# Characterization of Semicrystalline Polymers by Inverse Gas Chromatography. 2. A Blend of Poly(vinylidene fluoride) and Poly(ethyl methacrylate)

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ABSTRACT: The compatibility of a blend of semicrystalline poly(vinylidene fluoride) and poly(ethyl methacrylate) was characterized by using the inverse gas chromatography method above and below the PVF2 melting point. The IGC method was found to be capable of detecting the melting point depression of a polymer blend containing a crystallizable homopolymer. The thermodynamics of PVF2-PEMA miscibility obtained from the melting point depression are discussed. The values of the PVF2-PEMA interaction parameter and the energy parameter were found to be -0.33 and -3.15 cal/mL, respectively. The obtained values from the IGC method are in excellent agreement with the values obtained by the calorimetric method. Comparisons are made for the interaction parameters obtained from the melting point depression using the IGC and the calorimetric method. Our obtained values of interaction parameters and interaction energy revealed the miscibility of PVF2 and PEMA over weight fractions of 25-75% of PVF2 and over a temperature range of 140-195 °C. The interaction parameters for PVF2-PEMA blends were found independent of a number of carbons in the series of the three families, the composition of the blends, and the temperature range used. The molar heats of sorption of acetates into the blend layer were calculated for all the blend compositions. They ranged from -9.50 to -8.32 kcal/mol, indicating the miscibility of the PVF2-PEMA blend. The miscibility of the blend is achieved at all weight fractions used, and it is mostly noticed when the composition of the blend is at 50:50 w/w compositions of the blend.

## Introduction

Polymer blends have been known since the 1940s. However, only recently have they become important technologically.[1-10] Today, there is an intensive interest in polymer blends because this approach is a rapid and less expensive route than in developing new polymers. The characterization of polymer blends depends strongly on the miscibility (compatibility) of the pair of polymers. Miscibility occurs when specific interaction forces develop between the backbones of the two polymers. Specific interactions may be in the form of hydrogen bonding,[11] charge-transfer complexes, acid-base type interactions, dipole moments, and electron donor-acceptor complexes,[12,13] etc. These specific interactions are of a highly directional nature and are present in addition to the dispersive forces. Thus, the interaction between unlike polymers is "repulsive" for the majority of orientations that bring into proximity the interacting groups.[14] It is generally known that the thermodynamic basis for the evaluation of miscibility of polymer blends is an exothermic heat of mixing.[7-9]

The structure of polymers and their miscibility can be obtained by quantifying the interaction parameters of a polymer pair by experimental means. The main problems, however, is how this quantification of the interaction parameters will be made. Unfortunately, little data exist in the literature on polymer blends, and the number of methods available for measuring polymer-polymer interactions are few. A few techniques that have emerged to date are promising. Among them is the inverse gas chromatography method. Direct methods used for this purpose are measurement of the glass transition temperature, number of thermal and mechanical methods,[15,16] NMR method,[17] electron spin resonance method,[18] solvent vapor sorption method, heat of mixing measurements, small-angle light scattering,[19] small-angle X-ray scattering, small-angle neutron scattering,[20,21] and inverse gas chromatography (IGC).[22-35,49] Unfortunately, most of these techniques are beset by a number of technical problems; for instance, in the vapor sorption method, a long time is needed to attain equilibrium between the vapor and the polymer. While in the IGC method, the concentration of the probe is always vanishingly small, which results in a fast establishment of the equilibrium between the gas phase and the polymer in the chromatographic column.

The characterization and the thermodynamics of a blend containing semicrystalline poly(vinylidene fluoride) (PVF2) and a series of amorphous counterpolymers, mainly acrylates, have been the subject of extensive studies.[18,36-43,53] A variety of methods were utilized in these studies and were used to explore the miscibility of PVF2 and the counterpolymer. Among these studies, IGC has only been applied to two polymer blend systems (PVF2-PMMA[23] and PVF2-PEMA.[36]) The calorimetric method was also applied to miscible blends of PVF2 and counterpolymers involving poly(methyl methacrylate) (PMMA), poly($\epsilon$-caprolactone) (PCL), poly(vinyl methyl ether) (PVME), and poly(vinyl methyl ketone) (PVMK).[38,40,53] The blend of PVF2-PMMA was further characterized by using methods other than the calorimetric method such as the spin label method,[18] photolysis and spin probe methods,[37] and the X-ray diffraction method.[39] On the other hand, the compatibility of PVF2 and poly(ethyl methacrylate) (PEMA) was also investigated by using the calorimetric method.[42,43] All PVF2-counterpolymers blends mentioned above were found to be fully compatible.

Deshpande et al.[44] were the first to apply the IGC method to a blend system. They suggested that the method is useful in characterizing a mixture of two low molecular

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weight polymers. They were able to calculate $\chi_{23}$ for the polymer blend, which depended on the chemical nature of the solute. They could not eliminate this dependence either by using the molar volumes of the probes or the molar surfaces. Olabisi[45] supported Deshpande's findings: in characterizing a series of polymer blends system, he attributed the solvent dependency to the inability of the modified Flory–Huggins theory to account for all the polymer–solute interactions. In our recent examination of a blend of poly(methyl acrylate)–polyepichlorohydrin, we reached a similar conclusion.[22] We showed that $\chi_{23}$ may contain other solute-dependent contributions to the free energy of mixing that are not properly accounted for by the polymer solution thermodynamic theories. In addition, we pointed out, in the same study, that the variation of $\chi_{23}$ from solute to solute is partly due to the experimental errors and artifacts. Then we undertook a series of critical and corrective procedures that yielded a considerable reduction of the experimental errors.[46–48] Munk et al.[49] were able to calculate the interaction parameter $B$ of a poly($\epsilon$-caprolactone)–polyepichlorohydrin blend and to correlate this parameter with the Hildebrand solubility parameter of the solute. This correlation was a successful attempt, for the first time, to obtain a manageable way by which a binary interaction data can be obtained on polymer blend system.

In this paper, we examined the thermodynamics of a blend of PVF2 and PEMA by the IGC method in our effort to promote the IGC as a reliable method for polymer and polymer blend characterization. Recently, there has been an increasing interest in blends of semicrystalline PVF2 and a number of amorphous counterpolymers, because they are industrially important. Recently, we applied the IGC method to the characterization of PVF2, as a homopolymer, above and below its melting temperature[50] and of PEMA close to its decomposition temperature.[51] We concluded that a wealth of information can be obtained on semicrystalline and amorphous polymers using the IGC method. We are, in this paper, extending the application of the IGC method to a blend of semicrystalline–amorphous polymers (PVF2–PEMA). We will show, for the first time, that miscibility of polymer blends containing a semicrystalline polymer can be obtained, with reliable precision, by measuring the melting point depression for the crystalline–amorphous mixture using the IGC method. All previous melting point depressions of blends containing crystallizable polymers were obtained by using the calorimetric method. The melting point depression was never obtained by the IGC method previously. We will relate the polymer–polymer interaction coefficient $\chi_{23}$ to the interaction energy parameter $B_{23}$. We will show that our thermodynamic parameters, based on melting point depression data obtained by the IGC method, are in excellent agreement with those obtained by the calorimetric method. We will relate the thermodynamic quantities of the blend to the structure and the interactions between PVF2 and PEMA.

