

Relationships between polymer interaction parameters

Isaac C. Sanchez*

Alcoa Laboratories, Alcoa Center, PA 15069, USA

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Experimental methods that determine binary polymer-polymer χ interaction parameters may probe the mixture's free energy, its first derivative, or its second derivative. In general, there are four different χ parameters that are required to describe a binary polymer mixture, but if one is determined experimentally, the other three can be calculated. This allows for the determination of both the spinodal and two-phase coexistence curves. Theoretical Henry's law constants that govern gas sorption in polymers are derived which can be used to facilitate the determination of polymer-polymer interaction parameters by inverse gas chromatography.

(Keywords: interaction parameters; mixture; gas sorption; inverse gas chromatography)

INTRODUCTION

Now that small-angle neutron scattering (SANS) measurements are being used to determine binary polymer-polymer χ interaction parameters¹⁻⁹, it has raised the question as to how these SANS measured χ values compare with other experimentally determined values of χ . Among other methods, polymer-polymer χ interaction parameters can in principle be determined by measuring melting-point depressions¹⁰, heats of mixing¹¹⁻¹³, cloud points¹⁴⁻¹⁶, light scattering¹⁷, osmotic pressure¹⁸, interdiffusion via forward recoil spectrometry¹⁹⁻²¹ and gas sorption via inverse gas chromatography (i.g.c.)²²⁻²⁷.

When an interaction parameter depends on composition, it is not generally recognized that a proper thermodynamic description of a binary polymer mixture requires four different χ parameters; only one of these is determined in a SANS measurement. The χ parameter that is measured depends on whether the experiment probes the free energy directly, its first derivative, or its second derivative. However, when one of the four parameters is known, the other three can be determined. In this paper these four χ interaction parameters are defined and rigorous thermodynamic relationships are derived between them.

Determination of polymer-polymer interaction parameters by i.g.c., an experimental method which showed so much promise a decade ago, has been frustrated because the values obtained depend on the probe gas used in the measurement²⁷. Classical theory predicts otherwise. It is clearly shown that this difficulty is related to the compositional dependence of the interaction parameters. More importantly, it is shown how this difficulty can be circumvented by using an equation-of-state model and a theoretically derived Henry's law constant.

* Now at: Department of Chemical Engineering and Center for Polymer Research, University of Texas, Austin, TX 78712, USA

FREE ENERGY

The classical Flory-Huggins free energy of mixing^{28,29} can be expressed as³⁰:

$$\Delta f = \Delta f_{\text{comb}} + \Delta f_{\text{ex}} \quad (1)$$

where Δf_{comb} is the combinatorial entropy:

$$\Delta f_{\text{comb}}/kT = (\phi_1/v_1)\ln \phi_1 + (\phi_2/v_2)\ln \phi_2 \quad (2)$$

and Δf_{ex} is the excess free energy:

$$\Delta f_{\text{ex}}/kT = \phi_1\phi_2\chi \quad (3)$$

and where ϕ_i and v_i are the volume fraction and molar volume of component i , respectively; χ is an interaction parameter that in general is composition-dependent; kT has its usual significance and $kT\chi$ has units of energy density (energy/volume).

For a binary mixture the chemical potentials are given by³⁰:

$$\Delta\mu_1 = v_1[\Delta f + \phi_2(d\Delta f/d\phi_1)] \quad (4)$$

$$\Delta\mu_2 = v_2[\Delta f + \phi_1(d\Delta f/d\phi_2)]$$

Substituting equations (1)-(3) into (4) yields:

$$\Delta\mu_1/kT = \ln \phi_1 + (1 - v_1/v_2)\phi_2 + v_1\chi_{\mu 1}\phi_2^2 \quad (5)$$

$$\Delta\mu_2/kT = \ln \phi_2 + (1 - v_2/v_1)\phi_1 + v_2\chi_{\mu 2}\phi_1^2$$

where

$$kT\phi_2^2\chi_{\mu 1} = \Delta f_{\text{ex}} + \phi_2(d\Delta f_{\text{ex}}/d\phi_1) \quad (6)$$

and a similar expression for $\chi_{\mu 2}$ is obtained by interchange of the indices 1 and 2 in equation (6). If χ in equation (3) is composition-independent, then

