deviate substantially from unity, so that the effects of free volume and contact site dissimilarities included in $g°_T$ and in $\chi°_T$ are always large.

Concluding Remarks

If some previous applications of the FPP theory of λ and Y have failed, one of the main reasons could be the use of too simplified formulas containing approximations which, when applied to calculate interaction parameters, are equivalent to neglecting the dependence of g_{12} on mixed-solvent composition and to not properly taking into account the polymer concentration dependence of g_{13} and g_{23}.

We now have developed the equations of the FPP theory for λ and Y to a more detailed level, equivalent to a proper description of these dependencies of g_{i3}'s on φ_3 and of g_{12} on u_1.

The equations to be used for a comparison of the theory with experiment are eq 50–52. These still contain the approximations called set A. If desired, even this set of approximations can be avoided by using the complete equations for the M_{ij}^{R}'s (see eq 33 and 34). These may be useful to describe some particular systems.

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Registry No. PIB (homopolymer), 9003-27-4; PS (homopolymer), 9003-53-6; PMMA (homopolymer), 9011-14-7.

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Predictability of Properties in Ternary Solvent (1)/Solvent (2)/Polymer (3) Systems from Interaction Parameters of the Binary Systems. 1. General Considerations and Evaluation of Preferential Solvation Coefficients

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ABSTRACT: The ternary interaction potential, $g_T°$, and its derivative with polymer concentration $(\partial g_T/\partial\phi_3)_{u_1,\phi_3\to0}$, which, according to the Flory–Huggins formalism as generalized by Pouchlý, describe the sorption equilibrium in ternary solvent (1)/solvent (2)/polymer (3) systems, have been evaluated for diverse systems, and a correlation between them has been found, namely, $g_T° = K(g_{12} + (\partial g_T/\partial\phi_3)_{u_1,\phi_3\to0})$. This correlation has been explained by analyzing the contributions to g_T of the possible dependences of the binary interaction parameters, g_{ij}, on the third component in the ternary phase. On these grounds, $K = g_{13}°g_{23}°$ and both $g_T°$ and its derivative $(\partial g_T/\partial\phi_3)_{u_1,\phi_3\to0}$ may be defined solely in terms of binary interaction parameters and, as a consequence, so may any property of the sorption equilibrium. As an example, preferential sorption coefficients, λ, evaluated from data of the binary systems are compared with experimental values for two polystyrene, two poly(methyl methacrylate), and two poly(dimethylsiloxane) ternary systems.

Introduction

Total (Y) and preferential (λ) sorption coefficients describe sorption equilibrium in ternary solvent (1)/solvent (2)/polymer (3) systems.[1-3] The equations defining Y and λ according to the Flory–Huggins formalism (FH) generalized to ternary systems are not simple functions of system composition. They depend on binary (g_{ij}) and ternary (g_T) interaction potentials and on some derivatives of both kinds of potentials with system composition.[4,5] g_T and its derivatives are unknown, their evaluation from experimental data being the main task when intending to apply FH formalism to ternary systems. According to this for-

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malism, g_T may be evaluated from λ data. The evaluation method, as proposed by Munk et al.,[6,7] exactly solves the differential equation in g_T defining λ. Munk's method demands λ data over the whole composition range of the binary solvent mixture and evaluates g_T as a function of solvent mixture composition; therefore the first derivative of g_T with respect to that variable must be also known. As in the equation defining Y, the last remaining unknown is the derivative of g_T with polymer concentration $(\partial g_T/\partial\phi_3)_{u_1,\phi_3\to 0}$; this may be evaluated from Y data. In this context, this derivative looks like a parameter adjusting at one the λ and Y experimental data; therefore it is not possible to predict Y values from experimental λ data or vice versa.

Few attempts have been made to try to solve the above problem. Van der Berg and Altena[8] calculated Y values from $[\eta]$ data through the Flory–Fox model[9]. Assuming cubic expansions for g_T and its derivative with polymer concentration, they calculated the coefficients of both cubic polynomials from Y input values by a computer program. As the authors admitted, their calculated values did not reproduce those obtained by Munk from A_2 and λ data.

On the other hand, two approximate methods have been proposed by Pouchlý.[10,11] In his first approach, he assumed proportionality between g_T and g_{12}, namely $g_T = a_g g_{12}$, and he was able to calculate the constant a_g from experimental data. Once a_g was evaluated, g_T was known and also its derivatives with solvent mixture composition. With this approximate approach the problem of the adjusting character of the g_T derivative with polymer concentration still remains unsolved as well as the impossibility of predicting Y values from experimental λ ones. In his second approach, Pouchlý assumes that both g_T and χ_T (ternary interaction parameter) are proportional to g_{12}. He then eliminates g_T in the equation defining λ and eliminates g_T and its derivative with polymer concentration in the equation defining Y, establishing a correlation between Y data.

Whichever approach is followed and because of the unpredictable character of g_T, the applicability of the generalized formalism seems to be constrained to establish correlations between the magnitudes defining the sorption equilibrium, but the formalism is unable to predict any experimental property of the ternary system in terms of those of the respective binary ones. In this paper, a new approach is explored. It defines g_T as a function of the binary parameters. Its consequences are thoroughly studied and tested for several ternary systems.