## Theory

In a polymer blend mixture, the key term in the miscibility of a polymer–polymer pair is the free energy of mixing.

$$\Delta G_m = \Delta H_m - T\Delta S_m \tag{1}$$

The negative value of $\Delta G_m$ indicates that the polymer pairs are miscible. However, this is not a sufficient condition since stability considerations require in addition, for binary mixtures, that

$$\partial^2 \Delta G_m / \partial \phi_i^2 > 0 \tag{2}$$

where $\phi_i$ is the volume fraction of $i$th component. The volume fraction term was first introduced by the Flory–Huggins theory, which describes polymer solutions with reasonable success.[52] The free energy of mixing as described by the Flory–Huggins theory is

$$\Delta G_m = RT\{n_1 \ln \phi_1 + n_2 \ln \phi_2 + n_1\phi_2\chi\} \tag{3}$$

where $n_i$ is the number of moles of the $i$th component. $RT$ has its usual meaning and $\chi$ is a parameter that is inversely proportional to the absolute temperature. Parameter $\chi$ was introduced as an enthalpic contact parameter; the two logarithmic terms represent the (combinatory) entropy of mixing.

The combinatory entropy of mixing was well approximated by Flory[52] to read

$$\Delta S_m = -R(V_1 + V_2)\left[\frac{\phi_1 \ln \phi_1}{V_1} + \frac{\phi_2 \ln \phi_2}{V_2}\right] \tag{4}$$

where $V_1$ and $V_2$ are the molar volumes of these components compromising the mixture. This model further assumes that the heat of mixing is described by a Van Laar expression

$$\Delta H_m = (V_1 + V_2)B\phi_1\phi_2 \tag{5}$$

where $B$ is a binary interaction energy parameter. If we relate $B$ to the parameter $\chi$, the relationship reads

$$\frac{B}{RT} = \frac{\chi_1}{V_1} = \frac{\chi_2}{V_2} = \chi_{12} \tag{6}$$

Equation 6 can be extended to multicomponent mixtures as follows

$$\frac{\Delta H_m}{V} = \sum_{i>j} B_{ij}\phi_i\phi_j \tag{7}$$

where $V$ = total volume of the mixture, $\sum_i V_i$. While the sign of the combinatorial entropy always favors mixing, it is clear from eq 4 that its magnitude is greatly diminished for molecular weights (or molar volumes) on the order of those for the most important polymers; particularly, in our case, the molecular weights of both polymers used are high. Thus, in the limit of high molecular weights, the conditions for miscibility can only be satisfied by a negative interaction parameter $\chi_{23}$, leading to the conclusion that exothermic mixing is a requirement for miscibility in high molecular weight polymer–polymer blends.

Recently, we examined the elution behavior on the chromatographic column and analyzed the thermodynamics of inverse gas chromatography.[22] The reduced specific retention volume $V_g°$, is commonly used to describe the elution behavior of solutes, and it is defined as

$$V_g° = \Delta t \frac{F}{W} \frac{273.15}{T_r} \frac{3}{2} \frac{(P_i/P_o)^2 - 1}{(P_i/P_o)^3 - 1} \tag{8}$$

Here, $\Delta t = t_p - t_m$ is the difference between the retention time of the solute, $t_p$, and that 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 solute on a chromatographic column shows that $V_g°$ is related to the partition coefficient ($c_1^{l}/c_1^{g}$) as

$$V_g^\circ = (c_1^{l}/c_1^{g})v_2(273.15/T) \qquad (9)$$

Here, $c_1$ is the concentration of the solute, 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 the column temperature, $T$.

If the stationary and mobile phases on the column are at equilibrium, then $V_g^\circ$ is amenable to thermodynamic interpretation. At equilibrium, the chemical potential of the solute in the gas phase is given by

$$\Delta\mu_1^{g} = RT \ln \frac{RTc_1^{g}}{M_1P_1^\circ} - B_{11}P_1^\circ \qquad (10)$$

where $M_1$ is the molecular weight of the solute, $R$ is the gas constant, and $B_{11}$ is the second virial coefficient of the solute in the gaseous state. It should be noted that the last term in eq 10 represents the correction for the nonideality of the solute and that higher virial terms may be neglected.

While the chemical potential of the solute in the liquid phase, the polymer used in our case, is

$$\Delta\mu_1^{l} = -V_1P_1^\circ + (\partial\Delta G_{mix}/\partial n_1) \qquad n = l, p, T \qquad (11)$$

where $n_1$ is the number of moles of component 1 in a mixture and $V_1$ is its molar volume. At equilibrium, both chemical potentials are equal to each other. Combination of the derivative of eq 11 and eqs 3, 9, and 10 yields

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

Equation 12 has been routinely used for calculation of $\chi_{12}$ from IGC experiments.

When a polymer pair is used as a stationary (liquid) phase in a chromatographic column, we will use subscripts 2 and 3 to represent polymers 1 and 2, respectively. Then the interaction between the two polymers is expressed in terms of the free energy of mixing, $\Delta G_m$, which is an extension of eq 3 for three-component systems

$$\Delta G_m = RT[n_1 \ln \phi_1 + n_2 \ln \phi_2 + n_3 \ln \phi_3 + n_1\phi_2\chi_{12} + n_1\phi_3\chi_{13} + n_2\phi_3\chi_{23}] \qquad (13)$$

where $\chi_{23}$ is the interaction parameters between the polymer–polymer pair. Recognizing that, for a polymer mixture, $v_2$ in eq 9 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 14: Usually

$$\ln \frac{273.15R(w_2v_2 + w_3v_3)}{V_g^\circ V_1P_1^\circ} - 1 - \frac{B_{11} - V_1}{RT}P^\circ = \phi_2\left\{\chi_{12} - \frac{V_1}{M_2v_2}\right\} + \phi_3\left\{\chi_{13} - \frac{V_1}{M_3V_3}\right\} - \frac{V_1}{V_2}\phi_2\phi_3\chi_{23} \qquad (14)$$

a new parameter $\chi'_{23}$ is introduced as

$$\chi'_{23,app} = (V_1/V_2)\chi_{23} \qquad (15)$$

Comparison of eqs 14 and 12 suggests that, to obtain $\chi_{23}$ for the blends, in IGC experiments, $\chi_{12}$ and $\chi_{13}$ have to be known. In this case three columns are usually 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 identical conditions of column temperature, carrier gas flow rate, inlet pressure of the carrier gas, and the same solutes. In this case, all auxiliary parameters ($P_1^\circ$, $T$, $M_2$, $M_3$, $V_1$, $v_2$, $v_3$, $B_{11}$) will be identical for the three experiments, and a combination of eq 12 (taken twice for two homopolymers) and eq 14 for the blend will yield:

$$\chi'_{23,app} = \left[\ln \frac{V_{g,blend}}{w_2v_2 + w_3v_3} - \phi_2 \ln \frac{V_{g,2}}{v_2} - \phi_3 \ln \frac{V_{g,3}}{v_3}\right]\phi_2\phi_3 = \chi'_{23} \qquad (16)$$

Here, the second subscript of $V_g^\circ$ identifies the nature of the column. From eq 16, $\chi'_{23}$ may be calculated even for probes for which the parameters $P_1^\circ$, $B_{11}$, and $V_1$ are not known or are known with insufficient accuracy.