$\chi = \chi_{\mu 1} = \chi_{\mu 2}$; in general, χ depends on composition so that substitution of equation (3) into (6) yields:

$$\chi_{\mu 1} = \chi + \phi_1(d\chi/d\phi_1) \equiv \chi + \phi_1\chi' \quad (7)$$

$$\chi_{\mu 2} = \chi + \phi_2(d\chi/d\phi_2) \equiv \chi - \phi_2\chi'$$

Notice from equation (7) that:

$$\chi_{\mu 1} - \chi_{\mu 2} = \chi' \quad (8)$$

and

$$\chi = \phi_2\chi_{\mu 1} + \phi_1\chi_{\mu 2} \quad (9)$$

Thus, the interaction parameter that appears in the chemical potential, χ_{μ} , depends on χ and its concentration derivative, χ' .

In a scattering experiment, there is yet another interaction parameter, χ_{sc} , that is determined. The well known de Gennes formula³¹ for the static structure factor, $S(q)$, of a binary mixture is used to determine χ_{sc} :

$$S^{-1}(q) = \frac{1}{v_1\phi_1S_1(q)} + \frac{1}{v_2\phi_2S_2(q)} - 2\chi_{sc} \quad (10)$$

where the $S_i(q)$ are the single-chain structure factors (Debye functions) and are normalized so that $S_i(0) = 1$. At zero scattering angle ($q = 0$), $S^{-1}(0)$ is equal to the second concentration derivative of the free energy:

$$S^{-1}(0) = \frac{1}{v_1\phi_1} + \frac{1}{v_2\phi_2} - 2\chi_{sc} = \frac{d^2(\Delta f/kT)}{d\phi_1^2} \quad (11)$$

and thus from equation (3)

$$\chi_{sc} = -\frac{1}{2}d^2(\Delta f_{ex}/kT)/d\phi_1^2 \quad (12)$$

which yields:

$$\chi_{sc} = \chi + (\phi_1 - \phi_2)\frac{d\chi}{d\phi_1} - \frac{1}{2}\phi_1\phi_2\frac{d^2\chi}{d\phi_1^2} \quad (13)$$

Notice that χ_{sc} depends on χ , χ' and χ'' . Using equations (7) and (9), equation (13) can be written in more symmetrical form:

$$\chi_{sc} = \phi_1\chi_{\mu 1} + \phi_2\chi_{\mu 2} - \frac{1}{2}\phi_1\phi_2\chi'' \quad (14)$$

RELATIONSHIPS BETWEEN $\chi_{\mu 1}$, $\chi_{\mu 2}$ AND χ_{sc}

Chemical potentials satisfy a Gibbs–Duhem relation, i.e.:

$$\frac{\phi_1}{v_1}d(\Delta\mu_1) + \frac{\phi_2}{v_2}d(\Delta\mu_2) = 0 \quad (15)$$

which implies

$$d(\phi_1^2\chi_{\mu 2}) = -(\phi_1/\phi_2)d(\phi_2^2\chi_{\mu 1}) \quad (16)$$

Integrating equation (16) yields:

$$\chi_{\mu 2} = \frac{1}{\phi_1^2} \int_0^{\phi_1} \chi_{\mu 1} d\phi_1' - \frac{\phi_2}{\phi_1} \chi_{\mu 1} \quad (17)$$

In a polymer–solvent system, the solvent chemical potential parameter $\chi_{\mu 1}$ is usually determined. Equation (17) allows the polymer chemical potential parameter $\chi_{\mu 2}$ to be determined also.

Now from equation (4)

$$\frac{d(\Delta\mu_1/v_1)}{d\phi_1} = \phi_2 \frac{d^2\Delta f}{d\phi_1^2} \quad \text{and} \quad \frac{d(\Delta\mu_2/v_2)}{d\phi_2} = \phi_1 \frac{d^2\Delta f}{d\phi_2^2} \quad (18)$$

which implies by equations (5) and (12) that:

$$\chi_{sc} = \frac{1}{2\phi_2} \frac{d(\phi_2^2\chi_{\mu 1})}{d\phi_2} = \frac{1}{2\phi_1} \frac{d(\phi_1^2\chi_{\mu 2})}{d\phi_1} \quad (19)$$

Integrating equation (19) yields:

$$\chi_{\mu 1} = (2/\phi_2^2) \int_0^{\phi_2} \phi_2' \chi_{sc} d\phi_2' \quad (20)$$

$$\chi_{\mu 2} = (2/\phi_1^2) \int_0^{\phi_1} \phi_1' \chi_{sc} d\phi_1'$$

Equation (19) allows χ_{sc} to be determined from χ_{μ} measurements and equation (20) allows the determination of $\chi_{\mu 1}$ and $\chi_{\mu 2}$ from χ_{sc} .

