}/V_i \equiv (\chi_{ij})_{\text{Tompa}}/v \tag{4b}$$

In the present case, if components 2 and 3 are polymers, $(\chi_{23})_{\text{Flory}}$ becomes inconveniently large since it is proportional to V_2. For this interaction at least, it is advantageous to deal with χ_{23}/V_2 or α_{23}. Writing eq 2 in terms of these ratios, combining eq 2 with eq 1 and using γ_φ^∞ in Table I, we have

$$\left(\frac{\mu_1 - \mu_0}{RT}\right)_{\text{noncomb}} = \chi_{1(23)} = \left[\left(\frac{\chi_{12}}{V_1}\right)\varphi_2 + \left(\frac{\chi_{13}}{V_1}\right)\varphi_3 - \left(\frac{\chi_{23}}{V_2}\right)\varphi_2\varphi_3\right]V_1 = \ln\frac{273.2R(w_2v_{2,\text{sp}} + w_3v_{3,\text{sp}})}{P_1^\circ V_g^\circ V_1} - \left(1 - \frac{V_1}{V_2}\right)\varphi_2 - \left(1 - \frac{V_1}{V_3}\right)\varphi_3 - \frac{P_1^\circ}{RT}(B_{11} - V_1) \tag{5}$$

As is intuitively evident, a positive value of χ_{23} lowers the overall $\chi_{1(23)}$ for interaction between the probe and the mixed column. It is clear that when the stationary phase contains a single component, one recovers eq 2 of ref 3b

Table II
Column Description

Stationary Phase	Wt Support in Column (g)	Wt % Stationary Phase/Support	Wt Composition Stationary Phase		
			n-C$_{24}$	DOP	PDMS(L)
n-C$_{24}$	7.4707	12.00	1.000		
DOP	4.4896	10.65		1.000	
PDMS(L)	5.1373	10.22			1.000
n-C$_{24}$–DOP	5.7416	17.69	0.405	0.595	
n-C$_{24}$–PDMS(L)	5.6515	13.93	0.440		0.560

used previously. Experiments with the mixed and single component stationary phases will allow χ_{12}/V_1, χ_{13}/V_1, and χ_{23}/V_2 to be determined. These ratios, *i.e.*, the α_{ij}, are symmetrical and should be characteristic only of the chemical nature of molecules i and j, and independent of their chain lengths. Thus, we might expect that two n-alkanes, components 1 of different chain length, will have equal χ_{12}/V_1 values for interaction with a component 2 of some other chemical nature, *e.g.*, DOP or PDMS.

Recent Theories of Corresponding States Type. Recent theories[13] of polymer solution thermodynamics differ from the older Flory–Huggins theory in a number of ways.

(1) A thermodynamic effect arises from a difference in free volume between the components which leads to a volume change during the mixing process. (2) The interaction between molecules is associated with *surfaces* of the molecules considered as "hard cores." In the Flory–Huggins theory the interaction is between volumes, no differentiation being made between hard core volumes and "macroscopic volumes." (3) The combinatorial entropy is expressed in terms of segment fractions which deal with the hard core volumes, not the macroscopic volumes used in the familiar volume fractions of the Flory–Huggins theory.

The newer theories have so far been written for two-component systems, but an extension to three components may be made.[14] Using the corresponding states formulation of the Prigogine–Flory theory, the noncombinatorial Gibbs free energy per gram of a ternary mixture, g, may be related to a dimensionless reduced quantity $\tilde{G}(\tilde{T})$ by

$$g = u^*\tilde{G}(\tilde{T}) \qquad (6)$$

Here u^* is a reduction parameter (per gram) for quantities having dimensions of energy. It is related to the corresponding u_i^* of the pure components through

$$u^* = w_1u_1^* + w_2u_2^* + w_3u_3^* - w_1\theta_2v_1^*X_{12} - w_1\theta_3v_1^*X_{13} - w_2\theta_3v_2^*X_{23} \qquad (7)$$

