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On The Application of Inverse Gas Chromatography to Interactions in Mixed Stationary Phases

Z. H. Shi and H. P. Schreiber*

Department of Chemical Engineering, Ecole Polytechnique, P.O. Box 6079, Station A, Montreal, Quebec, Canada H3C 3A7

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ABSTRACT: The application of inverse gas chromatography (IGC) to measure polymer interaction thermodynamics refocuses attention on the dependence of thermodynamic parameters for mixed stationary phases on the selection of vapor probes. A critical portion of the problem is attributed to the spurious assumption that the surface composition of a mixed stationary phase is identical with its bulk composition. A method is proposed to correct for differences in these compositions. A second contributing factor to the probe dependence of IGC data, the nonrandom partitioning of vapor-phase molecules, is also examined, using a characteristic two-component stationary phase consisting of a polypropylene host and a minor amount of fluorochemical additive. It is shown that the proposed procedures substantiate the inherent attractiveness of IGC as a convenient route to the determination of reliable interaction parameters for mixed (polymeric) stationary phases.

Introduction

The use of inverse gas chromatography (IGC) has increased rapidly, due in large part to its convenient application to the measurement of thermodynamic parameters for polymeric stationary phases. The IGC method has been the subject of recent reviews,[1,2] which note both the strengths and the limitations of the technique. Early in the development of IGC, it was shown[3,4] that Flory–Huggins or Prigogine interaction parameters for two-component polymer–vapor probe systems could be measured with high accuracy over substantial temperature ranges and with relevance to practical cases, the polymer phase being at very high concentration. Subsequent developments have extended IGC methods to studies of interactions in more complex systems.[5–11] By analyzing the interactions between probe (1) and each of two nonvolatile components (2 and 3), it was possible to combine components 2 and 3 at any desired concentration and measure χ_{23}, thereby generating potentially valuable miscibility–concentration relationships for polymer blends, filled, reinforced, or plasticized polymers, etc. In this context, however, difficulties arose when it was noted that the χ_{23} parameter varied with the vapor probe used in measurements.[3,9–15] Since, formally, χ_{23} should be independent of the vapor-phase composition, this appeared to limit the applicability of IGC.

Numerous attempts have been reported to resolve the problem of vapor-phase-dependent interaction parameters.[3–9] The present paper also addresses the problem. It does so in the light of evidence, reported from various independent sources,[3–9] that surface and bulk compositions in multicomponent polymer systems generally differ and, further, that the partitioning of vapor-phase molecules between the components of a solid's surface layer is likely to be nonrandom. A procedure is suggested for establishing the true surface composition for a two-component polymer system, and this is tested by determinations of χ_{23} for a polypropylene matrix blended with limited amounts of a fluorochemical additive.

Review of Basic Concepts

A brief review of thermodynamic expressions applied to IGC is helpful for our purpose. The traditional expression for calculating χ_{23} is as follows:

$$\chi_{23} = \frac{V_2}{V_1}\left[\ln\left(\frac{V^\circ_{g23}}{\omega_2\nu_2 + \omega_3\nu_3}\right) - \phi_2 \ln\left(\frac{V^\circ_{g2}}{\nu_2}\right) - \phi_3 \ln\left(\frac{V^\circ_{g3}}{\nu_3}\right)\right]\Big/(\phi_2\phi_3) \quad \text{(1a)}$$

where V_1 is the molar volume of the solutes, V_2 is the molar volume of one of the polymers in the blend, ω_i are the weight fractions of the components i in the blend, ϕ_i are the volume fractions of the components i in the blend, and ν_i are the specific volumes of the components i in the blend.

Since χ_{23} is proportional to V_2, which for a polymer is likely to be large, this leads to inconveniently large values of the interaction parameter. Consequently, in practice, a "normalized" or apparent interaction parameter χ'_{23} is introduced[3–9] via

$$\chi'_{23} = \left[\ln\left(\frac{V^\circ_{g23}}{\omega_2\nu_2 + \omega_3\nu_3}\right) - \phi_2 \ln\left(\frac{V^\circ_{g2}}{\nu_2}\right) - \phi_3 \ln\left(\frac{V^\circ_{g3}}{\nu_3}\right)\right]\Big/(\phi_2\phi_3) \quad \text{(1b)}$$

