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Study of Polymer–Polymer Interaction Coefficients in Polymer Blends Using Inverse Gas Chromatography[†]

Zeki Y. Al-Saigh and Petr Munk*

Department of Chemistry and Center for Polymer Research, University of Texas, Austin, Texas 78712.
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ABSTRACT: A blend of poly(methyl acrylate) and poly(epichlorohydrin) was studied by inverse gas chromatography. In agreement with older studies on polymer blends, the apparent polymer–polymer interaction coefficient was found to be dependent on the chemical nature of the probe. An analysis of the experimental errors showed that the dependence is real and not an artifact. A probe-dependent term in the apparent interaction coefficient can be readily understood when the thermodynamic analysis is based on an expression for ΔG_{mix} which is more general and/or reflects a different model of interaction than the simple expression employed routinely. Analysis is presented for two expressions for ΔG_{mix}. Thus the apparent variability of the polymer–polymer interaction coefficient changes from an experimental nuisance into a valuable tool for understanding the thermodynamics of polymer blends.

Introduction

The pioneering work of Smidsrod and Guillet[1] has shown that gas chromatography using the polymeric stationary phase can reveal a number of interesting properties of the polymer. Because the stationary phase is the phase of interest (in contrast to traditional gas chromatography) the method is called inverse gas chromatography (IGC). Soon this method was used extensively for the measurement and evaluation of the thermodynamic interaction of polymers (above their glass transition) with low molecular weight probes.[2-31] While some authors caution that the thermodynamic data from IGC should be carefully analyzed to eliminate the effects of surface adsorption, most authors claim a reasonable agreement between the IGC data and data obtained by other methods (whenever available). At the present time, the papers and data quoted above represent the bulk of experimental knowledge of polymer–probe interaction, especially at elevated temperatures.

Deshpande et al.[11] were the first to suggest the use of IGC for studying polymer blends. Starting from the Flory–Huggins expression for the change of free enthalpy in mixing ΔG_{mix} which was extended to three-component systems, they proposed a method of analysis of IGC measurements on polymer blends which yielded the polymer–polymer interaction coefficient. They tested the method on a mixture of two low molecular weight compounds (tetracosane and dioctyl phthalate) and on a mixture of tetracosane with poly(dimethylsiloxane). Su et al. studied poly(vinyl chloride) plasticized by dioctyl phthalate.[17] Su and Patterson studied a blend of oligomeric polystyrene with poly(vinyl methyl ether).[18] DiPaola-Baranyi and Degre used blends of oligomeric polystyrene with poly(n-butyl methacrylate).[23]

Studies on blends of true high polymers are rare. Olabisi studied blends of poly(ϵ-caprolactone) with poly(vinyl chloride),[12] Walsh and McKeown reported the measurements on blends of poly(vinyl chloride) with several acrylates and methacrylates,[26] Doubé and Walsh analyzed the IGC of blends of poly(vinyl chloride) with chlorinated polyethylene,[27] and Walsh et al. studied blends of chlorinated polyethylene and ethylene–vinyl acetate copolymer.[28]

In all the papers quoted, the polymer–polymer interaction coefficient exhibited a significant dependency on the chemical nature of the probe.[11,12,17,18,23,26-28] Thus, the value of IGC for the measurement of the polymer–polymer interaction seemed to be severely compromised.

Recognizing that IGC is presently the only experimental technique that yields thermodynamic information on polymer blends with a relative ease, we decided to reexamine the situation. In this study we will focus on two aspects of IGC. First, we will show that the quantity that was in previous studies identified with the polymer–polymer interaction coefficient may actually contain other probe-dependent terms if a more general expression is used for ΔG_{mix}. Thus the variation of the apparent interaction coefficient with the probe may be real and its study may provide valuable information about the thermodynamics of polymer blends in the presence of low molecular weight compounds. Second, we will attempt an experimental verification of the above-described dependence on probe. A closer examination of the quoted papers convinced us that there was a possibility of experimental errors which may have led to some improper conclusions. Specifically, in a number of cases the experimental temperature was too close to the glass transition temperature T_g. For example, T_g for poly(vinyl chloride) is about 80 °C; most IGC measurements of its blends are done at 120 °C.[12,17,26,27] Yet the older IGC literature recommends that the IGC measurements of thermodynamic properties should be made at a temperature at least 50 °C higher than T_g to avoid the problems with a slow attainment of the equilibrium on the column.[2] Another possible source of error may be inadequate precision in the estimation of elution times in those cases when the specific retention volume V_g is very small, i.e., when the elution times of the marker and the probe are quite close.

For our experiments, we selected a blend of two polymers which both exhibit T_g at room temperature or below it. This gives us an opportunity to do the IGC experiments sufficiently far from T_g of either component while still safely below the decomposition temperature of the polymers. The experiments were designed to assess the experimental error in measurement of the apparent polymer–polymer interaction parameter and to find out whether its dependence on the nature of the probe is real or whether it is an experimental artifact.