A SIMPLE EXAMPLE

To illustrate these relations between the various interaction parameters, let us assume that χ depends linearly on composition, i.e.:

$$\chi = \phi_1\chi_1 + \phi_2\chi_2 \quad (21)$$

where χ_1 and χ_2 are constants. Thus, by equation (7):

$$\chi_{\mu 1} = 2\phi_1\chi_1 + (\phi_2 - \phi_1)\chi_2 \quad (22)$$

$$\chi_{\mu 2} = 2\phi_2\chi_2 + (\phi_1 - \phi_2)\chi_1$$

From equation (14), we have:

$$\chi_{sc} = (3\phi_1 - 1)\chi_1 + (3\phi_2 - 1)\chi_2 \quad (23)$$

The variation of χ , $\chi_{\mu 1}$, $\chi_{\mu 2}$ and χ_{sc} with composition is illustrated in Figure 1.

This simple example also serves as a check on the validity and self-consistency of equations (17), (19) and (20).

POLYMER–SOLVENT SYSTEM EXAMPLE

The concentration dependence of χ_{μ} in polymer solutions is well known³². At room temperature, the solvent chemical potential interaction parameter $\chi_{\mu 1}$ in polystyrene–cyclohexane solutions varies approximately with polymer volume fraction ϕ_2 as:

$$v_1\chi_{\mu 1} = 0.5 - 0.32\phi_2 + 1.4\phi_2^2$$

$$= 0.5\phi_1^2 + 0.68\phi_1\phi_2 + 1.58\phi_2^2 \quad (24)$$

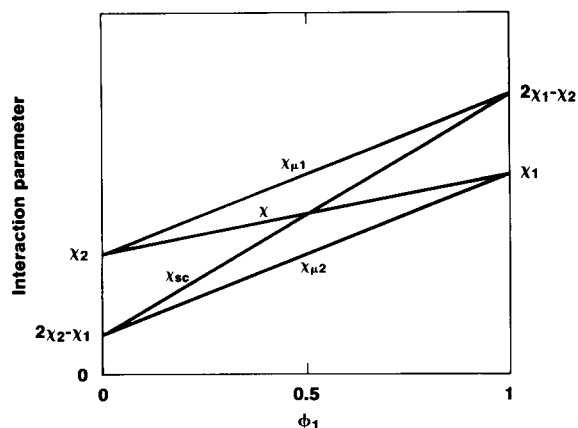


Figure 1 A simple example that illustrates the relationship between χ , $\chi_{\mu 1}$, $\chi_{\mu 2}$ and χ_{sc} . See equations (21)–(23)

Substituting equation (24) into (17) yields:

$$v_1 \chi_{\mu 2} = 0.82 + 0.60\phi_2 + 1.4\phi_2^2 \quad (25)$$

Substituting equations (24) and (25) into (9) yields χ :

$$v_1 \chi = 0.82 + 0.28\phi_2 + 0.48\phi_2^2 \quad (26)$$

Substituting equations (24) or (25) into (19) yields χ_{sc} :

$$v_1 \chi_{sc} = 0.5 - 0.48\phi_2 + 2.8\phi_2^2 \quad (27)$$

The behaviour of the four interaction parameters is shown in *Figure 2*.

The above equations have also recently been applied to the polystyrene–poly(vinyl methyl ether) system to determine χ , $\chi_{\mu 1}$ and $\chi_{\mu 2}$ from χ_{sc} (ref. 1).

IMPLICATIONS FOR INVERSE GAS CHROMATOGRAPHY

I.g.c. in principle can be used to determine polymer–polymer interaction parameters in miscible blends^{22–27}. In the i.g.c. experiment, the solubility of a probe gas in the blend is measured; the solubility is related to the polymer–polymer interaction parameter. Classical theory with composition-independent interaction parameters predicts that the measured polymer–polymer interaction parameter should be independent of the probe gas, but this is never observed²⁷. Below an analysis of the problem is carried out and a resolution is proposed.