Equations 14 and 16 have been routinely used for calculation of $\chi'_{23}$ and produced values that depend upon the nature of the probe. On the other hand, theory embodied in eq 13 predicts that $\chi'_{23}/V_1 = \chi'_{23}/V_2$ is independent of the nature of the probe and depends only on the nature of the two polymers.

In a blend containing a semicrystalline polymer, like PVF2, the polymer–polymer interaction coefficient, $\chi'_{23}$, and the interaction energy parameter, $B_{23}$, can be obtained experimentally in a different way than explained earlier. The melting point depression of a polymer mixture (blend) containing a semicrystalline polymer can be useful for quantifying the heat of mixing of the polymer pair.[41–43,53–55] A simple model for polymer–polymer mixtures, one of them crystallizable, is the Flory–Huggins theory.[41,52,53] Information can only be obtained close to the pure semicrystalline polymer melting point. However, the melting point measured is influenced by the number of factors (perfection, size, and environment of crystals) that can be accounted for. A careful analysis of melting point depression yields an approximation of the polymer blend interaction parameters adequate for the purpose of exploring the miscibility of the blend and its relationship with their molecular structure.

From Flory–Huggins theory[52] and Scott's thermodynamic treatment for mixing a semicrystalline polymer with a miscible diluent, we have

$$\frac{1}{T_m} - \frac{1}{T_m^\circ} = -R(V_{2u}/\Delta H_{2u})[\rho_2 \ln v_2/M_2 + (\rho_2/M_2 - \rho_3/M_3)v_3 + (B_{23}/RT_m)v_3^2] \qquad (17)$$

where subscripts 2 and 3 refer to PVF2 and PEMA, respectively. $T_m$ and $T_m^\circ$ are the melting points of polymer 2 (PVF2) in the mixture and pure PVF2, respectively. The quantities $v_2$, $v_3$, $\rho_2$, $\rho_3$, $M_2$, and $M_3$ are the volume fractions, density, and molecular weights of PVF2 (2) and PEMA (3), respectively. The quantity $\Delta H_{2u}/V_{2u}$ is the heat of fusion of PVF2 per unit volume; it was taken from ref 53 as 44.00 cal/mL. $B_{23}$ is the polymer–polymer interaction energy, which is related to Flory–Huggins interaction parameter $\chi_{23}$ as in the following equation where $V_3$ is the molar volume of component 3 (PEMA).

The first two terms in eq 17 are the entropic contribution, and the third term is the enthalpic contribution. Since the molecular weights of both PVF2 and PEMA used in this work are high, then the entropic contribution represents less than 1 °C, which plays a minor role in the melting point depression. Therefore, the values of the first two terms will be very small and can be neglected. Then eq 17 reads

$$B_{23} = RT_m^\circ(\chi_{23}/V_3) \qquad (18)$$

Rearrangement of eq 19 yields

$$\frac{1}{T_m} - \frac{1}{T_m^\circ} = -(V_{2u}/\Delta H_{2u})(B_{23}/T_m)v_3^2 \qquad (19)$$

**Table I**
**Stationary Phase and Columns Description**

| column no. | PVF2 wt, g | PEMA wt, g | PVF2 wt fraction | support wt, g | load, % | column length, cm |
|---|---|---|---|---|---|---|
| 1 | 0.5585 | 0 | 0 | 8.0010 | 6.98 | 152 |
| 2 | 0.1395 | 0.4189 | 0.2498 | 8.0001 | 6.98 | 152 |
| 3 | 0.2804 | 0.2797 | 0.5006 | 7.9985 | 7.00 | 152 |
| 4 | 0.3386 | 0.2272 | 0.5984 | 8.0004 | 7.07 | 152 |
| 5 | 0.4178 | 0.1415 | 0.7470 | 8.0004 | 6.99 | 152 |
| 6 | 0 | 0.5635 | 0 | 8.0023 | 7.04 | 152 |

Equation 20 can be rewritten in the following form:

$$\frac{T_m^\circ - T_m}{T_m T_m^\circ} = -(V_{2u}/\Delta H_{2u})(B_{23}/T_m)v_3^2 \qquad (20)$$

Equation 21 is used, in this work, to calculate the polymer–polymer interaction energy for a PVF2–PEMA blend.

$$\Delta T_m = T_m^\circ - T_m = -T_m^\circ (V_{2u}/\Delta H_{2u})B_{23}v_3^2 \qquad (21)$$

## Experimental Section

**Materials.** Fifteen polar and nonpolar probes were used in this study. They were selected to provide several groups of a chemically different nature and polarity. They all were purchased from Aldrich Chemical Co. as chromatographic grade, their purity being checked by gas chromatography prior to use. Poly(ethyl methacrylate) was supplied by Aldrich Chemical Co. in powder form. Its molecular weight was estimated from intrinsic viscosity, $[\eta] = 0.46$ dL/g in 2-butanone at 23 °C, to be 215 000 by using published Chinai and Samuels constants[18] ($a = 0.79$, $K = 0.002\,83$ mL/g). Poly(vinylidene fluoride) (PVF2) was obtained from Aldrich Chemical Co. in powder form. Its molecular weight was determined earlier as 250 000 by using the GPC technique.[50] Chromosorb W (AW-DMCS treated, 60/80 mesh) was obtained from Analabs.

**Instrumentation and Procedures.** All chromatographic measurements were run on a modified Varian 1800 Aerograph gas chromatograph equipped with both thermal conductivity and flame ionization detectors. The thermal conductivity detector was selected over the FID detector for reasons discussed elsewhere.[50,51] The control of the carrier gas flow, marker retention time, experimental setup, temperature measurements, and inlet and outlet carrier gas pressure were discussed in an earlier publication.[50,51]

The control of the mass of the homopolymers and the polymer blends in the stationary phase that has been accomplished by using a soaking type method for coating the polymer on the support was recently developed by us with excellent precision.[22] Six columns were prepared with 5-ft-long copper tubing, with $^1/_4$ in. o.d. The copper tubings were washed with methanol and were annealed prior to use. Table I shows the description of these columns. Six weight fractions of PVF2 and PEMA were used, ranging from 0% to 100% PVF2. The resulting load of the blend on the column was almost 7%, in all columns, by weight of the polymer blend relative to the weight of the solid support. Blending was achieved by dissolving certain weights of PVF2 and PEMA in hot *N,N*-dimethylacetamide (DMA) solution and deposited onto the solid support. Columns were conditioned at 80 °C and a fast carrier gas glow rate for 24 h prior to use. Probes were injected onto the columns with 1-μL Hamilton syringes. Three consecutive injections were made for each probe at each set of measurements. An injection volume of 0.2 μL was selected so as to remain within a safe region with a minimum effect on the retention volumes.[50] The retention times of the probes were measured with high precision by using an analog to digital converter (digital multimeter interfaced with IEEE-488 Keithley), which was interfaced with an IBM compatible personal computer via IEEE-488 card. The automation of our chromatographic system, the correction for the solid "inert" support, the detection, and integration of the chromatographic signal were reported earlier.[50,51] The automation procedure saved a tremendous amount of time and reduced the experimental error in retention time considerably.