Thermodynamics of Inverse Gas Chromatography

The elution behavior of volatile substances on gas chromatographic columns is usually described by means of the reduced specific retention volume $V_g°$, defined as

$$V_g° = \Delta t \frac{F}{w} \frac{273.15}{T_r} \frac{3}{2} \frac{(P_i/P_o)^2 - 1}{(P_i/P_o)^3 - 1} \qquad (1)$$

Here, $\Delta t = t_p - t_m$ is the difference between retention time

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[†] Dedicated to Professor W. H. Stockmayer on the occasion of his 70th birthday.

of the probe t_p and of the marker t_m. F is the flow rate of the carrier gas measured at room temperature T_r, w is the mass of the stationary phase, and P_i and P_o are the inlet and outlet pressures, respectively.

A routine analysis of the transport of a probe on a chromatographic column shows that V_g° is related to the partition coefficient (c_1^l/c_1^g) as

$$V_g^\circ = (c_1^l/c_1^g)v_2(273.15/T) \tag{2}$$

Here, c_1 is the concentration of the probe, and the superscripts l and g denote the liquid and gas phases, respectively; v_2 is the specific volume of the liquid phase (the polymer) at column temperature T.

If the stationary and mobile phases on the column are at equilibrium, then V_g° is amenable to thermodynamic interpretation. At equilibrium, the difference of $\Delta\mu_1$ of the chemical potential of the probe in either phase from the chemical potential in the reference state is the same.

$$\Delta\mu_1^l = \Delta\mu_1^g \tag{3}$$

The reference state is routinely chosen to be pure probe at the temperature of the column T and at a saturated vapor pressure P_1° at this temperature. Obviously, the reference chemical potential is then the same for both liquid and vapor phases.

In all the following considerations we will assume that both c_1^l and c_1^g are very small (ideal dilution) everywhere on the column. The thermodynamics of nonideal gases then yields

$$\Delta\mu_1^g = RT \ln \frac{RTc_1^g}{M_1P_1^\circ} - B_{11}P_1^\circ \tag{4}$$

where M_1 is the molecular weight of the probe, R is the gas constant, and B_{11} is the second virial coefficient of the probe in the gaseous state. It should be noted that the last term in eq 4 represents the correction for the nonideality of the gaseous probe under the assumption that the nonideality is moderate and that higher virial terms may be neglected. However, in many IGC experiments, temperatures above 100 °C and often up to 200 °C are used; frequently alkanes as low as pentane are used at these temperatures. Under these circumstances, P_1° may be very high (and the significance of the last term in eq 4 also high) and the truncation of the virial expansion may not be warranted. In fact, when enough care is not exercised the critical temperature of the probe may be exceeded, invalidating the whole thermodynamic analysis. In any case, when P_1° is very high the nonideal term should be treated with caution. Fortunately, while this consideration may be quite important in the calculation of the interaction parameters of the probe with a homopolymer, all the correction terms cancel out when the polymer–polymer interaction coefficient is calculated.

The thermodynamics of liquids and liquid mixtures yields for $\Delta\mu_1^l$

$$\Delta\mu_1^l = -V_1P_1^\circ + (\partial\Delta G_{\text{mix}}/\partial n_1)_{n\neq 1,P,T} \tag{5}$$

where n_j is the number of moles of component j in a mixture and V_j is its molar volume.

To proceed further we need an analytical expression for ΔG_{mix}. When the Flory–Huggins expression

$$\Delta G_{\text{mix}} = RT[n_1 \ln \phi_1 + n_2 \ln \phi_2 + \chi_{12}n_1\phi_2] \tag{6}$$

is used, the derivative in eq 5 will read

$$D_G = RT[\ln \phi_1 + 1 - V_1/V_2 + \chi_{12}] \tag{7}$$

In these equations, subscripts 1 and 2 denote the probe and the polymer, respectively, ϕ_i is the volume fraction of component i, χ_{12} is the Flory–Huggins interaction parameter, and D_G is a shorthand notation for the derivative in eq 5. If χ in eq 6 is considered to be a function of concentration, eq 7 will still apply: the value of χ_{12} at the infinite dilution of the probe should be used. Combination of eq 2–5 and 7 yields

$$\chi_{12} = \ln \frac{273.15Rv_2}{V_g^\circ V_1P_1^\circ} - 1 + \frac{V_1}{M_2v_2} - \frac{B_{11} - V_1}{RT}P_1^\circ \tag{8}$$

Equation 8 has been routinely used for calculation of χ_{12} from IGC experiments.

When the interaction of the probe with a blend of two polymers (subscripts 2 and 3) is considered, an expression for ΔG_{mix} of a three-component system is used which is an extension of eq 6 for three components (cf. Scott[32]).

$$\Delta G_{\text{mix}} = RT[n_1 \ln \phi_1 + n_2 \ln \phi_2 + n_3 \ln \phi_3 + n_1\phi_2\chi_{12} + n_1\phi_3\chi_{13} + n_2\phi_3\chi_{23}] \tag{9}$$

Equation 9 is usually considered satisfactory for nonpolar mixtures. In eq 9 the binary interaction coefficients χ_{ij} are considered to be parameters independent of the composition of the mixture. The derivative of eq 9 reads

$$D_G = RT\left[\ln \phi_1 + 1 - \frac{V_1}{V_2}\phi_2 - \frac{V_1}{V_3}\phi_3 + \phi_2\chi_{12} + \phi_3\chi_{13} - \frac{V_1}{V_2}\phi_2\phi_3\chi_{23}\right] \tag{10}$$