The system of interest is ternary: gas (1), polymer (2) and polymer (3). The free energy of this system is:

$$\begin{aligned} \Delta f &= \Delta f_{\text{comb}} + \Delta f_{\text{ex}} \\ \Delta f_{\text{comb}}/kT &= \sum_{i=1}^3 (\phi_i/v_i) \ln \phi_i \\ \Delta f_{\text{ex}}/kT &= \sum_{i<j}^3 \phi_i \phi_j \chi_{ij} \end{aligned} \quad (28)$$

Let us assume that the interaction parameters χ_{ij} are all composition-dependent and are homogeneous functions of degree n . A homogeneous function F of degree n has the following two properties:

$$F(\lambda\phi_1, \lambda\phi_2, \lambda\phi_3) = \lambda^n F(\phi_1, \phi_2, \phi_3) \quad (29)$$

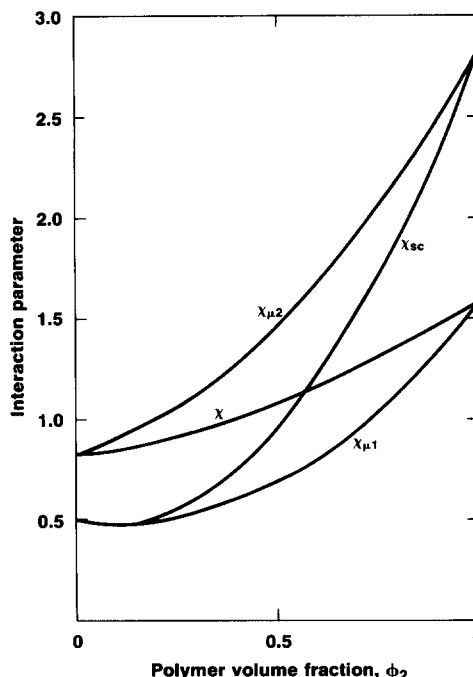


Figure 2 Variation of χ , $\chi_{\mu 1}$, $\chi_{\mu 2}$ and χ_{sc} for polystyrene–cyclohexane solutions at room temperature. See equations (24)–(27)

for arbitrary λ and

$$\sum_{i=1}^3 \phi_i (\partial F / \partial \phi_i) = nF \quad (30)$$

For example, if $n=2$, then the χ_{ij} have a quadratic functional form:

$$\chi_{ij} = \sum_{k<l}^3 c_{kl}^{ij} \phi_k \phi_l \quad (31)$$

where the c_{kl}^{ij} are constants (e.g. see equation (24)). Thus, for this ternary system Δf_{ex} is homogeneous of degree $n+2$.

Chemical potentials for a multicomponent mixture can be expressed as³⁰:

$$\Delta \mu_i = v_i \left[\Delta f + \left(\frac{\partial \Delta f}{\partial \phi_i} \right)_{\phi'} - \sum_j \phi_j \left(\frac{\partial \Delta f}{\partial \phi_j} \right)_{\phi'} \right] \quad (32)$$

where the subscript ϕ' denotes that the derivative with respect to ϕ_i is taken holding all other ϕ_j ($i \neq j$) constant. Substituting equation (28) into (32) and using equation (30) yields:

$$\begin{aligned} \Delta \mu_i/kT &= \ln \phi_i + 1 - v_i \sum_j (\phi_j/v_j) \\ &+ v_i \left(\sum_j \phi_j \chi_{ij} - \sum_{k<l} \phi_k \phi_l [(n+1)\chi_{kl} - (\partial \chi_{kl} / \partial \phi_i)] \right) \end{aligned} \quad (33)$$

In the i.g.c. experiment the gas, component 1, is a minor component so that in the limit of $\phi_1 \rightarrow 0$, the infinite dilution limit, the chemical potential of the gas becomes:

$$\begin{aligned} \Delta \mu_1/kT &= \ln \phi_1 + 1 - v_1 (\phi_2/v_2 + \phi_3/v_3) + v_1 \{ \phi_2 \chi_{12}^\infty + \phi_3 \chi_{13}^\infty \\ &- \phi_2 \phi_3 [(n+1)\chi_{23}(\phi_1=0) - (\partial \chi_{23} / \partial \phi_1)_{\phi_1 \rightarrow 0}] \} \end{aligned} \quad (34)$$

where χ_{12}^∞ and χ_{13}^∞ are the infinite-dilution gas-polymer interaction parameters (constants). The polymer-polymer interaction parameter χ_{23} determined from i.g.c. data is identified with the two terms in the square brackets in equation (34):

$$\chi_{23}(\text{i.g.c.}) = (n+1)\chi_{23}(\phi_1=0) - (\partial\chi_{23}/\partial\phi_1)_{\phi_1 \rightarrow 0} \quad (35)$$