It is evident from eq 1a that χ_{23} is proportional to the molar volume of one, but not both, of the polymers involved in a polyblend. This is somewhat surprising since, a priori, there is no advantage in choosing one polymer over another in such a situation. A review of Flory–Huggins theory, however, reduces this problem to triviality, showing that χ_{23} as well as χ'_{23} should be independent of the polymer molar volumes. The more serious problem, as already stated, has to do with the conflict between Flory–Huggins theory, which shows χ_{23} to be defined by the properties of the stationary-phase components only, and experiments,[3,9–15] which show that χ'_{23} is a function of the vapor probe. The original Flory–Huggins expression is symmetric and given by[16–19]

$$\Delta G_\phi = RT[\phi_1 \ln \phi_1 + (V_1/V_2)\phi_2 \ln \phi_2 + \chi_{12}\phi_1\phi_2] \quad \text{(2a)}$$

for a two-component system, while for a three-component system

$$\Delta G_\phi = RT[\phi_1 \ln \phi_1 + (V_1/V_2)\phi_2 \ln \phi_2 + (V_1/V_3)\phi_3 \ln \phi_3 + \chi_{12}\phi_1\phi_2 + \chi_{13}\phi_1\phi_3 + \chi_{23}\phi_2\phi_3] \quad \text{(2b)}$$

Here, ΔG_ϕ is the change of free enthalpy of mixing per

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mole of lattice sites, T is the experimental temperature, R is the gas constant, and χ_{12} and χ_{13} are the Flory–Huggins interaction parameters of solute(1)–polymer(2) and solute(1)–polymer(3), respectively.

Given that V_1 of the solvent molecule is much smaller than the V_i of the polymer molecule (i = 2 or 3 in a two-component blend), the Flory–Huggins lattice model[16] considers that for each site occupied by a solvent molecule there are V_i/V_1 sites occupied by a polymer. The total number of lattice sites in a complex is V/V_1. The total change in the free enthalpy of mixing is given by

$$\Delta G_{\text{mix}} = \frac{V}{V_1}\Delta G_\phi = RT(n_1 \ln \phi_1 + n_2 \ln \phi_2 + n_1\phi_2\chi_{12}) \tag{3a}$$

for a two-component system, while for three components

$$\Delta G_{\text{mix}} = \frac{V}{V_1}\Delta G = RT[n_1 \ln \phi_1 + n_2 \ln \phi_2 + n_3 \ln \phi_3 + n_1\phi_2\chi_{12} + n_1\phi_3\chi_{13} + (n_1\phi_2\phi_3/\phi_1)\chi_{23}] \tag{3b}$$

where n_i is the number of moles of component i (i = 1, 2, or 3), $V = n_1V_1 + n_2V_2 + n_3V_3 = \sum n_iV_i$, and $\phi_i = n_iV_i/V$.

IGC is a process that involves the distribution of a gaseous solute between the stationary and the mobile phases. The specific retention volume, V°_g is related to the partition coefficient for solute between the two phases (C_1^l/C_1^g) as follows:

For a column containing only one polymer, 2

$$V^\circ_{g2} = \frac{C_1^{\,l}}{C_1^{\,g}}\nu_2\frac{T^\circ}{T} \tag{4a}$$

while for a column containing a mixture of polymers 2 and 3

$$V^\circ_{g23} = \frac{C_1^{\,l}}{C_1^{\,g}}(\omega_2\nu_2 + \omega_3\nu_3)\frac{T^\circ}{T} \tag{4b}$$

In the above equations C_1^l is the concentration of solute (1) in stationary phase l in terms of the amount of solute absorbed per volume of polymer, C_1^g is the concentration of solute (1) in terms of the molar number of solute in the gas phase of volume V, and T° = 273.15 K.

At infinite dilution of the solute, the concentration of probes in both the stationary phase and the mobile gas phase (C_1^l, C_1^g) is very small. The thermodynamics of nonideal gases gives the chemical potential in the gas phase, $\Delta\mu_1^g$:[4]

$$\Delta\mu_1^{\,g} = RT \ln \frac{RTC_1^{\,g}}{M_1P_1^\circ} - B_{11}P_1^\circ \tag{5}$$

where M_1 is the molecular weight of the probe, B_{11} is the second virial coefficient of the probe in the gaseous state, and P_1° is the saturated vapor pressure at the temperature T.