Recognizing that for a polymer mixture v_2 in eq 2 should be replaced by $w_2v_2 + w_3v_3$, where w_2 and w_3 are the weight fractions of the two polymers in the blend, one can easily derive eq 11

$$\ln \frac{273.15R(w_2v_2 + w_3v_3)}{V_g^\circ V_1P_1^\circ} - 1 - \frac{B_{11} - V_1}{RT}P_1^\circ = \phi_2\left(\chi_{12} - \frac{V_1}{M_2v_2}\right) + \phi_3\left(\chi_{13} - \frac{V_1}{M_3v_3}\right) - \frac{V_1}{V_2}\phi_2\phi_3\chi_{23} \tag{11}$$

Usually a new parameter χ'_{23} is introduced as

$$\chi'_{23} \equiv (V_1/V_2)\chi_{23} \tag{12}$$

If the parameters χ_{12} and χ_{13} are known (for example, from IGC experiments on appropriate homopolymers), χ'_{23} may be calculated from eq 11 as the only unknown.

Comparison of eq 11 and 8 suggests that the IGC study of blends is performed in the following way: three columns are prepared—two from homopolymers and a third from a blend using the same samples of homopolymers to make the blend. The three columns should be studied under conditions as identical as possible. Then all auxiliary parameters (P_1°, T, M_2, M_3, V_1, v_2, v_3, B_{11}) will be identical for the three experiments, and combination of eq 8 (taken twice for two homopolymers) and eq 11 for the blend will yield

$$\chi'_{23,\text{App}} \equiv \left[\ln \frac{V_{g,\text{blend}}}{w_2v_2 + w_3v_3} - \phi_2 \ln \frac{V_{g,2}}{v_2} - \phi_3 \ln \frac{V_{g,3}}{v_3}\right] \Big/ \phi_2\phi_3 = \chi'_{23} \tag{13}$$

Here, the second subscript of V_g identifies the nature of the column. From eq 13, χ'_{23} may be calculated even for probes for which the parameters P_1°, B_{11}, and V_1 are not known or are known with insufficient accuracy.

Equations 11 and/or 13 have been routinely used for calculation of χ'_{23} and produced values that depended upon the nature of the probe. On the other hand, theory embodied in eq 9 predicts that $\chi'_{23}/V_1 \equiv \chi_{23}/V_2$ is independent of the nature of the probe and depends only on the nature of the two polymers. We will now show that the discrepancy disapears when relations for ΔG_{mix} which are different from eq 9 are used in the calculations. Then $\chi'_{23,\text{App}}$ (defined by eq 13) may not be equal to χ'_{23}.

Equations 6 and 9 imply that the interaction free enthalpies are proportional to the volume fractions of the components. However, many authors have suggested that the molecular surfaces and not the volumes are important for contact interaction. Thus one of the possible forms of the expression for ΔG_{mix} may read

$$\Delta G_{\text{mix}} = RT[n_1 \ln \phi_1 + n_2 \ln \phi_2 + n_3 \ln \phi_3 + n_1\sigma_2\gamma_{12} + n_1\sigma_3\gamma_{13} + n_2\sigma_3\gamma_{23}] \quad (14)$$

$$\sigma_i = n_iS_i/\sum_j n_jS_j \quad (15)$$

Here, S_i is the molar interacting surface for component i, σ_i is its surface fraction, and γ_{ij} represents contact interaction parameters similar to χ_{ij} but defined with respect to surface fractions. If ΔG_{mix} is given by eq 14, D_G reads

$$D_G = RT\left[\ln \phi_1 + 1 - \frac{V_1}{V_2}\phi_2 - \frac{V_1}{V_3}\phi_3 + \sigma_2\gamma_{12} + \sigma_3\gamma_{13} - \frac{S_1}{S_2}\sigma_1\sigma_2\gamma_{23}\right] \quad (16)$$

Thus if the molar surfaces are known, the surface interaction coefficient $\gamma'_{23} \equiv \gamma_{23}(S_1/S_2)$ may be derived from experimental data similarly as in previous cases. It should be noted that a similar approach was used by Deshpande et al.[11] in conjunction with the equation-of-state theory. However, it is interesting to find out what would happen if the system obeys eq 14–16 but we try to interpret it in terms of volume fractions (this is actually done routinely). Let us convert eq 16 into volume fractions. For that purpose, it is convenient to introduce the surface-to-volume ratios $a_i \equiv S_i/V_i$. D_G now reads

$$D_G = RT\left\{\ln \phi_1 + 1 - \frac{V_1}{V_2}\phi_2 - \frac{V_1}{V_3}\phi_3 + \frac{\phi_2\gamma_{12}}{1 - \phi_3(1 - a_3/a_2)} + \frac{\phi_3\gamma_{13}}{1 - \phi_2(1 - a_2/a_3)} - \frac{(S_1/S_2)\phi_2\phi_3\gamma_{23}}{[1 - \phi_3(1 - a_3/a_2)][1 - \phi_2(1 - a_2/a_3)]}\right\} \quad (17)$$