**Table II**
**Specific Retention Volumes of Solutes at 175, 185, and 195 °C and Various Weight Fractions of PVF2**

| probe | 0% PVF2 | 25% PVF2 | 50% PVF2 | 75% PVF2 | 100% PVF2 |
|---|---|---|---|---|---|
| | | A. At 175 °C | | | |
| octane | 5.46 | 4.33 | 3.24 | 2.33 | 1.47 |
| nonane | 9.02 | 7.24 | 5.45 | 3.94 | 2.56 |
| decane | 13.46 | 10.62 | 8.06 | 5.74 | 3.65 |
| undecane | 22.52 | 17.12 | 12.21 | 8.32 | 5.02 |
| dodecane | 35.35 | 25.25 | 17.12 | 10.57 | 5.69 |
| methyl acetate | 3.94 | 3.91 | 4.01 | 4.32 | 5.18 |
| ethyl acetate | 4.91 | 4.99 | 5.29 | 5.93 | 7.45 |
| propyl acetate | 7.56 | 7.56 | 7.78 | 8.43 | 10.16 |
| butyl acetate | 11.75 | 11.47 | 11.53 | 12.11 | 13.88 |
| methanol | 2.21 | 2.14 | 2.16 | 2.31 | 2.76 |
| ethanol | 2.57 | 2.41 | 2.31 | 2.35 | 2.61 |
| 2-propanol | 3.71 | 3.32 | 3.01 | 2.82 | 2.84 |
| butanol | 9.57 | 8.64 | 7.92 | 7.54 | 7.71 |
| 2-pentanol | 9.76 | 8.79 | 8.04 | 7.63 | 7.82 |
| | | B. At 185 °C | | | |
| octane | 4.26 | 3.49 | 2.71 | 2.02 | 1.37 |
| nonane | 7.58 | 6.16 | 4.72 | 3.49 | 2.33 |
| decane | 11.62 | 9.22 | 7.04 | 5.11 | 3.36 |
| undecane | 18.61 | 14.32 | 10.51 | 7.19 | 4.50 |
| dodecane | 29.31 | 21.36 | 14.55 | 9.31 | 5.13 |
| methyl acetate | 2.83 | 2.87 | 3.06 | 3.41 | 4.36 |
| ethyl acetate | 4.01 | 4.06 | 4.28 | 4.79 | 6.04 |
| propyl acetate | 6.74 | 6.61 | 6.64 | 7.01 | 8.16 |
| butyl acetate | 9.41 | 9.17 | 9.21 | 9.64 | 11.16 |
| methanol | 1.78 | 1.79 | 1.88 | 2.14 | 2.74 |
| ethanol | 2.26 | 2.26 | 2.35 | 2.65 | 3.41 |
| 2-propanol | 2.86 | 2.75 | 2.75 | 2.92 | 3.46 |
| butanol | 8.02 | 7.37 | 6.89 | 6.67 | 7.12 |
| 2-pentanol | 8.19 | 7.52 | 7.08 | 6.87 | 7.39 |
| | | C. At 195 °C | | | |
| octane | 3.42 | 2.87 | 2.35 | 1.81 | 1.30 |
| nonane | 6.07 | 5.03 | 4.01 | 3.11 | 2.17 |
| decane | 9.73 | 7.86 | 6.24 | 4.58 | 3.15 |
| undecane | 14.79 | 11.62 | 8.78 | 6.26 | 4.13 |
| dodecane | 23.68 | 17.62 | 12.39 | 8.11 | 4.72 |
| methyl acetate | 2.11 | 2.21 | 2.42 | 2.82 | 3.80 |
| ethyl acetate | 3.18 | 3.26 | 3.45 | 3.98 | 5.10 |
| propyl acetate | 5.46 | 5.39 | 5.47 | 5.83 | 6.85 |
| butyl acetate | 7.18 | 7.12 | 7.28 | 7.84 | 9.37 |
| methanol | 1.21 | 1.23 | 1.29 | 1.46 | 1.91 |
| ethanol | 1.83 | 1.83 | 1.91 | 2.12 | 2.69 |
| 2-propanol | 2.17 | 2.11 | 2.11 | 2.25 | 2.72 |
| butanol | 6.36 | 5.89 | 5.58 | 5.48 | 5.95 |
| 2-pentanol | 6.74 | 6.44 | 6.34 | 6.62 | 7.70 |

## Results and Discussion

**Specific Retention Volumes.** Specific retention volumes, $V_g^\circ$, of 15 solutes were obtained for homopolymers, PVF2, PEMA, and blends of PVF2–PEMA. The solutes were selected to provide information about the type and the strength of the interactions of solute–homopolymer and solute–blend systems. Solutes from three different families, alkanes, acetates, and alcohols, were selected. To accomplish this goal, six columns of homopolymers and different weight fractions of blends were prepared (Table I). An additional column packed with only the solid support was used to obtain the $V_g^\circ$ values of solutes with 0% polymers. These $V_g^\circ$ values were subtracted from the apparent $V_g^\circ$ values obtained with columns packed with different loadings of homopolymers and the blend. This measure was taken to correct for the contribution of the inert solid support effect.[50] Four different compositions of the blends were prepared so that they will provide wide distribution of the weight fractions of the blend. $V_g^\circ$ values obtained with different homopolymer composition and three temperatures are listed in Table II. These $V_g^\circ$ values are obtained in a temperature range above the PVF2 melting point at which the blend of PVF2–PEMA is

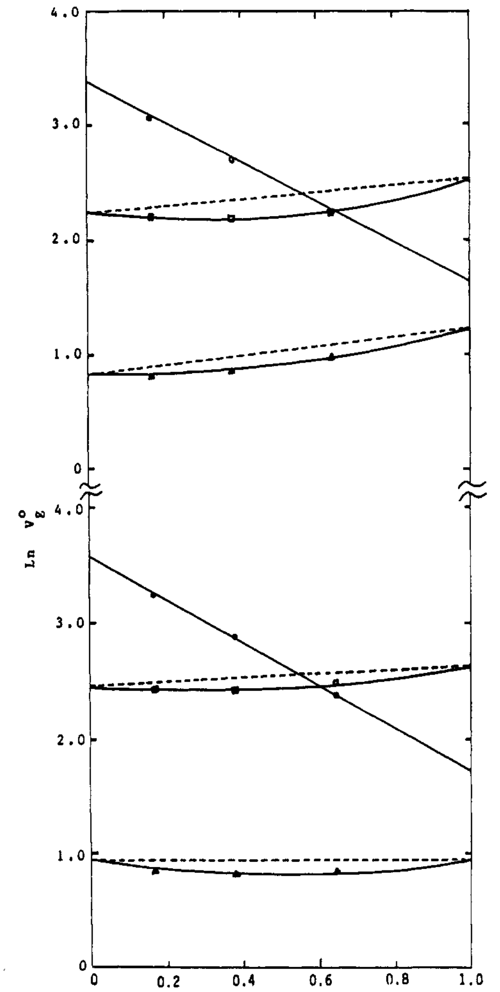

**Figure 1.** (—) Dependence of the ln $V_g°$ on the PVF2 volume fraction for selected solutes at 175 (lower) and 185 °C (upper): (○) dodecane; (□) *n*-butyl acetate; (△) ethanol. (- - -) Hypothetical logarithmic average for the pure PVF2 and PEMA.

completely at melt. The obtained $V_g°$ values are then amenable for thermodynamic calculations. A plot of the logarithm $V_g°$ vs the volume fractions of PVF2 may provide information about the dependence of the polymer–polymer interactions on the weight/volume fractions of the homopolymers. Figure 1 shows the relationship between the logarithm of $V_g°$ and the volume fraction of PVF2 using dodecane, *n*-butyl acetate, and ethanol as solutes. Acetates and alcohols show a curved relationship, with a minimum at 0.50–0.55 volume fraction of PVF2. This indicates that the miscibility of PVF2 and PEMA is greatly achieved when the blend mixture is at 50:50 w/w PVF2–PEMA. Munk et al.[49] found similar results for a blend of poly($\epsilon$-caprolactone)–polyepichlorohydrin. They called the dashed lines the hypothetical logarithmic average of the two pure homopolymers, which characterizes the behavior of hypothetical noninteracting blends. They attributed the strength of the polymer–polymer interactions to the deviation of the experimental ln $V_g°$ line from the hypothetical line. Alkanes, however, did not show this kind of behavior, simply because alkanes do not interact strongly with the blend, unlike acetates and alcohols.