Similarly, the thermodynamics of liquids and liquid mixture yields to the chemical potential in the liquid phase, $\Delta\mu_1^l$:[4]

$$\Delta\mu_1^{\,l} = -V_1P_1^\circ + \left(\frac{\partial \Delta G_{\text{mix}}}{\partial n_1}\right)_{n_2,n_3,P,T} \tag{6}$$

where $(\partial\Delta G_{\text{mix}}/\partial n_1)$ can be determined from the derivative of eq (3), which leads to

$$\partial\Delta G_{\text{mix}}/\partial n_1 = RT(\ln \phi_1 + 1 - V_1/V_2 + \chi_{12}) \tag{7a}$$

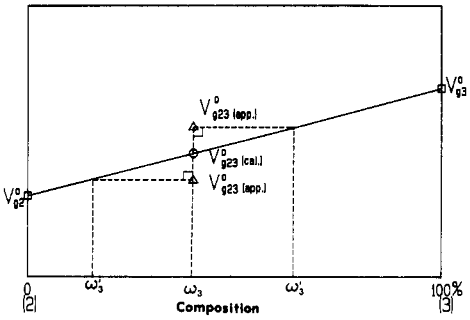

Figure 1. Ideal and experimental relationship in the retention volume–composition diagram of a two-component system.

and for a mixed stationary phase

$$\partial\Delta G_{\text{mix}}/\partial n_1 = RT[\ln \phi_1 + (1 - \phi_1) - (V_1/V_2)\phi_2 - (V_1/V_3)\phi_3 + (1 - \phi_1)\phi_2\chi_{12} + (1 - \phi_1)\phi_3\chi_{13} - \phi_2\phi_3\chi_{23}] \tag{7b}$$

Since, at equilibrium, the chemical potential of the solute in the mobile and stationary phases is the same, combining expressions 4 and 8, we have for a two-component system

$$\Delta\mu_1^{\,g} = \Delta\mu_1^{\,l} \tag{8}$$

$$RT \ln \frac{RT^\circ\nu_2\phi_1}{V^\circ_{g2}P_1^\circ V_1} - B_{11}P_1^\circ = -V_1P_1^\circ + RT\left(\ln \phi_1 + 1 - \frac{V_1}{V_2} + \chi_{12}\right) \tag{9}$$

and for three components

$$RT \ln \frac{RT^\circ\phi_1}{P_1^\circ V_1} - B_{11}P_1^\circ + RT \ln \frac{\omega_2\nu_2 + \omega_3\nu_3}{V^\circ_{g23}} = -V_1P_1^\circ + RT\left[\ln \phi_1 + 1 - \frac{V_1}{V_2}\phi_2 - \frac{V_1}{V_3}\phi_3 + \chi_{12}\phi_2 + \chi_{13}\phi_3 - \chi_{23}\phi_2\phi_3\right] \tag{10}$$

From the above equations we establish the basic statements for χ parameters:

$$\chi_{12} = \ln \frac{RT\nu_2}{V^\circ_{g2}V_1P_1^\circ} - 1 + \frac{V_1}{M_2\nu_2} - \frac{B_{11} - V_1}{RT}P_1^\circ \tag{11}$$

and

$$\chi_{23} = \left[\ln\left(\frac{V^\circ_{g23}}{\omega_2\nu_2 + \omega_3\nu_3}\right) - \phi_2 \ln\left(\frac{V^\circ_{g2}}{\nu_2}\right) - \phi_3 \ln\left(\frac{V^\circ_{g3}}{\nu_3}\right)\right]/(\phi_2\phi_3) \tag{12}$$

A comparison with the literature shows that χ_{12} as given by eq 11 retains its usual form. However, χ_{23} as given by eq 12 corresponds to χ'_{23}. This eliminates the V_2 term and avoids the inconvenience of excessively large parameter values.