Here the w_i are the weight fractions and θ_i surface or site fractions of the components in the mixture

$$\theta_i = w_iv_i^*s_i/\Sigma w_iv_i^*s_i \qquad (8)$$

The v_i^* are reduction parameters (per gram) for volume and the s_i are molecular surface:volume ratios. The u_i^* may also be written in terms of the pressure reduction parameters: $u_i^* = p_i^*v_i^*$. The X_{ij} are contact interaction parameters as introduced in the theory of Flory and collaborators. The reduced temperature $\tilde{T}$ of the ternary mixture is related to the $\tilde{T}_i$ of the pure components through

$$\tilde{T} = (\Sigma w_iu_i^*\tilde{T}_i)/u^* \qquad (9)$$

It is also necessary to define $\tilde{T}_0$, the reduced temperature of the stationary phase, given by eq 9 through $w_1 \rightarrow 0$. It is possible to obtain the chemical potential of component 1 in the mixture through differentiation of eq 6. At infinite dilution, $w_1 \rightarrow 0$, we have

$$\left(\frac{\mu_1 - \mu_1^\circ}{RT}\right)_{\text{noncomb}} = \chi_{1(23)} = \left[\left(\frac{X_{12}}{s_1}\right)\theta_2 + \left(\frac{X_{13}}{s_1}\right)\theta_3 - \left(\frac{X_{23}}{s_2}\right)\theta_2\theta_3\right]\left[\frac{s_1M_1v_1^*}{RT}\{-\tilde{U}(\tilde{T}_0)\}\right] + [\tilde{U}(\tilde{T}_0) - \tilde{U}(\tilde{T}_1) + \tilde{T}_1\{\tilde{S}(\tilde{T}_1) - \tilde{S}(\tilde{T}_0)\}]\left(\frac{p_1^*M_1v_1^*}{RT}\right) \qquad (10)$$

In the Flory model, $\tilde{U} = -\tilde{V}^{-1}$ and $\tilde{S} = \ln(\tilde{V}^{1/3} - 1)$ with $\tilde{T} = (\tilde{V}^{1/3} - 1)\tilde{V}^{-4/3}$, and these explicit relations will be used in eq 10.

When the stationary phase contains only one component, eq 10 reduces to equations used previously for binary polymer solutions, *e.g.*, eq 12 or 17 of ref 15. Both terms of eq 10 are positive contributions to $\chi_{1(23)}$. The second term of eq 10 has no analog in the Flory–Huggins eq 5 since it is due to the free volume change occurring during the mixing process. However, the first term is analogous to the whole of $\chi_{1(23)}$ in eq 5. The X_{ij}, like their χ_{ij} counterparts, are not symmetrical, being proportional to s_i. Equation 10 introduces the symmetrical quotients X_{ij}/s_i. Surface fractions, θ, replace the volume fractions, φ, of eq 5 and the quantity $s_1M_1v_1$, which is the molecular surface of a mole of component 1, replaces V_1. Glc experiments with columns containing pure polymers 2 and 3 and with the mixed (2–3) column allow the parameters X_{12}/s_1, X_{13}/s_1, and X_{23}/s_2 to be obtained, corresponding to the χ_{ij}/V_i as characteristics of ij interactions. The X_{ij} parameters refer to free energies of interaction, and enthalpic data may lead to rather different values of these parameters.

Experimental Section

Apparatus and Materials. The dual-column glc apparatus used in this work has been described previously.[3b]

Stationary phases included n-C$_{24}$ obtained from Aldrich Chemical Co. at 99% purity and used as received. Plasticizer-grade DOP was obtained from Witco Chemical Co. Two PDMS samples were involved The higher molecular weight sample ($\bar{M}_v \sim 5 \times 10^5$) was the same material used previously.[3b] Because of limited miscibility of this polymer with n-C$_{24}$, a lower molecular weight sample was also used. This was a 50-cs Dow-Corning silicones fluid which had been heated for several days at 110° to remove any low boiling components. A molecular weight of 3700 was obtained for this material from inherent viscosity measurements in toluene. The two samples will be denoted by PDMS(H) and PDMS(L), respectively.