Thus, if the χ_{ij} depend on composition, the experimentally determined $\chi_{23}(\text{i.g.c.})$ depends on the probe gas through the last term in equation (35). Only when the χ_{ij} are independent of composition ($n=0$), does $\chi_{23}(\text{i.g.c.})$ equal the χ_{23} parameter that appears in the free energy.

A resolution of this problem is possible by using a non-classical model for the free energy such as the Flory-Orwoll-Vrij-Eichinger equation-of-state model³³⁻³⁶ or lattice fluid (LF) model^{30,37-40}. In the i.g.c. experiment the solubility of a probe gas is measured which at low pressures follows Henry's law. If w_1 is the weight fraction of the gas absorbed by the polymer, then:

$$w_1 = HP \quad (36)$$

where H is the Henry's law constant and P is the gas pressure. For the LF model the Henry's law constant for a gas (component 1) dissolved in a pure polymer (component 2) is given by (a derivation is given below):

$$H = (M_1/RT\rho_2)\exp\{\tilde{\rho}_2(M_1/\rho_1^*)(P_1^*/kT - \chi_{12}) - r_1[1 + (1 - \tilde{\rho}_2)\ln(1 - \tilde{\rho}_2)/\tilde{\rho}_2]\} \quad (37)$$

where M_1 is the molecular weight of the gas, ρ_2 is the mass density of the polymer and χ_{12} is the 'bare' gas-polymer interaction parameter and is composition-independent. The remaining undefined quantities are equation-of-state parameters and variables; the LF equation of state is:

$$\tilde{\rho}^2 + \tilde{P} + \tilde{T}[\ln(1 - \tilde{\rho}) + (1 - 1/r)\tilde{\rho}] = 0 \quad (38a)$$

or equivalently

$$\tilde{\rho} = 1 - \exp[-(\tilde{\rho}^2 + \tilde{P})/\tilde{T} - (1 - 1/r)\tilde{\rho}] \quad (38b)$$

where $\tilde{\rho}$, \tilde{P} and \tilde{T} are the reduced (dimensionless) mass density, pressure and temperature, respectively. The mass density, pressure and temperature are reduced by their respective equation-of-state parameters ρ^* , P^* and T^* ; r is a dimensionless size parameter proportional to the molecular weight (M):

$$r = M(P^*/kT^*\rho^*) \quad (39)$$

P^* is the hypothetical cohesive energy density of the liquid at absolute zero and ρ^* is the corresponding mass density; T^* does not have a clear physical significance³⁰.

A pure component is completely characterized by the three equation-of-state parameters; they have been tabulated for many small molecules³⁷ as well as for several polymers⁴¹. For small molecules, the parameters can be determined from a latent heat of vaporization and a liquid density⁴²; for polymers, a density, thermal expansion coefficient and isothermal compressibility are required^{39,41}. In equation (37) $\tilde{\rho}_2$ is the reduced mass density of the polymer which is calculated from the

equation of state. The only unknown parameter in equation (37) is χ_{12} and it is given by:

$$\chi_{12} = [(P_1^* + P_2^* - 2\xi(P_1^*P_2^*)^{1/2})/kT] \quad (40)$$

where ξ is a dimensionless parameter; if both the gas and polymer are non-polar, it is expected that $\xi = 1$ (geometric mean approximation) so that:

$$\chi_{12} = (\sqrt{P_1^*} - \sqrt{P_2^*})^2/kT \quad (41)$$

Equations (37) and (41) when combined yield excellent Henry's law constants for 10 different probe gases in polystyrene⁴³. In general however, χ_{12} must be determined experimentally, which can be done with the i.g.c. determined Henry's law constant and equation (37).