To get a better feeling for the significance of eq 17 we will assume that the ratio a_3/a_2 is close (but not equal) to unity, i.e., that the two polymers have similar surface-to-volume ratios. After a few manipulations, we get

$$D_G = RT\left\{\ln \phi_1 + \left(1 - \frac{V_1}{V_2} + \gamma_{12}\right)\phi_2 + \left(1 - \frac{V_1}{V_3} + \gamma_{13}\right)\phi_3 - \phi_2\phi_3\left[\frac{S_1}{S_2}\gamma_{23}\left(\phi_2\frac{a_2}{a_3} + \phi_3\frac{a_3}{a_2}\right) + \gamma_{12}\left(1 - \frac{a_3}{a_2}\right) + \gamma_{13}\left(1 - \frac{a_2}{a_3}\right)\right]\right\} \quad (18)$$

When the calculations that led to eq 13 are repeated for the present case, the following relation is obtained:

$$\chi'_{23,\text{App}} = \gamma_{23}\frac{S_1}{S_2}\left(\phi_2\frac{a_2}{a_3} + \phi_3\frac{a_3}{a_2}\right) + \gamma_{12}\left(1 - \frac{a_3}{a_2}\right) + \gamma_{13}\left(1 - \frac{a_2}{a_3}\right) \quad (19)$$

The first term in the above expression for $\chi'_{23,\text{App}}$ is proportional to the polymer–polymer interaction coefficient (γ_{23}/S_2) and depends on the nature of the probe only through its molar surface S_1 in a way quite analogous to the dependence of χ'_{23} on V_1. However, the last two terms in eq 19 show that $\chi'_{23,\text{App}}$ depends also on the individual values of the coefficients γ_{12}, γ_{13}. The significance of this dependence varies from blend to blend: if the surface-to-volume ratio is very closely the same for both polymers forming the blend, the variation is insignificant. Otherwise, it may be quite appreciable, specifically if the interaction coefficients γ_{12} and γ_{13} are very different.

The variation of $\chi'_{23,\text{App}}$ with the probe is not quite unpredictable, however. If the individual values of γ_{1i} are measured for all probes and reasonable assumptions are made about the probe molar surfaces S_1, then values of $\chi'_{23,\text{App}}$ for all probes could be correlated by using only one adjustable parameter a_2/a_3.

Both eq 9 and 14 are based on models where the thermodynamic interaction in a ternary system may be expressed as a combination of the corresponding binary interactions. We have previously studied another type of ternary system: a polymer in a mixed solvent.[33,34] It proved necessary to use a more general expression for ΔG_{mix}. We have used a phenomenological relation suggested by Pouchlý et al.[35]

$$\Delta G_{\text{mix}} = RT[n_1 \ln \phi_1 + n_2 \ln \phi_2 + n_3 \ln \phi_3 + n_1\phi_2g_{12} + n_1\phi_3g_{13} + n_2\phi_2g_{23} + n_1\phi_2\phi_3g_{\text{T}}] \quad (20)$$

Here, g_{T} is a phenomenological function of the composition of the mixture, which is *defined* by eq 20 while all other quantities are specified. The three binary interaction functions g_{ij} are similarly defined for the three corresponding binary systems. The parameters g have a significance quite analogous to χ's of the older literature. The new symbol was introduced to stress that they depend on the composition of the mixture. In the newer symbolism, the parameter χ is related to g but has a slightly different significance.[33,34] In fact, it is given by the expression in the parentheses of eq 21; obviously, it is dependent on the composition of the blend, provided g_{23} depends on it.

When the manipulations that led to eq 13 are performed by using eq 20 instead of eq 9, the result reads

$$\chi'_{23,\text{App}} = \frac{V_1}{V_2}\left(g_{23} + \phi_2\frac{\mathrm{d}g_{23}}{\mathrm{d}\phi_2}\right) - g_{\text{T}} \quad (21)$$

Equation 21 predicts that the measured interaction parameters should change with the composition of the blend and with the nature of the probe due to the probe-dependent values of g_{T}. (The g_{T} values depend, of course, also on the composition of the mixture.) In other words, the IGC method does not measure directly the elusive parameter g_{23} or χ'_{23} but only its combination with another probe-dependent parameter, g_{T}.

Equation 21 is completely general and capable of describing all experimental data. However, because it is based on the phenomenological eq 20, it does not provide any clue to the physical significance of the parameter g_{T}. The significance can be deduced only after a large number of values are measured and analyzed for different probes and polymer blends.

Experimental Section

As we will describe later in this section, we have adapted a gas chromatograph for the IGC measurements using the procedures routinely used in this field of study.