The specific retention volumes of the PVF2–PEMA blend showed a linear relationship with temperature above the melting point of PVF2 as we expected. At this temperature range, the establishment of equilibrium between the vanishing small amount of solutes and the blend is very fast. Figure 2 shows that acetate solutes and the PVF2–PEMA blend are indeed in equilibrium. Two more plots like Figure 2 were generated for alkanes and alcohols at different compositions, which showed similar behavior to the acetates. The slopes of the straight lines in Figure 2 are meaningful for obtaining thermodynamic sorption quantities for the sorption process of solutes with the blend layer (discussed in the following section).

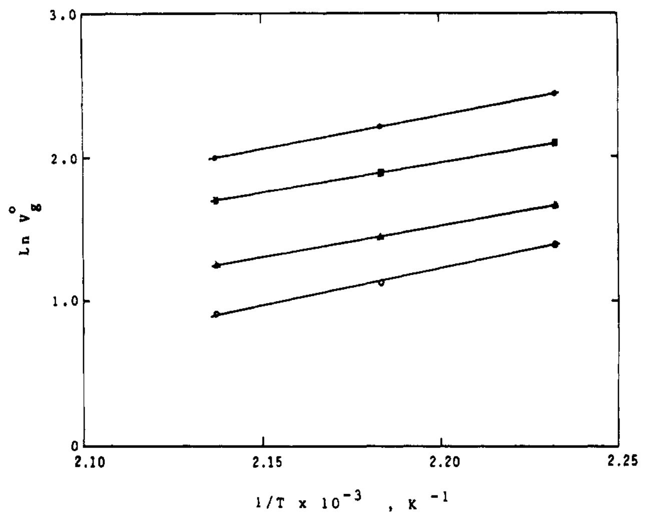

**Figure 2.** Dependence of ln $V_g°$ on the inverse of temperature for a PVF2–PEMA blend containing 50% PVF2: (●) *n*-butyl acetate; (□) propyl acetate; (△) ethyl acetate; (○) methyl acetate.

**Thermodynamic Parameters.** The PVF2–PEMA interaction parameters $\chi'_{23}$ were calculated at three temperatures, 175–195 °C, and various weight fractions of the homopolymers (Table III). Alcohols showed more negative values than acetates and alkanes for all compositions and temperatures. Since the negative value of the interaction parameter $\chi'_{23}$ or the exothermic heat of mixing is an indication of miscibility of the system, it is clear, from Table III, that PVF2 and PEMA are compatible in the temperature range used. PVF2–PEMA and PVF2–PMMA were previously found to be compatible by the calorimetric method above the PVF2 melting point. Our data indicate that the IGC method is comparable to the other methods used in polymer characterization and indeed has several advantages: speed and reliability. $\chi'_{23}$ values were −0.33 for alcohols, −0.22 for acetates, and almost zero for alkanes. All these values indicate the compatibility of the PVF2–PEMA pair over the weight fraction and temperatures used. $\chi'_{23}$ values were found to be temperature independent; values varied within experimental error with the change of temperature. Also, $\chi'_{23}$ values were found to be independent of the following factors: the number of carbons in the series of the three families, the compositions of the blend, and the temperatures used. Figure 3 shows the relationship between $\chi'_{23}$ and the number of carbons in the series of alkanes, acetates, and alcohols at 50% by weight of PVF2 and 175 °C. Similar plots were obtained for the other compositions and temperatures. For alkanes, the points are more scattered than those of acetates and alcohols, particularly for undecane, but they clearly indicate no dependence on the number of carbons. Our results are in good agreement with the results obtained, by Munk et al.,[49] on poly($\epsilon$-caprolactone)–polyepichlorohydrin blends for a given solute. They found no dependence of $\chi'_{23}$ on the weight fractions of the blend. In contrast, DiPaola-Baranyi[23] reported controversial results: they found a dependence of $\chi'_{23}$ on the PVF2–PMMA composition. Their results show that, at 90% PVF2, $\chi'_{23}$ has a larger negative value than the other composition.

**Table III**
**PVF2–PEMA Interaction Parameters, $\chi'_{23}$ at 175, 185, and 195 °C and Various Weight Fractions of PVF2**

| probe | 25% PVF2 | 50% PVF2 | 75% PVF2 |
|---|---|---|---|
| A. At 175 °C | | | |
| octane | 0.05 | 0.02 | 0.07 |
| nonane | 0.08 | 0.01 | 0.03 |
| decane | 0.01 | 0.04 | 0.05 |
| undecane | −0.02 | −0.06 | −0.03 |
| dodecane | −0.08 | −0.02 | −0.04 |
| methyl acetate | −0.24 | −0.23 | −0.24 |
| ethyl acetate | −0.24 | −0.22 | −0.22 |
| propyl acetate | −0.21 | −0.22 | −0.23 |
| butyl acetate | −0.23 | −0.22 | −0.21 |
| methanol | −0.36 | −0.32 | −0.31 |
| ethanol | −0.34 | −0.35 | −0.31 |
| 2-propanol | −0.33 | −0.33 | −0.33 |
| butanol | −0.33 | −0.33 | −0.31 |
| 2-pentanol | −0.34 | −0.34 | −0.33 |
| B. At 185 °C | | | |
| octane | 0.07 | 0.03 | 0.04 |
| nonane | 0.07 | 0.01 | 0.03 |
| decane | −0.03 | −0.01 | 0.01 |
| undecane | −0.03 | −0.02 | −0.06 |
| dodecane | −0.03 | −0.05 | −0.01 |
| methyl acetate | −0.28 | −0.23 | −0.27 |
| ethyl acetate | −0.26 | −0.25 | −0.25 |
| propyl acetate | −0.23 | −0.24 | −0.24 |
| butyl acetate | −0.25 | −0.23 | −0.25 |
| methanol | −0.34 | −0.33 | −0.28 |
| ethanol | −0.35 | −0.36 | −0.33 |
| 2-propanol | −0.37 | −0.34 | −0.32 |
| butanol | −0.32 | −0.32 | −0.35 |
| 2-pentanol | −0.35 | −0.32 | −0.36 |
| C. At 195 °C | | | |
| octane | 0.04 | 0.08 | 0.05 |
| nonane | 0.03 | 0.02 | 0.08 |
| decane | −0.03 | 0.05 | −0.01 |
| undecane | −0.06 | −0.04 | −0.06 |
| dodecane | −0.04 | −0.04 | −0.05 |
| methyl acetate | −0.23 | −0.23 | −0.26 |
| ethyl acetate | −0.25 | −0.28 | −0.22 |
| propyl acetate | −0.22 | −0.23 | −0.23 |
| butyl acetate | −0.24 | −0.24 | −0.24 |
| methanol | −0.29 | −0.33 | −0.33 |
| ethanol | −0.32 | −0.31 | −0.31 |
| 2-propanol | −0.33 | −0.35 | −0.35 |
| butanol | −0.33 | −0.32 | −0.34 |
| 2-pentanol | −0.34 | −0.34 | −0.33 |