A total of 11 aliphatic and aromatic hydrocarbon probes were used in the various parts of this research. These were analytic grade materials used without further purification. Analytic grade CCl$_4$ also was used as received.

Column Description and Composition Analysis. All columns were made of 0.25-in. o.d. copper tubing, methanol washed prior to use. The supporting solid throughout was Chromosorb W (60–80 mesh, acid washed, and DMCS treated). The stationary phases studied were: n-C$_{24}$, DOP, PDMS(L), and the n-C$_{24}$-DOP and n-C$_{24}$-PDMS(L) mixtures. All stationary phases were deposited

Table III
Specific Retention Volumes, V_g° (ml/g), for Two- and Three-Component Systems

Probe	*n*-C_{24}	DOP	PDMS(L)	*n*-C_{24}–DOP	*n*-C_{24}–PDMS(L)
Column temperature (°C):	60	75	60	75	60
n-Pentane	43.27	15.46	24.76	25.49	41.64
n-Hexane	115.25	39.14	60.91	61.65	93.09
n-Heptane	298.53	90.68	144.30	147.68	234.42
n-Octane	761.55	208.15	332.14	352.40	580.61
n-Nonane		470.53	765.38		
2-Methylpentane	86.21	29.98	46.96	47.07	72.36
3-Methylpentane	98.65	34.14	52.65	53.79	80.40
2-Methylhexane	216.25	69.57	107.76	110.33	
2,4-Dimethylpentane	152.13	49.79	78.97	80.03	122.19
Cyclohexane	207.45	77.49	106.14	112.82	162.24
Carbon tetrachloride	180.07	98.92	105.71	117.15	
Benzene	169.65	120.20	105.46	126.10	145.22

onto Chromosorb from *n*-hexane solutions. Following removal of excess hexane, the coated support was dried in a vacuum evaporator and finally oven-dried at 100° for several hours to remove last traces of hexane. Composition analysis varied somewhat, depending on the particular system. The concentration of pure PDMS was determined by Soxhletting the coated support for 72 hr again using *n*-hexane. Concentrations of DOP and *n*-C_{24} were evaluated by the ashing method of Martire and Riedl.[16]

In choosing mixed stationary phases, preliminary experiments were carried out to test the compatibility of the constituents. Mixtures of PDMS and DOP were turbid in the temperature and concentration range of interest and this system was therefore rejected. The *n*-C_{24}-PDMS(H) system was also incompatible at the operating temperature, but this problem was not encountered with the lower molecular weight sample. Although several *n*-C_{24}-PDMS(H) columns were prepared to study incompatibility effects, results will be reported for only the *n*-C_{24}-PDMS(L) system. To eliminate any possibility of phase separation, the column was packed and stored in an oven at 60°. When required for use, it was transferred rapidly into the glc apparatus bath, again maintaining its temperature above 60°.

Triplicate determinations of the total percentage of supported mixed stationary phase (*n*-C_{24}-PDMS(L) or *n*-C_{24}-DOP) were made by Soxhlet extraction. In *n*-C_{24}-DOP mixtures, the composition balance was determined from refractive index measurements at 45°. A calibration curve for mixtures of known composition had been previously established for this application.

Extracted *n*-C_{24}-PDMS mixtures were first exposed at 100° to remove *n*-hexane, then mixed with σ-xylene to give 5% w/v solutions. The flow times of these solutions were measured at 30° using Cannon-Fenske viscometers, giving reference flow times for σ-xylene greater than 200 sec. Compositions were calculated from a calibration curve of flow times against known *n*-C_{24}-PDMS ratios.

Details of column composition are given in Table II. All analytic results are averages of three separate determinations, with deviations from the stated data not exceeding 1%.

Retention Times. Procedures for the determination of retention times were followed precisely after those described earlier.[3b] As in previously reported work, symmetrical elution peaks were obtained in all cases, indicating attainment of equilibrium sorption conditions.