The only exception was the method of coating of polymer (or polymer mixture) onto the inert support. Routinely, this is done by dissolving the polymer in a suitable solvent, adding the support, slowly evaporating the solvent (usually in a rotary evaporator),

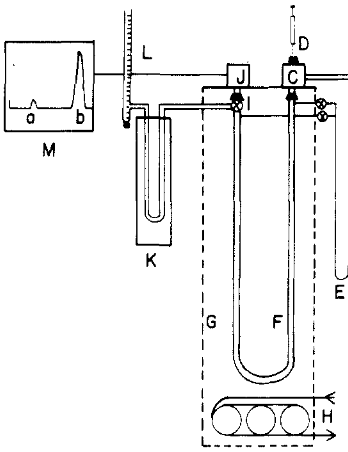

Figure 1. Schematic diagram of the adapted gas chromatograph: (A) carrier gas cylinder, (B) precision needle valve, (C) injection port, (D) microsyringe, (E) manometer, (F) column, (G) column oven, (H) cooling coil, (I) three-way valve, (J) detector, (K) Dewar flask, (L) bubble flow meter, (M) recorder ((a) marker, (b) probe).

drying the coated support in the oven and, sometimes, resieving it. During this lengthy procedure a significant part of the polymer may be lost on the walls of the evaporating vessel. Further losses may occur during resieving. The amount of the polymer on the column is one of the key quantities in calculation of V_g and the polymer loss may be very significant. (For example, a 5-ft column, $^1/_4$-in. o.d., may hold 10 g of support. With typical 7% loading, a loss of 7 mg of the polymer would cause 1% error in calculated V_g values. This is much more than is acceptable for a single source of error.) Consequently, most researchers analyze the coated support for its polymer content by either extraction or calcination. However, both methods were shown to be subject to significant errors.[36-38]

To achieve a better control of the amount of polymer we designed a new method (soaking method) for depositing the whole sample of polymer on support and into the column. In this method the polymer is dissolved in a solvent as usual. The support is piled on a watch glass or a similar dish and a small amount of the solution is applied on the top of the support pile. Care is taken to wet the pile as much as possible without letting the solution touch the surface of the dish, either around or under the pile. The solvent is allowed to evaporate and the pile is thoroughly mixed. Then a next portion of the solution is applied and the whole procedure is repeated until all the solution (including several rinsings of the solution flask) is used up. It takes typically 10–20 applications and requires only a few hours. In our experience no polymer was left on the surface of the dish. Then the support was dried in the oven and quantitatively transferred into the column with standard precautions of quantitative analytical chemistry. The method is fast, the amount of polymer is precisely known, and the analysis of the column material is avoided. We have compared a column prepared in the above-described manner with a column prepared by traditional coating in an evaporator. (The amount left on the walls of the evaporator vessel represented about 10% of the total polymer.) The chromatographic behavior of both columns was fully comparable. The small systematic differences in V_g° values on both columns could be accounted for by the uncertainty in the mass of polymer in the traditional column. In our opinion, these results fully justify the use of the new coating technique.

Apparatus and Procedures. Measurements were made on a modified Varian Aerograph Model 2100-40 gas chromatograph equipped with a flame ionization detector. Dried helium was used as a carrier gas. The flow rate was controlled by a precision needle valve, it was measured by a soap bubble flow meter. In order to be able to monitor the flow rate of the carrier gas frequently, we added a three-way 0.25-in. o.d. stainless steel valve at the column outlet (Figure 1). The valve would direct the carrier gas flow either to the detector or to the flow meter. The flow rate was measured at room temperature. The carrier gas was passed through a tube immersed in a Dewar flask filled with water at room temperature. The room and water temperatures were carefully monitored. The flow rate was monitored frequently by taking an average of three readings every time. These readings usually agreed within 0.5%. Our flow rate was typically about 11–16 mL/min; in a few preliminary experiments using twice as large flow rates we found no dependence of V_g values on the flow rate, within our experimental error.

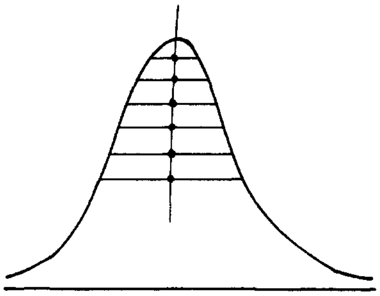

Figure 2. Graphical method for locating the peak maximum.

Table I
Description of Columns

column	I	II	III
Chromosorb W, g	7.5320	7.5098	7.9837
PECH, g	0.5049		0.2699
PMA, g		0.433	0.2639

The inlet and outlet pressures were frequently monitored by a mercury manometer. The inlet pressure was generally in the range of 900 mmHg (total pressure) while the outlet pressure was always atmospheric. Methane gas was used as a marker for retention time.

The probes were injected with 5-μL Hamilton syringes. To avoid the artifacts related to the overloading of the columns by the probe, we filled the syringe with the probe, emptied it two or three times, and then injected onto the column the air–probe vapor mixture left in the syringe. The amount injected in this way is not very reproducible, but the peaks obtained were always symmetrical. Two or three consecutive injections were made for each probe at each set of measurements; the retention times differed less than 2 s. The positions of peak maxima were obtained from the recorded plots of the elution peak by a method depicted in Figure 2: several lines parallel to the base line were drawn near the peak maximum, the distance between the two intersections of each line with the elution curve was halved, and the line connecting the midpoints was extrapolated to the top of the peak.