The corresponding Henry's law constant for a miscible blend (polymer 2 + polymer 3) is obtained by equating the chemical potential of the gas at temperature T and pressure P to the chemical potential of the gas absorbed in the polymer blend:

$$\mu_1^0(\text{free gas}) = \mu_1(\text{absorbed gas}) \quad (42)$$

If the gas density ρ_g is low, then:

$$\mu_1^0/kT = \ln \tilde{\rho}_g - r_1 + 1 \quad (43)$$

and ρ_g can be replaced by its ideal-gas value PM_1/kT so that:

$$\mu_1^0/kT = \ln(PM_1/kT) - \ln \rho_1^* - r_1 + 1 \quad (44)$$

In the dilute limit of gas absorption ($\phi_1 \rightarrow 0$) and high molecular weights (M_1 and $M_2 \rightarrow \infty$) the chemical potential of the absorbed gas is given by³⁰:

$$\begin{aligned} \mu_1/kT = & \ln \phi_1 + 1 + \tilde{\rho}(M_1/\rho_1^*)[-P_1^*/kT \\ & + (\phi_2\chi_{12} + \phi_3\chi_{13} - \phi_2\phi_3\chi_{23}) \\ & + r_1(1 - \tilde{\rho})\ln(1 - \tilde{\rho})/\tilde{\rho} + \ln \tilde{\rho} \end{aligned} \quad (45)$$

Substituting equations (44) and (45) into (42) yields Henry's law with a Henry's law constant of

$$\begin{aligned} H = & (M_1/RT\rho)\exp\{\tilde{\rho}(M_1/\rho_1^*)[P_1^*/kT \\ & - (\phi_2\chi_{12} + \phi_3\chi_{13} - \phi_2\phi_3\chi_{23}) \\ & - r_1[1 + (1 - \tilde{\rho})\ln(1 - \tilde{\rho})/\tilde{\rho}]\} \end{aligned} \quad (46)$$

The volume fractions ϕ_i are defined as

$$\phi_i = \frac{w_i/\rho_i^*}{\sum_i w_i/\rho_i^*} \quad (47)$$

where the w_i are weight fractions. In equation (46) ρ is the mass density and $\tilde{\rho}$ is the reduced mass density of the blend of composition $\phi_2 + \phi_3 = 1$. Assuming the molecular weights of the two polymers are very large, the equation of state for the blend, equation (38b), becomes:

$$\tilde{\rho} = 1 - \exp(-\tilde{\rho}^2 T^*/T - \tilde{\rho}) \quad (48)$$

where T^* is now given by³⁰:

$$T^* = (\phi_2 P_2^* + \phi_3 P_3^* - \phi_2 \phi_3 k T \chi_{23}) / (\phi_2 P_2^*/T_2^* + \phi_3 P_3^*/T_3^*) \quad (49)$$

Equation (48) can be rapidly solved by iteration.

Notice that as $\phi_3 \rightarrow 0$ equation (46) reduces to (37). The χ_{ij} that appear in equations (46) and (49) are 'bare' interaction parameters and are defined by the obvious generalization of equation (40). Of course, χ_{23} is the elusive polymer-polymer interaction parameter. χ_{12} and χ_{13} can be determined by i.g.c. on the appropriate gas-polymer systems. Thus, in equation (46) the only unknown is χ_{23} , but notice through equations (48) and (49) that $\bar{\rho}$ is also an implicit function of χ_{23} . Measurement of the Henry's law constant of a probe gas in a miscible binary blend is tantamount to determining χ_{23} —an interaction parameter that should be independent of the probe gas.

SUMMARY

There are two important points made in this paper. The first is that for a binary polymer mixture there are in general four different interaction parameters that can be defined and determined experimentally. One is associated with the free energy; two are associated with the chemical potentials which depend on the first concentration derivative of the free energy; and one is associated with the spinodal which depends on the second derivative of the free energy. If one of these interaction parameters is composition-dependent, which invariably is the case, then the other three are also composition-dependent. However, the interaction parameters are all related and if the composition dependence of one is known, then the remaining three can be calculated via equations (9), (17), (19) and (20). This allows, for example, the spinodal line to be determined as well as the two-phase coexistence line (binodal) from measurement of any one of the four parameters.

The second and equally important point is that the difficulty of determining polymer-polymer interaction parameters for miscible blends by i.g.c. is related to the compositional dependence of the interaction parameters. This situation can be rescued by using an equation-of-state model, such as the lattice fluid model, for data interpretation. Theoretical Henry's law constants that govern gas sorption have been derived for both polymer-gas and polymer-polymer gas systems which contain composition- and probe-independent interaction parameters; it is suggested that i.g.c. measurements should concentrate on determining these 'bare' interaction parameters.

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