The χ_{23} Conundrum: Previous and Present Approaches to Resolution

In theory, the retention volume for a two-component stationary phase, V°_{g23}, should satisfy the following equation:

$$V^\circ_{g23(\text{cal})} = \omega_2V^\circ_{g2} + \omega_3V^\circ_{g3} \tag{13}$$

A graphical representation of this is shown in Figure 1. The retention volume for any given probe should fall on a straight line linking the retention volumes for each of the pure solids. This assumes tacitly that the surface composition of the mixed stationary phase corresponds exactly to the system's stoichiometry. Now IGC reports on the state of interactions at, or near, the surface of the stationary phase. When that phase consists of polymers below their glass transition temperature, the *surface* alone is being probed. Even above the T_g, however, the probe molecules, swept by the carrier gas, report essentially on the surface state or, at best, on the condition of an interphase near the surface. Provided the ideal relationship is followed, it is possible to evaluate a calculated $\chi_{23(\mathrm{cal})}$ from

$$\chi_{23(\mathrm{cal})} = \left[\ln\left(\frac{\omega_2 V^\circ{}_{g2} + \omega_3 V^\circ{}_{g3}}{\omega_2 \nu_2 + \omega_3 \nu_3}\right) - \phi_2 \ln\left(\frac{V^\circ{}_{g2}}{\nu_2}\right) - \phi_3 \ln\left(\frac{V^\circ{}_{g3}}{\nu_3}\right)\right] / (\phi_2 \phi_3) \quad (14)$$

The literature shows clearly that the *calculated* and experimental, or *apparent*, χ'_{23} rarely agree. Various approaches have been proposed to obtain χ_{23} from eq 1 by making measurements on two-component stationary phases and on the corresponding pure components under strictly controlled, identical experimental conditions of temperature, gas flow rate, probe volume, etc. Probe-to-probe variations were somewhat reduced but far from eliminated. DiPaola-Baranyi et al.[12] ascribed probe-to-probe variations of χ in ternary systems partly to limitations in the ability of the modified Flory–Huggins theory to account for interactions in such complex systems. However, they also noted the possibility that nonrandom partitioning of probe molecules could affect the forces acting between molecules of the mixed stationary phases, so that IGC could be viewed as a unique source for information on interactions on a molecular rather than on a bulk scale. A similar point of view has been expressed by Schreiber and Lloyd.[2] An empirical and rather limited route to minimizing probe-to-probe variations of χ_{23} was reported recently by Klotz and co-workers,[20] who selected probes that were "thermodynamically symmetric" with respect to the polymers to be evaluated. Further, Sanchez[21,22] has argued that a full description of polymer mixture thermodynamics requires the definition of four different χ parameters: one associated with the free energy of the mixture, two with the first concentration derivative of the free energy, and the fourth with the second concentration derivative. Not surprisingly, in this point of view, a single value of χ will be open to variations due to changes in the chemistry and concentration of the vapor. Finally, we note recent work by Chee,[23] who has proposed an interaction density parameter to overcome probe-to-probe variations in χ_{23}. The use of this approach led to interaction values essentially independent of probe selection for the system ethylene–vinyl acetate/chlorinated PE.

In our view, the IGC experiment is reporting accurately on the state of surface interaction in a binary stationary phase. Two main factors are to be considered in this regard. The first is the tacit assumption, as expressed by eq 13, that the surface composition in a mixture of polymers will be the same as the bulk composition. This seems contentious on theoretical grounds since, at equilibrium, the need to minimize the surface free energy of a solid must drive to the surface an excess of the component with lower surface energy. The second is the widely discussed effect of nonrandom partitioning of the vapor phase. Indeed, nonrandom partitioning may be regarded as a thermodynamic requirement in all but those cases where χ_{12} and χ_{13} are identical. In fact, as already noted above,[1,2] the IGC experiment may be unique in providing information on this level of interactions.

Returning to the difference between surface and bulk compositions, we may cite experimental evidence to support the reality of this effect. Our recent studies of complex vinyl polymer systems[24] have led to the notion of compositional heterogeneity at all contacts between the system's constituents. Lipatov[25] has reported complex compositional variations among bulk, interphase, and surface regions in multicomponent polymer systems. Differences between bulk and surface regions may also arise in single polymers, due to the ability of the polymer to restructure in keeping with thermodynamic drives to minimize surface free energies. Schultz,[26] Schreiber,[27] Ratner,[28] and their co-workers are among those who have generated experimental evidence supporting this effect. In terms of Figure 1, then, the failure of $V^\circ{}_{g23}$ to lie on the line joining the $V^\circ{}_g$ for the pure component systems arises from the two basic causes introduced above and should be used to evaluate an effective surface composition in the binary stationary phase. This is illustrated in Figure 1 by the constructions leading to the definitions of ω'_3. The protocol implicated in this figure leads to the following:

$$\omega'_2 = \frac{V^\circ{}_{g23(\mathrm{app})} - V^\circ{}_{g3}}{V^\circ{}_{g2} - V^\circ{}_{g3}} \quad (15a)$$

and

$$\phi'_2 = \frac{\nu_2 \omega'_2}{\nu_2 \omega'_2 + \nu_3 \omega'_3} \quad (15b)$$

with $\omega'_2 + \omega'_3 = 1$ and $\phi'_2 + \phi'_3 = 1$. By using these corrected values, we determine an effective value of the interaction parameter, $\chi_{23(\mathrm{eff})}$ from

$$\chi_{23(\mathrm{eff})} = \left[\ln\left(\frac{V^\circ{}_{g23(\mathrm{app})}}{\omega'_2 \nu_2 + \omega'_3 \nu_3}\right) - \phi'_2 \ln\left(\frac{V^\circ{}_{g2}}{\nu_2}\right) - \phi'_3 \ln\left(\frac{V^\circ{}_{g3}}{\nu_3}\right)\right] / (\phi'_2 \phi'_3) \quad (16)$$

Experimental Section

To test the utility of eq 16, we have evaluated the interaction parameter for two-component stationary phases consisting of polypropylene (PP) as host and fluorochemical (FC) additive at concentrations of 0.1, 1.0, and 10%. The PP was a commercially available resin with $M_w = 1.2 \times 10^5$ and $M_n = 1.67 \times 10^4$. The fluorochemical had a formula molecular weight of 852. Compounding utilized the Brabender Plasticorder apparatus, operating at a temperature of 180 °C and 50 rpm.

Chromatographic columns were prepared for each of the pure components and for mixed components, using Chromosorb W (AW-DMCS treated, 60/80 mesh) as the support. The support was coated from xylene solutions of the desired stationary-phase materials and, following the usual drying and ashing procedures,[29,30] was packed in steel tubes 0.60 cm in diameter and about 60 cm long. In all cases, the supported stationary-phase concentration was in the 7–8 wt % range. Prior to measurements, all columns were conditioned overnight at 110 °C under a helium flow. Measurements involved a Perkin-Elmer Sigma 2 apparatus, equipped with a thermal conductivity detector. Pure helium was the carrier gas at flow rates of 10 mL/min in keeping with the findings of Galin and associates,[31] who found that these flow rates and stationary-phase concentrations optimized the reproducibility of $V^\circ{}_g$ values. Experiments were carried out in the temperature range 30–80 °C. Retention times were measured in at least triplicate, with reproducibility of better than 3%. A total of 13 probes was employed; these are identified in the tables of results.

Table I
Flory-Huggins Interaction Parameter $\chi_{23(\mathrm{cal})}$ for Various PP-Additive Blends at 40 °C

	ω_3 (%) additive										
probe	0.05	0.1	0.2	0.4	0.6	0.8	1	1.2	1.4	1.6	1.8
n-C6[a]	0.69	0.62	0.57	0.55	0.55	0.54	0.53	0.54	0.54	0.54	0.54
n-C7[a]	0.68	0.60	0.56	0.54	0.54	0.53	0.53	0.53	0.53	0.53	0.53
n-C8[a]	0.62	0.54	0.50	0.48	0.48	0.48	0.47	0.47	0.47	0.47	0.47
n-C9[a]	0.57	0.49	0.45	0.44	0.43	0.43	0.43	0.43	0.42	0.42	0.42
$CHCl_3$	0.39	0.31	0.27	0.25	0.25	0.24	0.24	0.24	0.24	0.24	0.24
THF	0.54	0.46	0.42	0.40	0.40	0.40	0.39	0.39	0.39	0.39	0.39
ether	0.50	0.42	0.38	0.36	0.36	0.35	0.35	0.35	0.35	0.35	0.35
acetone	0.43	0.35	0.31	0.29	0.29	0.28	0.28	0.28	0.27	0.27	0.28
EtAc[b]	0.43	0.35	0.31	0.29	0.29	0.28	0.28	0.28	0.28	0.28	0.28
xylene	0.47	0.40	0.36	0.34	0.33	0.33	0.33	0.33	0.32	0.32	0.32
C_6H_6	0.42	0.34	0.31	0.29	0.28	0.28	0.28	0.28	0.27	0.27	0.27
CCl_4	0.45	0.37	0.33	0.31	0.31	0.30	0.30	0.30	0.30	0.30	0.30
toluene	0.40	0.32	0.29	0.27	0.26	0.26	0.26	0.26	0.25	0.25	0.25