Results and Discussion

Specific Retention Volumes. Values of the specific retention volume, $V_g{}^0$, calculated from the expression of Littlewood and coworkers[17] are found in Table III. The quoted data are averages of six determinations corresponding to two inlet pressures and triplicate retention times. Their precision is ±1%.

Thermodynamic Interaction Parameters. Various quantities are required in order to obtain and interpret the thermodynamic interaction parameters. Virial coefficients were computed from corresponding states equations of McGlashan and Potter,[18] using critical constants taken from Driesbach's compilation.[19] Parameters for use in eq 10 are found in Table IV. The starred reduction parameters are obtained from equation of state data at 25°, and are taken to be independent of temperature.

Table IV
Parameters for X_{ij} Calculations

Probe	T*(°K)	v_{sp}* (cm^3/g)	p* (J/cm^3)	s (A^{-1})
n-C_5	4096[a]	1.173[a]	423[a]	1.08[h]
n-C_6	4446[a]	1.155[a]	436[a]	1.04[h]
n-C_7	4707[a]	1.133[a]	428[a]	1.00[h]
n-C_8	4863[a]	1.120[a]	428[a]	0.98[h]
2-Methylpentane	4365[b]	1.158[b]	411[b]	1.00[i]
3-Methylpentane	4435[b]	1.147[b]	418[b]	1.00[i]
2,4-Dimethylpentane	4540[b]	1.154[b]	408[b]	0.85[j]
Cyclohexane	4719[c]	1.001[c]	531[c]	0.93[j]
Carbon tetrachloride	4697[c]	0.488[c]	569[c]	0.97[j]
Benzene	4708[a]	0.889[a]	620[a]	1.00[j]
Toluene	5026[a]	0.918[a]	561[a]	0.93[j]
n-C_{24}	5843[d]	1.039[d]	471[d]	0.87[h]
PDMS(L)	5578[e]	0.855[e]	353[a]	0.48[k]
DOP	6003[f]	0.850[f]	552[g]	0.99[l]

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Pure Stationary Phases. Values of χ_{12} are found in Table V for the probes interacting with *n*-C_{24}, DOP, and PDMS of low and high molecular weights. These values have been obtained using eq 2 of ref 3b or the present eq 5 putting $\varphi_3 = 0$. In previous work[3] we have evaluated χ_{12}* parameters, given by a variant of the Flory-Huggins theory which uses segment fractions and "hard-core volumes" in the combinatorial term of eq 2. This has also been done here, but no new feature is apparent for the mixed columns and the χ_{12}* are not reported.

In a simple view of the Flory-Huggins theory, the ratio χ_{12}/V_1 should be independent of the size of the probe molecule and be characteristic of the chemical natures of the interacting molecules. The χ_{12} values in Table V, if converted to χ_{12}/V_1, would not fulfil this expectation. This is particularly evident in the decrease of χ_{12}/V_1 for the series of *n*-alkane probes of increasing molecular weight. The difficulty is largely due to the neglect in the Flory-Huggins theory of the free volume difference between the probe and stationary-phase liquids. The main