This observed dependence is possibly due to the lack of correction of many experimental artifacts. Our values in Table III suggest that $\chi'_{23}$ depended strongly on the chemical nature of the probe used. As we pointed out earlier,[22] this dependence is real and not an artifact. This dependence is due to the deficiency in the Flory–Huggins theory and not due to the experimental artifacts. Galin and Maslinko[36] found similar results in the PVF2–PEMA blend system. They estimated $\chi'_{23}$ to be −0.32, which is in good agreement with our results. Their $\chi'_{23}$ showed also slight sensitivity to temperature between 160 and 200 °C and composition of the blend.

the molar heats of sorption, $\Delta H_1{}^s$, of acetates were calculated as the slopes of the linear relationship of ln $V_g{}^\circ$ for the blend with $1/T$ (similar to Figure 2) for all the weight fractions used. An exothermic values of −9.50 kcal/mol for 25% PVF2, −9.75 kcal/mol for 50% PVF2, and −8.32 kcal/mol for 75% PVF2 were obtained. These values support our results in Figure 1 that miscibility of the PVF2–PEMA blend is mostly achieved at 50:50 w/w composition of the blend.

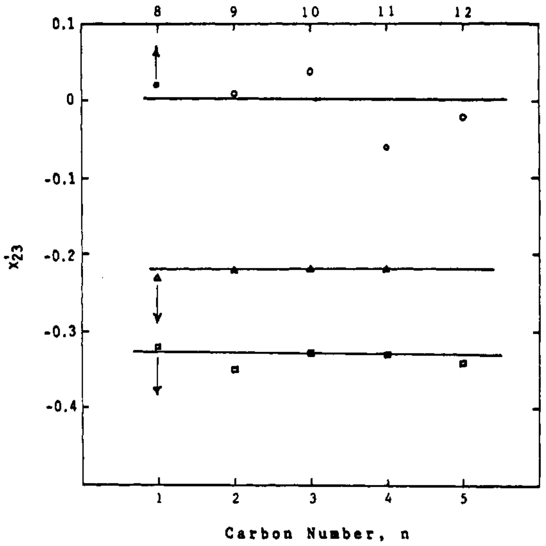

Figure 3. Dependence of the PVF2–PEMA interaction parameters on the number of carbons of the three families at 175 °C and for a blend containing 50% PVF2: (○) alkanes; (△) acetates; (□) alcohols.

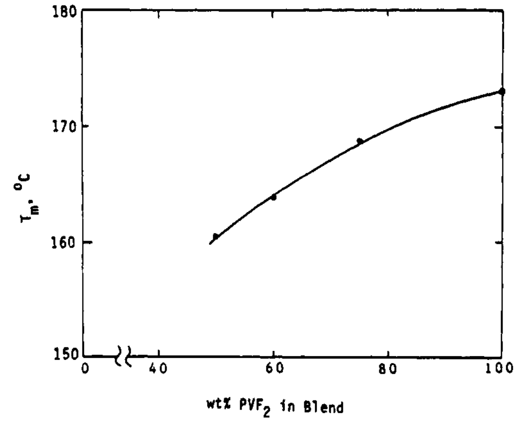

Figure 4. Dependence of the PVF2 melting point on the weight fraction of PVF2 in the blends.

**Melting Point Depression.** To support our results for the miscibility of PVF2 and PEMA, and since PVF2 is crystallizable below its melting temperature, we performed experiments below the PVF2 melting temperature (140–175 °C) for all the weight fractions of the blend. Indeed, the melting point of PVF2 dropped from 174 °C for 100% PVF2 to 160.0 °C for 50% PVF2. The depression of the melting point was not clearly detectable for a blend having less than 35% PVF2. We selected one family for this purpose. Acetates were used to measure the melting point depression of PVF2, because acetates interact strongly with the PVF2–PEMA blend. A series of experiments were performed by using four acetate solutes, and the melting point of PVF2 was obtained for each individual acetate solute, which differed by 2% from one solute to another. Then the melting point depressions were averaged to obtain one melting point for the whole family at a given weight fraction. The averaging method eliminated the dependency of $B_{23}$ on the contribution of individual solute; it depended only on the family of solutes, as we will discuss later. Figure 4 shows the depression in the PVF2 melting point as its weight fraction decreases in the mixture. As we stated in the Introduction, the melting point depression of a polymer mixture, containing crystallizable homopolymers, was usually obtained by using the calorimetric method. The melting point depression obtained from the calorimetric method on PVF2 blends was very useful for the evaluation of polymer blend miscibility. $B_{23}$ and $\chi'_{23}$ were calculated from the melting point depression and used as an indicator for the miscibility as in eqs 18–21. No previous attempts were made to detect

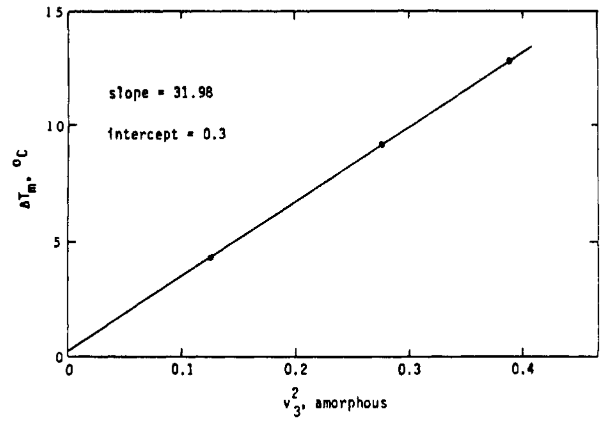

**Figure 5.** PVF2 melting point depression vs the volume fraction of PEMA.

the melting point depression of a blend or to evaluate its miscibility by the inverse gas chromatography method. However, there is only one report on the depression of the PVF2 melting point when it was blended with PMMA.[23] No evaluation of the miscibility of the blend was based on the melting point depression.