	ω_3 (%) additive										
probe	2	4	6	8	10	15	20	30	50	70	90
n-C6[a]	0.54	0.54	0.55	0.56	0.57	0.58	0.62	0.67	0.85	1.17	2.66
n-C7[a]	0.53	0.54	0.54	0.55	0.56	0.58	0.61	0.67	0.83	1.17	2.65
n-C8[a]	0.47	0.48	0.48	0.49	0.50	0.52	0.54	0.59	0.75	1.07	2.53
n-C9[a]	0.42	0.43	0.43	0.44	0.45	0.46	0.49	0.53	0.68	0.99	2.43
$CHCl_3$	0.24	0.24	0.24	0.25	0.25	0.27	0.28	0.32	0.44	0.73	2.13
THF[b]	0.39	0.39	0.40	0.41	0.41	0.43	0.45	0.50	0.64	0.94	2.37
ether	0.35	0.35	0.36	0.36	0.37	0.38	0.40	0.45	0.58	0.88	2.30
acetone	0.28	0.28	0.28	0.29	0.29	0.31	0.32	0.36	0.49	0.78	2.19
EtAc[b]	0.28	0.28	0.28	0.29	0.30	0.31	0.33	0.37	0.49	0.78	2.19
xylene	0.32	0.33	0.33	0.34	0.34	0.36	0.38	0.42	0.55	0.84	2.26
C_6H_6	0.27	0.27	0.28	0.28	0.29	0.30	0.32	0.36	0.48	0.77	2.18
CCl_4	0.30	0.30	0.31	0.31	0.32	0.33	0.35	0.39	0.52	0.81	2.22
toluene	0.25	0.25	0.26	0.26	0.27	0.28	0.30	0.34	0.46	0.75	2.15

[a] *n*-C6, *n*-C7, *n*-C8, and *n*-C9 refer to *n*-hexane, *n*-heptane, *n*-octane, and *n*-nonane, respectively. [b] THF and EtAc refer to tetrahydrofuran and ethyl acetate, respectively.

Table II
Flory-Huggins Interaction Parameter $\chi_{23(\mathrm{app})}$ for PP-Additive Blends at 40 °C

probe	$\omega_3 = 0.1\%$	$\omega_3 = 1\%$	$\omega_3 = 10\%$
n-C6	-20.41	-3.79	-0.79
n-C7	-33.08	-5.86	-0.77
n-C8	-63.96	-13.38	-2.51
n-C9	-31.58	-4.27	-1.55
THF	-104.91	-21.09	-3.93
ether	-44.23	-9.37	-2.76
acetone	-64.68	-11.22	-2.24
EtAc	-94.92	-23.92	-2.92
xylene	-83.57	-9.69	-1.51
C_6H_6	-78.68	-15.22	-2.09
CCl_4	-55.86	-5.54	-1.44
toluene	-58.32	-12.40	-2.02

Table III
Flory-Huggins Interaction Parameter $\chi_{23(\mathrm{eff})}$ for PP-Additive Blends at 40 °C

probe	0.1% add. (ω'_3)	1% add. (ω'_3)	10% add. (ω'_3)
n-C6	0.38 (4.4)	0.39 (9.4)	0.43 (29.2)
n-C7	0.45 (6.6)	0.47 (12.7)	0.52 (28.5)
n-C8	0.40 (13.1)	0.43 (27.2)	0.51 (53.0)
n-C9	0.33 (7.2)	0.34 (10.9)	0.40 (41.9)
$CHCl_3$	0.10 (23.1)	0.10 (44.4)	0.11 (70.1)
THF	0.32 (23.8)	0.36 (45.4)	0.43 (77.6)
ether	0.24 (11.6)	0.26 (24.6)	0.30 (66.7)
acetone	0.16 (21.9)	0.17 (37.5)	0.19 (71.9)
EtAc	0.16 (31.1)	0.19 (72.2)	0.20 (86.1)
xylene	0.22 (22.7)	0.23 (27.1)	0.25 (47.2)
C_6H_6	0.15 (27.0)	0.17 (50.4)	0.18 (69.8)
CCl_4	0.18 (17.1)	0.18 (18.0)	0.21 (48.8)
toluene	0.12 (23.4)	0.13 (48.2)	0.14 (76.6)