Materials. We selected a blend (kindly suggested by Prof. D. R. Paul from the Department of Chemical Engineering of this University) of poly(epichlorohydrin) and poly(methyl acrylate). Using differential scanning calorimetry, Prof. Paul's group has shown that these two polymers form a well-compatible blend. Both of these polymers have rather low glass transition temperatures (−22 and +18 °C, respectivey), making it possible to perform the measurements at relatively low temperatures and thus avoid problems with polymer degradation.

The sample of poly(methyl acrylate) (PMA) had intrinsic viscosity in butanone at 20 °C $[\eta] = 116$ mL/g ($M_v = 381\,000$). The poly(epichlorohydrin) (PECH) had at 20 °C in tetrahydrofuran $[\eta] = 48.2$ mL/g.

The polymers dissolved in tetrahydrofuran were coated onto Chromosorb W, 60–80 mesh. The support was acid washed and treated with dimethyldichlorosilane. The coated supports were packed into 5-ft copper columns, 0.25-in. o.d., previously washed with methanol. The columns were conditioned in the oven of the chromatograph for at least 6 h above 80 °C. The column parameters are given in Table I.

The probes were purchased from known sources and their purities checked chromatographically prior to use. The probes were selected to provide several groups of meaningfully related compounds. The groups differed significantly in their chemical nature.

Computations. The solute specific retention volume V_g° corrected to 0 °C was calculated from eq 1. Parameters χ were obtained from eq 8, where the term $V_1/(M_2v_2)$ was neglected.

Table II
Specific Retention Volumes V_g° (cm^3/g) for Poly(epichlorohydrin) (PECH), Poly(methyl acrylate) (PMA), and Polymer Blend of PECH and PMA at 76 and 125 °C

	PECH		PMA		blend	
	76 °C	125 °C	76 °C	125 °C	76 °C	125 °C
n-pentane	3.43		2.25		3.96	
n-hexane	7.22		4.69		8.03	
n-heptane	15.44	3.08	12.10	4.43	14.80	4.79
n-octane	30.19	6.76	23.35	7.72	28.05	7.90
n-decane	124.11	23.72	88.88	19.97	107.57	21.82
n-undecane		41.82	166.78	31.44	211.69	35.62
n-dodecane		68.31	321.54	51.33	462.25	59.22
methanol		5.51	33.88	10.11	28.12	7.54
ethanol	23.57	6.81	44.93	12.06	36.73	10.34
isopropyl alcohol	25.78	6.75	48.20	13.36	36.97	9.82
tert-butyl alcohol	24.54	6.20	45.81	12.18	35.90	9.87
ethyl acetate	51.06	11.63	53.11	16.58	51.41	13.89
tert-butyl acetate	61.48	13.21	57.91	15.81	58.76	14.92
methylene chloride	26.68	8.70	43.29	13.54	35.45	10.80
chloroform	46.14	11.80	77.78	20.57	60.14	16.91
carbon tetrachloride	33.51	9.50	39.03	13.19	37.15	11.30
trichloroethylene	60.49	15.01	78.63	21.35	69.13	17.84
cyclohexane	18.45	6.68	16.09	6.87	18.70	6.88
benzene	67.51	17.32	66.94	19.01	66.05	18.44
toluene	141.57	30.14	126.05	31.13	129.83	30.21
p-fluorochlorobenzene	263.70	48.82				
acetone		9.75	35.82	12.70	34.78	11.79
2-butanone	67.80	16.21	62.11	18.35	64.35	16.99
tetrahydrofuran	58.58	15.12	45.87	14.76	53.83	15.58

Table III
Interaction Parameters χ for Poly(epichlorohydrin) (PECH), Poly(methyl acrylate) (PMA), and Polymer Blend of PECH and PMA at 76 and 125 °C

	PECH		PMA		blend	
	χ_{12}		χ_{13}		$\chi'_{23,\mathrm{App}}$	
	76 °C	125 °C	76 °C	125 °C	76 °C	125 °C
n-pentane	1.50		2.36		1.47	
n-hexane	1.62		2.27		1.35	
n-heptane	1.66	1.82	2.05	1.59	0.36	1.01
n-octane	1.78	1.65	2.18	1.65	0.26	0.36
n-decane	1.96	1.62	2.43	1.93	0.14	0.04
n-undecane		1.67	2.59	2.09		−0.03
n-dodecane		1.79	2.73	2.20		0.04
methanol		1.24	1.38	0.77		−0.02
ethanol	1.52	0.92	1.01	0.48	0.42	0.49
isopropyl alcohol					0.13	0.07
tert-butyl alcohol					0.21	0.45
ethyl acetate	0.29	0.43	0.38	0.21	−0.05	−0.03
tert-butyl acetate					−0.05	0.12
methylene chloride	0.11	0.05	−0.24	−0.25	0.12	−0.06
chloroform	0.07	0.23	−0.32	−0.19	−0.03	0.27
carbon tetrachloride	0.61	0.57	0.60	0.37	0.10	0.01
trichloroethylene	0.42	0.42	0.29	0.20	−0.01	−0.05
cyclohexane	1.23	0.93	1.51	0.91	0.35	0.07
benzene	0.11	0.12	0.26	0.05	−0.06	0.06
toluene	0.15	0.18	0.40	0.29	−0.09	−0.05
acetone						0.21
2-butanone					−0.02	−0.07
tetrahydrofuran					0.19	0.18