Munk et al. was the first to introduce the relationship between $B_{23}$ and $\chi'_{23}$ of polymer blends (PCL-PECH) using the IGC method.[49] The $B_{23}$ term differed according to the chemical nature of the solutes and as the number of carbons changed within the family itself. Within a given solute family, the apparent value of $B_{23}$ increased progressively with increasing aliphatic content in the solute molecule. This increase in $B_{23}$ is a result of the mathematical dependence of $\chi'_{23}$ on the molar volume of the given solute (similar to eq 18). However, in our case, this dependence is less pronounced as $\chi'_{23}$ depended on the molar volume of the miscible diluent polymer, which is PEMA. From our results of melting point depression, $B_{23}$ did not change from one solute to another within the same family, but it changed with the chemical nature of the family only. Using eq 21, we plotted the melting point depression of PVF2 vs the square of the volume fraction of PEMA in Figure 5. The quantity ($\Delta H_{2u}/V_{2u}$) is the heat of fusion of pure PVF2 per unit volume, which was taken from ref 53 as 44 cal/mL. A linear relationship was obtained; the slope of the straight line was incorporated to calculate $B_{23}$. We must mention, however, that the straight line has a nonzero intercept, and the $y$ intercept was found to be 0.3 °C. This small intercept may be attributed to a small entropic contribution. A value of −3.15 cal/mL was obtained for $B_{23}$. To our satisfaction, this value of $B_{23}$ is in good agreement with the $B_{23}$ value obtained by Barlow[43] on PVF2-PEMA (−3.18 cal/mL) and −2.98 cal/mL obtained by Kwei et al.[42] for PVF2-PEMA blends using the calorimetric method. Our $B_{23}$ value is also in good agreement with the value obtained by Nishi and Wang[53] on PVF2-PMMA (−2.98 cal/mL) by the calorimetric method. It is obvious that $B_{23}$ values obtained in this work and others indicate an exothermic heat of mixing of the PVF2 and PEMA arising from strong specific interactions between the two polymers. A value of −0.295 for $\chi'_{23}$ of the PVF2-PMMA blend was obtained by Nishi and Wang[53] at 160 °C from the melting point depression using the calorimetric method. A value of −0.34 for $\chi'_{23}$ of the PVF2-PEMA blend was also obtained by Kwei et al.[42] using the calorimetric method. From Table III, it is clear that $\chi'_{23}$ values obtained by refs 42 and 53 are in good agreement with our $\chi'_{23}$ values obtained in this work for the most interacting solutes (acetates and alcohols) at all compositions used. It is evident that both the thermodynamics of the IGC method and the melting point depression by using calorimetric method yielded similar polymer-polymer interaction parameters. Other investigators[40] also obtained similar values for $B_{23}$ using melting point depression by calorimetry. A value ranged from −1.71 to −3.88 cal/mL for a blend of PVF2-counterpolymers containing ester, ketone, or ether groups. These values depended on the strength of the interaction forces between PVF2 and its counterpolymer; the ketone group interacted more strongly (more exothermic) than the ether group with PVF2.

## Conclusion

It is clear from our discussions on PVF2-PEMA blend miscibility studied by the IGC method that a new feature of the IGC method has been obtained. We have shown that the IGC method can be used for the measurement of the melting point depression of a pair of polymers containing crystallizable polymer. The melting point depression is used as an indicator for the miscibility of a polymer pair. Thus, we consider the IGC method as a promising method for polymer and polymer blend characterization. It is characterized mainly by its speed, reliability, and versatility. In this work, we demonstrated that PVF2 is miscible with PEMA below and above the PVF2 melting temperature. The miscibility arises from the negative interaction parameter ($\chi'_{23}$) obtained from the thermodynamic calculations and from the exothermicity of the interaction energy $B_{23}$ obtained from the melting point depression. We showed that the IGC method was capable of detecting the depression in the melting point of a semicrystalline polymer when a miscible diluent was added. Our obtained $B_{23}$ depended only on the nature of the families used and not on the individual solute.

## Appendix

The probe specific retention volumes, $V_g°$, the interaction coefficients, $\chi_{12}$ and $\chi_{13}$, and the polymer-polymer interaction coefficients, $\chi'_{23}$, were calculated according to eqs 8, 12, and 16. The vapor pressure, $P_1°$, was calculated from the Antoine equation as

$$\log P_1° = A - B/(t + C) \qquad \text{(A1)}$$

where $t$ is the temperature in degrees Celsius and the constants $A$-$C$ were taken from Dreisbach's compilation.[56] The molar volumes of the solutes $V_1$ were calculated using eqs 2-4

$$V_1 = M_1/\rho_L \qquad \text{(A2)}$$

$$\rho_L + \rho_V = a - bt \qquad \text{(A3)}$$

$$\rho_V = P_1° M_1/RT \qquad \text{(A4)}$$

where $\rho_L$ and $\rho_V$ are the densities of the liquid solute and its saturated vapor, respectively, $M_1$ is the molecular weight of the solute, and $P_1°$ is the pressure calculated from eq A1. The constants $a$ and $b$ are also taken from Dreisbach's compilation.[56] Second virial coefficients $B_{11}$ were computed by using the equation[57]

$$B_{11}/V_c = 0.430 - 0.886(T_c/T) - 0.694(T_c/T)^2 - 0.0375(n - 1)(T_c/T)^{4.5} \qquad \text{(A5)}$$

where $V_c$ and $T_c$ are the critical molar volume and the critical temperature of the solute, respectively, and $n$ is the number of carbon atoms in alkanes or the number of corresponding groups in non-alkane solutes.

The molar heat (enthalpy) of sorption of probe absorbed by the amorphous part of the blend ($\Delta H_1^s$) is given by the equation[58]

$$\Delta H_1^s = -R\,\delta \ln V_g^\circ/\delta(1/T) \qquad \text{(A6)}$$

where $V_g^\circ$ is the net specific retention volume corrected for the support dependence (as discussed in the Results and Discussion Section). $T$ is the column temperature.

The average partial molar heat of mixing at infinite dilution of the probe was calculated as

$$\Delta \bar{H}_1^\infty = R\,\delta \ln \Omega_1^\infty/\delta(1/T) \qquad \text{(A7)}$$

where $\Omega_1^\infty$ is the weight fraction activity coefficient of the solute probe at infinite dilution, which is calculated according to the equation

$$\Omega_1^\infty = \frac{273.15R}{V_g^\circ P_1^\circ M_1}\exp[-P_1^\circ(B_{11} - V_1)]RT \qquad \text{(A8)}$$

where $P_1^\circ$, $V_1$, and $B_{11}$ were defined in eq 12, and $M_1$ is the molecular weight of the probe. Equation 8 was developed by Patterson et al.[59] to replace the original equation for the infinite dilution activity coefficient developed by Everett.[60] The original equation depended on an uncertain quantity: the molecular weight of the polymer.

The partial molar free energy of mixing at infinite dilution is calculated from the weight fraction activity coefficient of the solute as

$$\Delta G_1^\infty = RT \ln \Omega_1^\infty \qquad \text{(A9)}$$

where $RT$ has the usual meaning.

The partial molar free energy of sorption at infinite dilution is calculated as

$$\Delta G_1^s = -RT \ln [M_1 V_g^\circ/273.15R] \qquad \text{(A10)}$$

By incorporating eqs A6 and A10, we calculated the entropy of sorption of solutes as