Table V
Interaction Parameters

	Interaction between Probe (Component 1) and Pure Stationary Phase (Component 2)									Interaction between Two Components (2 and 3) in the Stationary Phase			
	n-C$_{24}$				DOP		PDMS(L)		PDMS (H)	n-C$_{24}$–DOP		n-C$_{24}$–PDMS (L)	
Probe	χ_{12} 60°	X_{12}/s_1 × 10^8 J cm^{-2} 60°	χ_{12} 75°	X_{12}/s_1 × 10^8 J cm^{-2} 75°	χ_{12} 75°	X_{12}/s_1 × 10^8 J cm^{-2} 75°	χ_{12} 60°	X_{12}/s_1 × 10^8 J cm^{-2} 60°	χ_{12} 60°	$V_1\chi_{23}/V_2$ cm^{-3} 75°	X_{23}/s_2 × 10^8 J cm^{-2} 75°	$V_1\chi_{23}/V_2$ cm^{-3} 60°	X_{23}/s_2 × 10^8 J cm^{-2} 60°
n-C$_5$	0.32	4.5	0.32^c	4.4^c	0.76	21.2	0.45	12.5	0.44^b	0.86	33.9	1.01	34.6
n-C$_6$	0.24	4.6	0.24^a	5.0^a	0.67	19.2	0.43	13.4	0.45^b	0.72	25.5	0.48	11.7
n-C$_7$	0.20	4.2	0.20^a	4.6^a	0.67	18.8	0.45	13.8	0.49^b	0.77	25.5	0.55	12.1
n-C$_8$	0.17	3.4	0.17^a	3.8^a	0.68	17.6	0.49	13.4	0.54^b	0.87	26.4	0.64	12.6
2-Methylpentane	0.26	5.0	0.27^a	5.9^a	0.69	20.1	0.42	13.0	0.43^b	0.72	26.8	0.57	15.9
3-Methylpentane	0.23	4.6	0.24^a	5.4^a	0.66	19.7	0.41	13.4		0.74	27.6	0.49	13.0
2,4-Dimethylpentane	0.26	5.0	0.26^c	5.4^c	0.70	21.3	0.42	13.4		0.77	28.5	0.49	13.0
Cyclohexane	0.17	5.4	0.17^c	5.9^c	0.48	19.2	0.44	19.2		0.62	28.5	0.42	10.9
Carbon tetrachloride	0.26	10.5	0.26^c	10.9^c	0.19	6.3	0.42	20.1		0.48	22.2		
Benzene	0.51	23.4	0.48^a	23.0^a	0.16	5.4	0.62	31.4	0.75^b	0.43	19.2	0.37	14.6
Toluene	0.35^d	15.5^d	0.36^a	16.3^a					0.76^b				

[a] Based on $V_g°$ values given by Y. B. Tewari, D. E. Martire, and J. P. Sheridan, *J. Phys. Chem.*, **74,** 2345 (1970). [b] Interpolated by using $V_g°$ values given by W. R. Summers, Y. B. Tewari, and H. P. Schreiber, *Macromolecules*, **5,** 12 (1972). [c] Estimated from values for 60°. [d] Estimated from values for 75°.

feature of the newer theories is the elimination of the free volume contribution to χ_{12} leaving the X_{12} parameter. Table V lists values of the similar, but somewhat more fundamental ratio X_{12}/s_1. They were obtained using eq 10 putting $\theta_3 = 0$ for the pure columns. The values of X_{12}/s_1 for the normal and branched-alkane probes are now similar for interactions with each of the three stationary phases. The closeness of normal and branched-alkane data indicates the similarity of methyl and methylene groups in their interactions, at least as far as free energies are concerned. The same conclusion was reached through an analysis[20] of literature data for a large range of normal and branched-alkane probes in n-C$_{18}$ and n-C$_{36}$. Values of X_{12}/s_1 for alkane probe-n-C$_{24}$ interactions are relatively independent of the probe. They are small, but still not zero as one might expect. It is possible[20] that the nonzero X_{12}/s_1 reflect an error in the free volume term in the theory. It may also be significant that there is an ordering or correlation of the orientations of neighboring long n-alkane chains such as n-C$_{24}$. This correlation has been shown[21] to have an important effect on the enthalpy of interaction of the n-alkane with a component, such as an alkane of low carbon number, where the correlation is absent. The effect in the enthalpy is apparently compensated to a great extent by a corresponding effect in the entropy of interaction. However, it is still possible that the free energy and X_{12} may reflect the lack of orientational ordering of neighboring n-C$_{24}$ and alkane probe molecules.

Dioctyl phthalate is a rather poor solvent for the normal and branched alkanes as reflected by the high values of X_{12}/s_1 and χ_{12}. As expected, a drastic reduction in X_{12}/s_1 and χ_{12} is observed when the probe is aromatic. The low value of the interaction parameters for DOP-CCl$_4$ is particularly interesting when it is recalled that DOP is a strong plasticizer for chlorine-containing vinyl polymers.