The vapor pressures P_1° were calculated from the Antoine equation

$$\log P_1^\circ = A - B/(t + C) \tag{22}$$

where t is temperature in °C, and the constants, A, B, and C were taken from Dreisbach's compilation.[39] The molar volumes of the probes V_1 were calculated with eq 23

$$V_1 = M_1/\rho_L \tag{23a}$$

$$\rho_L + \rho_V = a - bt \tag{23b}$$

$$\rho_V = P_1^\circ M_1/RT \tag{23c}$$

where ρ_L and ρ_V are the densities of the liquid probe and its saturated vapor, respectively. M_1 is the molecular weight of the probe and P_1° is the pressure calculated from eq 22. The constants a and b are again taken from Dreisbach's compilation.[39] Second virial coefficients B_{11} were computed by using the equation[40]

$$B_{11}/V_c = 0.430 - 0.886(T_c/T) - 0.694(T_c/T)^2 - 0.0375(n - 1)(T_c/T)^{4.5} \tag{24}$$

where V_c and T_c are the critical molar volume and the critical temperature of the probe, respectively, and n is the number of carbon atoms in alkanes or the number of corresponding groups in other probes.

For PMA we used the value $v_2 = 0.846$ at 25 °C, which is the inverse of the density of poly(methyl methacrylate). We felt that this choice is reasonable because the two polymers have essentially the same partial molar volumes in several solvents.[41] The v_2 for

PECH ($v_2 = 0.735$) is an inverse of its density $\rho = 1.36$ g/mL at 20 °C.

Results and Discussion

Our measurements on PECH, PMA, and their blend are reported in Tables II and III. The values of $\chi'_{23,\mathrm{App}}$ were calculated by using eq 13. Thus they are not influenced by possible errors in the quantities V_1, $P_1°$, and B_{11}.

DiPaola-Baranyi and Guillet[21] reported the interaction parameters χ for a number of probes at three temperatures using PMA as a stationary phase. Their values were higher than ours by about 0.36; the difference was reduced to about 0.22 after we took into account the apparently different values for the specific volume of PMA in this work and the quoted paper. We cannot explain this discrepancy.

Values of χ reported in Table III are quite reasonable with respect to known solution behavior of the homopolymers. We are planning a more comprehensive measurement of these values and are therefore postponing their detailed analysis.

First, we needed to establish the reliability of our data and the overall experimental error. While our values of χ for both homopolymers show reasonable trends within each family of probes, we decided *not* to use these values of χ as a measure of the experimental error: they are unfavorably influenced by possibly large errors in the quantities V_1, $P_1°$, and B_{11}. The magnitude of these errors varies from probe to probe and depends on the reliability of the literature data. Moreover, $\chi'_{23,\mathrm{App}}$ are calculated by using eq 13, which does not contain these parameters: the experimental error depends only on the error in the observable quantities that constitute $V_g°$ according to eq 1 and 13.

In the analysis of our $\chi'_{23,\mathrm{App}}$ values we discount the values for pentane and hexane at 76 °C and the values for heptane and cyclohexane at 125 °C. Due to very low values of $V_g°$, these $\chi'_{23,\mathrm{App}}$ values are subject to very large errors. For the remaining data we assume that the difference of the $\chi'_{23,\mathrm{App}}$ values for the same probe at our two experimental temperatures is less than the experimental error. As is apparent from Table III, these differences for different probes are completely random: the difference is less than or equal to about 0.10 (with the exception of *tert*-butyl alcohol, *tert*-butyl acetate, methylene chloride, and chloroform). Thus we estimate the error in $\chi'_{23,\mathrm{App}}$ as about 0.10. Values of $\chi'_{23,\mathrm{App}}$ were calculated from eq 13, which implies that the combined error in values of $V_{g,2}°$, $V_{g,3}°$, and $V_{g,\mathrm{blend}}°$ is less than 3%; individual values of $V_g°$ suffer then an error of about 2%.

This estimate seems quite reasonable when the experimental procedures are considered. The values of $\chi'_{23,\mathrm{App}}$ in Table III (with the exception of the discounted ones) are between −0.09 and +0.49. This spread is much larger than our estimated error. Moreover, there is a clear difference between different families of probes. The nonpolar probes and the alcohols tend to exhibit positive values of $\chi'_{23,\mathrm{App}}$ while the polar probes have mainly negative values. These results lead to the conclusion that the differences for the $\chi'_{23,\mathrm{App}}$ values for different probes are real. If a more meaningful value $\chi'_{23,\mathrm{App}}/V_1$ is calculated, the differences between probes will remain about equally important. In Figure 3 we have plotted the $\chi'_{23,\mathrm{App}}$ values for alkanes against the number of carbons in the alkane. The scatter of points is clearly less than the overall trend in the plot, proving again that the differences are real. However, due to our still appreciable experimental error, we prefer not to speculate about the significance of the differences in $\chi'_{23,\mathrm{App}}$. We intend to show only that the differences are real and not artifacts.