$$\Delta G_1^s = \Delta H_1^s - T\Delta S_1^s \qquad \text{(A11)}$$

## References and Notes

(1) Utracki, L. A.; Walsh, D. J.; Weiss, R. A. *Polymer Alloys, Blend and Ionomers*; ACS Symposium Series 395; American Chemical Society: Washington, DC, 1989; pp 1–35.
(2) Utracki, L. A., Weiss, R. A., Eds. *Multiphase Polymers: Blends and Ionomers*; ACS Symposium Series 395; American Chemical Society: Washington, DC, 1989; p 517.
(3) Utracki, L. A. *Int. Polym. Process.* **1987**, *2*, 3.
(4) Utracki, L. A. *Multiphase Polymers: Blends and Ionomers*; ACS Symposium Series 395; American Chemical Society: Washington, DC, 1989; p 153.
(5) Paul, D. R. *Polymer Blends Mixtures*; NATO Advanced Study Institute Series 89; Plenum: New York, 1985; pp 1–23.
(6) Paul, D. R., Sperling, L. H., Eds. *Multicomponent Polymer Materials*; Advances in Chemistry Series 211; American Chemical Society: Washington, DC, 1986; p 354.
(7) Paul, D. R.; Barlow, J. W. Polymer Blends (or Alloys). *J. Macromol. Sci., Rev. Macromol. Chem.* **1980**, *C18*, 109.
(8) Solc, K., Ed. *Polymer Compatibility and Incompatibility: Principles and Practice*; MMI Press Symposium Series 2; MMI Press: Baltimore, MD, 1982.
(9) Barlow, J. W.; Paul, D. R. *Annu. Rev. Mater. Sci.* **1981**, *11*, 299.
(10) Sanchez, I. C. *Annu. Rev. Mater. Sci.* **1983**, *13*, 387.
(11) Pearce, E. M.; Kwei, T. K.; Min, B. Y. *J. Macromol. Sci., Chem.* **1984**, *A21*, 1181.
(12) Rodrigues-Parada, J. M.; Percec, V. *Macromolecules* **1986**, *19*, 55.
(13) Pugh, C.; Percec, V. *Macromolecules* **1986**, *19*, 65.
(14) ten Brinke, G.; Karasz, F. E. *Macromolecules* **1984**, *17*, 815.
(15) Bank, M.; Leffingwell, J.; Thies, C. *Macromolecules* **1971**, *4*, 43.
(16) Shultz, A. R.; Beach, B. M. *Macromolecules* **1974**, *7*, 902.
(17) Kwei, T. K.; Nishi, T.; Roberts, R. F. *Macromolecules* **1974**, *7*, 667.
(18) Shimada, Y.; Kashiwabara, H. *Macromolecules* **1988**, *21*, 3454.
(19) Roe, R. J.; Sin, W. C. *Macromolecles* **1980**, *13*, 1221.
(20) Haziioannou, G.; Stein, R. *Macromolecules* **1984**, *17*, 567.
(21) Jelenic, J.; Kirste, R. G.; Oberthur, R. C.; Schmitt-Strecker, S.; Schmitt, B. J. *Makromol. Chem.* **1984**, *185*, 129.
(22) Al-Saigh, Z. Y.; Munk, P. *Macromolecules* **1984**, *17*, 803.
(23) DiPaola-Baranyi, G.; Fletcher, S. J.; Degré, P. *Macromolecules* **1982**, *15*, 885.
(24) DiPaola-Baranyi, G. *Macromolecules* **1981**, *14*, 1456.
(25) Walsh, D. J.; McKeown, J. G. *Polymer* **1980**, *21*, 1335.
(26) Ward, T. C.; Sheehy, D. P.; McGrath, J. E. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1980**, *21* (2), 70.
(27) Ward, T. C.; Sheehy, D. P.; Riffle, J. S. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1981**, *22* (1), 187.
(28) Ward, T. C.; Sheehy, D. P.; McGrath, J. E.; Riffle, J. S. *Macromolecules* **1981**, *14*, 1791.
(29) Su, C. S.; Patterson, D. *Macromolecules* **1977**, *10*, 708.
(30) DiPaola-Baranyi, G.; Degre, P. *Macromolecules* **1981**, *14*, 1456.
(31) Galin, M.; Rupprecht, M. C. *Macromolecules* **1979**, *12*, 506.
(32) Shiom, T.; Karasz, F. E.; Macknight, W. J. *Macromolecules* **1986**, *19*, 2644.
(33) Tyagi, O. S.; Husain, S. *Ind. J. Technol.* **1984**, *22*, 435.
(34) El-Hibri, M. J.; Munk, P. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1987**, *28*, 154.
(35) Tyagi, O. S.; Sahid, S. M.; Husain, S. *Polymer* **1987**, *28*, 2329.
(36) Galin, M.; Maslinko, L. *Eur. Polym. J.* **1987**, *23*, 923.
(37) Tsay, P. D.; Kim, S. S.; Cebe, P. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1987**, *28*, 183.
(38) Cebe, P.; Chung, S. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1987**, *28*, 183.
(39) Rashmi, G. K. N.; Pillai, P. K. C. *J. Macromol. Sci. Phys.* **1987**, *B26*, 185.
(40) Bernstien, R. E.; Wahrmund, D. C.; Barlow, J. W.; Paul, D. R. *Polym. Eng. Sci.* **1978**, *18*, 1220.
(41) Paul, D. R.; Barlow, J. W.; Berstein, R. E.; Wahrnund, D. C. *Polym. Eng. Sci.* **1978**, *18*, 1225.
(42) Kwei, T. K.; Patterson, G. D.; Wang, T. T. *Macromolecules* **1976**, *9*, 780.
(43) Imken, R. L.; Paul, D. R.; Barlow, J. E. *Polym. Eng. Sci.* **1976**, *16*, 593.
(44) Deshpande, D. D.; Patterson, D.; Schreiber, H. P.; Su, C. S. *Macromolecules* **1974**, *7*, 530.
(45) Olabisi, O. *Macromolecules* **1975**, *8*, 316.
(46) Card, T. W.; Al-Saigh, Z. Y.; Munk, P. *J. Chromatogr.* **1984**, *301*, 261.
(47) Card, T. W.; Al-Saigh, Z. Y.; Munk, P. *Macromolecules* **1985**, *18*, 1030.
(48) Munk, P.; Al-Saigh, Z. Y.; Card, T. W. *Macromolecules* **1985**, *18*, 2196.
(49) El-Hibri, M. J.; Cheng, W.; Munk, P. *Macromolecules* **1988**, *21*, 3458.
(50) Chen, C. T.; Al-Saigh, Z. Y. *Macromolecules* **1989**, *22*, 2974.
(51) Chen, C. T.; Al-Saigh, Z. Y. *Polymer* **1990**, *31*, 1170.
(52) Flory, P. J. *Principles of Polymer Chemistry*; Cornell University Press: Ithaca, NY, 1953.
(53) Nishi, T.; Wang, T. T. *Macromolecules* **1975**, *8*, 909.
(54) Roerdink, E.; Challa, G. *Polymer* **1978**, *19*, 173.
(55) Martuscelli, E.; Demma, G.; Drioli, E.; Nicolais, L.; Spina, S.; Hopfenberg, H. B. Stannett, V. T. *Polymer* **1979**, *20*, 571.
(56) Dreisbach, R. R. *Physical Properties of Chemical Compounds*; Advances in Chemistry Series 15, 22, and 29; American Chemical Society: Washington, DC, 1955, 1959, 1961.
(57) McGlashan, M. L.; Potter, D. J. B. *Proc. R. Soc. London, Ser. A* **1967**, *267*, 478.
(58) Lipson, L. E. G.; Guillet, J. E., Dawkins, J. V. *Developments in Polymer Characterization*, 3rd ed.; Dawkins, J. V., Ed.; Applied Science Publishers: Barking, England, 1982; p 33.
(59) Patterson, D.; Tewari, Y. B.; Schreiber, H. P.; Guillet, J. E. *Macromolecules* **1971**, *4*, 356.
(60) Everett, D. H. *Trans. Faraday Soc.* **1965**, 1637.

**Registry No.** PVF$_2$, 24937-79-9; methyl acetate, 79-20-9; ethyl acetate, 141-78-6; propyl acetate, 109-60-4; butyl acetate, 123-86-4; poly(ethyl methacrylate), 9003-42-3.