Results and Discussion

In an initial survey of results, we assume that the bulk and surface compositions of mixed stationary phases are equivalent. From a knowledge of the V°_g for individual components we can therefore calculate the $\chi_{23(\mathrm{cal})}$ for mixtures over the entire composition range, as is done in Table I. The values entered are positive and lie in the range 0.2–2.5, suggesting that the host and additive polymers are immiscible or, at best, sparingly miscible. Experimental values of V°_g for the selected probes, of course, do not lie on a linear construction analogous to Figure 1. When these V°_g values are used in conjunction with the *apparent* compositions of mixed stationary phases, then very different *apparent* values $\chi_{23(\mathrm{app})}$ are obtained. The point is illustrated in Table II, using results at 40 °C. The variation with additive concentration is reasonably systematic for each of the probes, but the probe-to-probe variation is large, more particularly at lower additive concentrations. Furthermore, the unreasonably large, generally negative χ values suggest a high degree of miscibility, in contradiction with the calculated values of Table I. Clearly, very little confidence is generated by either the *calculated* or the *apparent* χ_{23}, and that for reasons which have already been noted earlier in this article.

The construction illustrated in Figure 1 permits an estimate to be made of the effective surface composition, ω'_3, for every mixed stationary phase in contact with each of the vapor probes. This procedure has been followed in the present case, with results illustrated in Table III, again at 40 °C. Tabulated are values of the real or *effective* $\chi_{23(\mathrm{eff})}$ and, in parentheses, the effective surface concentration of component 3, ω'_3. Since the glass transition temperature of the host polymer is below the experimental, it follows that the new composition parameter describes the near-surface interphase, though not necessarily the surface layer exclusively. Several points are noteworthy. First, the χ values now agree qualitatively with those in Table I, suggesting limited miscibility between host and

Table IV
Flory–Huggins Interaction Parameter $\chi_{23(\mathrm{eff})}$ for PP–Additive Blends at 80 °C

probe	0.1% add. (ω'_3)	1% add. (ω'_3)	10% add. (ω'_3)
n-C6			
n-C7	0.08 (3.4)	0.08 (20.4)	0.09 (66.0)
n-C8	0.10 (7.8)	0.11 (21.8)	0.12 (62.0)
n-C9	0.08 (8.1)	0.09 (26.2)	0.09 (62.0)
$CHCl_3$	0.05 (27.8)	0.06 (77.8)	0.06 (88.9)
THF	0.20 (11.0)	0.22 (28.0)	0.26 (69.5)
ether	0.15 (17.5)	0.16 (55.0)	0.19 (65.0)
acetone	0.04 (14.3)	0.05 (28.6)	0.05 (71.4)
EtAc	0.11 (23.7)	0.12 (47.4)	0.13 (79.0)
xylene	0.05 (34.2)	0.05 (62.8)	0.06 (75.0)
C_6H_6	0.01 (6.2)	0.01 (12.5)	0.01 (62.0)
CCl_4	0.07 (4.6)	0.08 (16.3)	0.08 (46.5)
toluene	0.00 (10.5)	0.00 (39.5)	0.00 (79.0)