We note further a significant difference in the χ_{12} values involving the two distinct PDMS samples. There is some divergence[7] of published $V_g{}^0$ data for high molecular weight samples of this polymer, but the internal reproducibility of data is excellent, and recent interlaboratory comparisons[7] confirm the reproducibility of values such as those given in Table III. The difference between PDMS-L and PDMS-H is, in our view, accounted for by the substantial difference in polymer molecular weight.

Two-Component Stationary Phases. Table V shows values of $V_1\chi_{23}/V_2$ and X_{23}/s_2 obtained using respectively eq 5 and 10 for the two mixed columns. If interactions are correctly taken account of by the theory, the quantities χ_{23}/V_2 and X_{23}/s_2 should be independent of the probe. Except in the case of n-C$_5$, X_{23}/s_2 in Table V is almost independent of probe. A larger, but still not unreasonable variation, would be found for χ_{23}/V_2 obtained from $V_1\chi_{23}/V_2$ values in Table V. Also, χ_{23}/V_2 and X_{23}/s_2 are measures of interactions of the alkane–DOP and alkane–PDMS type already examined in the binary systems. Thus, the parameters for these interactions should be the same as those found in the χ_{12}/V_1 and X_{12}/s_1 table columns for alkane probes interacting with DOP and PDMS. This check on data consistency is reasonably successful, particularly for the alkane-PDMS(L) interaction. Values of X_{ij} obtained with n-pentane as probe appear anomalous. This may be due to the extremely large free-volume term in the theory for this probe which is, in the present case, at a temperature far above the boiling point. In general, however, the consistency of the results suggests that glc is a promising method for the determination of interactions between the components of the stationary phase.

The values of X_{ij} depend to some extent on the values taken for the parameters in Table III. The calculation of s, in particular, requires rather arbitrary assumptions concerning the molecular shape. Fortunately, the X_{ij} values are not sensitive to a variation in the parameters and the general picture is unchanged.

Several columns were prepared with n-C$_{24}$-PDMS(H) stationary phases of different composition. In each case very small or negative χ_{23}/V_2 values were obtained for all probes, leading to negative values of the X_{23}/s_2 parameter. We believe these to be due to phase separation occurring in the supported stationary phase, and indeed phase separation was shown to occur in bulk samples of the n-C$_{24}$-PDMS(H) mixtures.

It is probably useful to comment on the parameter s, the molecular surface/volume ratio found in Table II. Flory uses an s defined as "the number of intermolecular contact sites per segment." In fact this parameter is not evaluated for individual components since the choice of a segment may be different for each system. In practice, however, it seems that all sites are taken of equal area and the segments of equal volume. Hence the definition used in this article is essentially the same as that of Flory.

In Table V we cite values of X_{12}/s_1 and X_{23}/s_2 rather than the simpler X_{12} and X_{23} which is the type of parameter familiar from the work of Flory and others. A typical value of X_{12}/s_1 in Table V would be 13.4×10^{-8} J cm^{-2} for n-C$_6$ + PDMS or 1.34 ergs cm^{-2}, whereas X_{12} itself would be 13.9 J cm^{-3} for this system. The X_{12} corresponds to the interchange free energy for forming contacts between the surfaces of molecules 1 and 2. It is, however, normalized to the surface area associated with 1 cm^3 of molecules of component 1 and is therefore not symmetrical. On the other hand, X_{12}/s_1 is the same interchange free energy expressed per cubic centimeter of surface of molecular contact and is hence symmetrical. If indeed the interaction is between molecular surfaces as current theories suggest, then X_{12}/s_1 appears the more meaningful quantity for comparing systems. (Since most molecules have similar surface/volume ratios, X_{12} is also useful.) The parameter X_{12}/s_1 corresponds to a molecular interfacial energy, and the value of 1.34 ergs cm^{-2} is of the same order as the interfacial free energy for polyethylene-PDMS,[22] 5.1 ergs cm^{-2}. A counterpart to X_{12}/s_1 is found in the theory of Huggins,[23] and indeed in the early solution theory of Langmuir,[24] both of which deal more directly with interaction between molecular surfaces than do the approaches of Prigogine and Flory.

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References and Notes

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