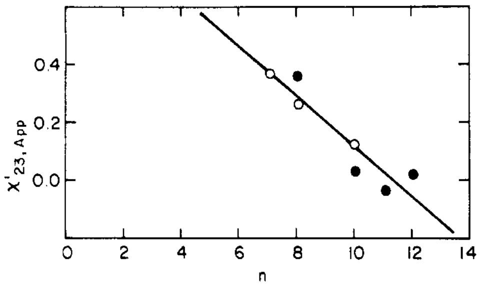

Figure 3. Blend of PMA and PECH. Dependence of $\chi'_{23,\mathrm{App}}$ on the number of carbons in straight-chain alkanes. Open symbols for data at 76 °C; full symbols for data at 125 °C.

It is also interesting to compare our spread of values of $\chi'_{23,\mathrm{App}}$ with the data reported in the literature. Deshpande et al.[11] measured a mixture of two low molecular weight compounds: tetracosane and dioctyl phthalate using mainly hydrocarbon probes. The $\chi'_{23,\mathrm{App}}$ varied with the probe between 0.43 and 0.86. Their other system was tetracosane mixed with poly(dimethylsiloxane). Again the $\chi'_{23,\mathrm{App}}$ varied with the probe (only hydrocarbons were used) between 0.37 and 1.01. In these systems, where at least one component of the stationary phase is a low molecular weight compound, the rather high $\chi'_{23,\mathrm{App}}$ value may not prevent the miscibility of the components, unlike in a two-polymer mixture. In both cases the variation of $\chi'_{23,\mathrm{App}}$ with the probe could not be eliminated by considering the molar volumes of either the probes or the molecular surfaces. Clearly, the spread of values obtained by Deshpande et al.[11] is comparable to the one we report here.

Su and Patterson[18] studied a blend of polystyrene ($M_n \sim 600$) with poly(vinyl methyl ether) ($M_v \sim 10000$). This polymer pair is considered to be well compatible. A polystyrene oligomer was selected to avoid the difficulties connected with the high glass transition temperature of polystyrene. For most probes, the $\chi'_{23,\mathrm{App}}$ values were between −0.10 and +0.30. (Similar values were observed for two different compositions; the blend richer in polystyrene yielded values smaller by about 0.1.) However, isopropyl alcohol (a poor solvent for both polymers) yielded values as high as 1.47; chloroform (the best solvent for both polymers) yielded 0.65. Again, the spread of values was comparable to ours.

DiPaola-Baranyi and Degre[23] studied blends of polystyrene with poly(*n*-butyl methacrylate). Because blends were incompatible when higher molecular weight polystyrene ($M_w \sim 110000$) was used, the relevant data were obtained by using an oligomer with $M_n \sim 1709$. While for individual columns the $\chi'_{23,\mathrm{App}}$ values were clustered closely together (the difference between the highest and lowest values was usually less than 0.2), there was a large unexplained variation of $\chi'_{23,\mathrm{App}}$ among different columns (differing in the polymer/polymer ratio). The highest average value, 0.42, was observed for a column with 30% polystyrene, while the lowest average value, −0.23, was found with 35% polystyrene.

In the papers which are concerned either with plasticized poly(vinyl chloride)[17] or with blends of poly(vinyl chloride) with other polymers,[12,26,27] a much broader spread of $\chi'_{23,\mathrm{App}}$ values is reported. This is also true for blends of chlorinated polyethylene and ethylene–vinyl acetate copolymer.[28] (It should be noted that the papers from Walsh's laboratory report $\chi'_{23,\mathrm{App}}/V_1$ values.[26-28] Because V_1 is typically about 100 mL/mol, their numerical values are smaller by about 2 orders of magnitude than the corresponding values of $\chi'_{23,\mathrm{App}}$.) It is possible that the large spread of experimental values in these studies was caused either by too close proximity to glass transition temperature (in the case of poly(vinyl chloride)) or by incipient phase separation in the latter system.

Conclusions

In our experimental system, the measured values of $\chi'_{23,\mathrm{App}}$ vary between −0.09 and +0.49, with an experimental error of about 0.10. Moreover, values within each family of probes are clustered together. Thus the dependence of $\chi'_{23,\mathrm{App}}$ (and also $\chi'_{23,\mathrm{App}}/V_1$) on the nature of the probe seems to be real. The magnitude of this variation is comparable to the magnitude reported in the literature.

We believe that our new coating technique brought under control the difficult-to-measure quantity: the amount of polymer on the chromatographic column. However, although the experimental precision was satisfactory for establishing the reality of the variation of $\chi'_{23,\mathrm{App}}$ with the probe, it is not fully satisfactory for quantitative measurement of that variation. Further improvement in measurement of the flow rate, retention time, and column pressure is needed to bring the error in $V_g°$ under 1%.

Using two plausible relations for ΔG_{mix} of the three-component system, we have shown that the dependence of $\chi'_{23,\mathrm{App}}/V_1$ on the nature of the probe can be predicted theoretically. Measurement of this dependence could provide valuable insight into the thermodynamics of polymer blends.

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Registry No. Poly(methyl acrylate) (homopolymer), 9003-21-8; poly(epichlorohydrin) (homopolymer), 24969-06-0; poly(epichlorohydrin) (SRU), 61419-11-2.

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