additive and eliminating the irrationally high absolute values seen in Table II. Second, the corrected ω'_3 is always higher than the additive concentration in solution. We conclude that either the host PP is preferentially adsorbed by the Chromosorb, leaving an excess of FC additive at the surface, or, due to its limited miscibility with the host, the FC migrates to the surface. The column conditioning steps at 110 °C would surely allow this to occur. The corrected composition variable ω'_3 continues to display variations due to probe selection. This is attributed in part to the nonrandom sorption of probes, the degree being dependent on the nature of each probe. Moreover, depending on the dispersive and nondispersive surface energies of probes and of surface regions in the stationary phase, probe species may penetrate the near-surface layer to varying depths, accounting for the effect of apparent composition changes. Finally, the $\chi_{23(\mathrm{eff})}$ still varies slightly with the probe selection. This may be due to incomplete sorption of certain probes at the experimental temperature. Adsorption processes would attain equilibria more rapidly at higher temperatures and indeed, at 80 °C, the probe-to-probe variation is reduced into the range of expected experimental uncertainties. The point is shown by the data summary in Table IV. We conclude that $\chi_{23(\mathrm{eff})}$ may be used as a reliable measure of the interaction between mixed stationary phase constituents, particularly when care is taken to attain adsorption equilibria in the IGC experiment. Additional experimental tests of the new approach to interaction measurements will be reported in future publications.

The temperature variation of interaction parameters remains a valuable element of thermodynamic information, and again the procedures followed here lead to rational and useful results. They are shown in Figure 2. The temperature dependence of the interaction number is shown for four of the probes, namely, *n*-heptane, $CHCl_3$, ether, and *o*-xylene. Throughout the experimental range, the $\chi_{23(\mathrm{eff})}$ remains positive, albeit the slopes are consistently negative, indicating that the miscibility of the PP/FC system improves as the temperature rises.

Conclusions

(1) A review of using Flory–Huggins theory in the IGC experiment shows that χ_{23} is independent of the molar volumes of the stationary-phase as well as volatile-phase components.

(2) The often-noted difficulty of probe dependence for χ_{23}, when determined by IGC methods, has been examined from the point of view of differences between bulk and surface compositions of the stationary phase. A method has been proposed to estimate the effective composition of the surface region. With this convention, the probe dependence of χ_{23} for a two-component PP/FC additive system has been reduced dramatically. The validity of the IGC approach to measuring interaction parameters for mixed stationary phases has been enhanced significantly.

(3) In the PP/FC system chosen for study it was found that the surface concentration of FC additive always exceeded the bulk composition, differences varying strongly with the choice of vapor probe. Proposed causes for this include the preferential adsorption of the host PP on the chromatographic support and the migration of the additive to the surface of the stationary phase. In addition, nonrandom partitioning of the vapor phase has been retained from previous literature as a contributing cause to different surface and bulk compositions.

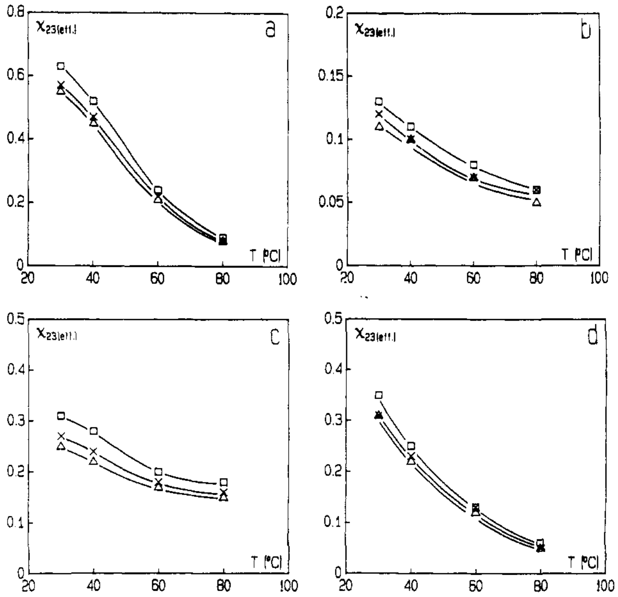

Figure 2. Dependence of $\chi_{23(\mathrm{eff})}$ on temperature for blends: (△) ω_3 = 0.1%; (×) ω_3 = 1%; (□) ω_3 = 10%. (a) Probe, *n*-C7; (b) probe, $CHCl_3$; (c) probe, ether; (d) probe, *o*-xylene.

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Registry No. PP, 9003-07-0; THF, 109-99-9; C_6, 110-54-3; C_7, 142-82-5; C_8, 111-65-9; C_9, 111-84-2; $CHCl_3$, 67-66-3; C_6H_6, 71-43-2; CCl_4, 56-23-5; EtAc, 141-78-6; acetone, 67-64-1; xylene, 1330-20-7; toluene, 108-88-3.