Theory

A dilute solvent (1)/solvent (2)/polymer (3) solution may be considered as formed by two phases coexisting in equilibrium: the bulk solvent and the domain of the coil, binary and ternary, respectively. Throughout the text the following nomenclature will be used to define the composition in both phases. ϕ_{i0} $(i = 1, 2)$ is the volume fraction of component i in the bulk solvent, and it is assumed to be equal to the compositon of the solvent mixture prior to polymer solution. ϕ_i $(i = 1, 2, 3)$ is the volume fraction of component i in the domain of the coil and u_i $(i = 1, 2)$ the volume fraction of the solvent mixture in this phase, being $u_i = \phi_i/(1 - \phi_3)$.[10]

According to the FH formalism, as generalized by Pouchlý,[4] the Gibbs energy of mixing is defined by

$$\Delta G_M = RT\left(\sum_{i=1}^{3} n_i \ln \phi_i + \sum_{i=1}^{3}\sum_{j>i}^{3} g_{ij} n_i \phi_j + g_T n_1 \phi_2 \phi_3\right) \qquad (1)$$

where n_i is the number of moles of the ith component. Total (Y) and preferential sorption (λ) coefficients defining sorption equilibrium are respectively given by

$$Y = \frac{V_1}{2RT}(M_{33} - M_{13}^2/M_{11}) \qquad (2)$$

$$\lambda = -\bar{v}_3 M_{13}/M_{11} \qquad (3)$$

where M_{ij} stands for the limit at polymer infinite dilution of the second derivative of the Gibbs energy of mixing with respect to u_i and u_j. The diverse M_{ij}'s are defined by

$$\frac{M_{11}V_1}{RT} = N_{11} = \frac{1}{\phi_{10}} + \frac{s}{\phi_{20}} - 2g_{12} + 2(\phi_{20} - \phi_{10})\frac{\mathrm{d}g_{12}}{\mathrm{d}\phi_{10}} + \phi_{10}\phi_{20}\frac{\mathrm{d}^2 g_{12}}{\mathrm{d}\phi_{10}^2} \qquad (4)$$

$$\frac{M_{13}V_1}{RT} = N_{13} = s - 1 + g_{13}^\circ - s g_{23}^\circ + (\phi_{10} - \phi_{20})(g_{12} - g_T^\circ) - \phi_{10}\phi_{20}\frac{\mathrm{d}g_{12}}{\mathrm{d}\phi_{10}} + \phi_{10}\phi_{20}\left(\frac{\partial g_T}{\partial u_1}\right)_{\phi_3\to 0} \qquad (5)$$

$$\frac{M_{33}V_1}{2RT} = N_{33} = \frac{1}{2}(\phi_{10} + s\phi_{20}) - \left(g_{13}^\circ - \frac{\mathrm{d}g_{13}}{\mathrm{d}\phi_3}\right)\phi_{10} - s\left(g_{23}^\circ - \frac{\mathrm{d}g_{23}}{\mathrm{d}\phi_3}\right)\phi_{20} + g_{12}\phi_{10}\phi_{20} - 2g_T^\circ\phi_{10}\phi_{20} + \phi_{10}\phi_{20}\left(\frac{\partial g_T}{\partial \phi_3}\right)_{u_1,\phi_3\to 0} \qquad (6)$$

where V_i $(i = 1, 2)$ is the molar volume of solvent i, $s = V_1/V_2$, $\bar{v}_3$ is the partial specific volume of the polymer, g_{13}° is the binary interaction parameter of solvent i/polymer at polymer infinite dilution, $g_{12}^\circ(\phi_{10})$ is the binary interaction potential between both solvents in the bulk solvent, and g_T is the ternary interaction potential. A detailed analysis of eq 4–6 may be worthwhile.

Analysis of Eq 4. Here, the $g_{12}(\phi_{10})$ function and its first and second total derivatives with bulk-solvent composition (or solvent mixture composition prior to polymer solution, as mentioned above) appear. Therefore, when the function $g_{12}(\phi_{10})$ is experimentally known, the $M_{11}(\phi_{10})$ function can unequivocally be calculated.

Analysis of Eq 5. In M_{13}, eq 5, $(s - 1 + g_{13}^\circ - sg_{23}^\circ)$, $g_{12}(\phi_{10})$ and its first derivative, g_T°, and the partial derivative $(\partial g_T/\partial u_1)_{\phi_3\to 0}$ appear:

(a) With respect to $g_{12}(\phi_{10})$ and its derivative the comments made above also apply here.

(b) The dependence of the interaction potential solvent/polymer function, $g_{13}(\phi_3)$, on polymer concentration (ϕ_3) may be expressed as a series in ϕ_3 powers.[12] At low polymer dilution ($\phi_3 \to 0$, as is the present case), quadratic and higher ϕ_3 powers can be neglected; therefore

$$g_{i3}(\phi_3) = g_{i3}^\circ + \phi_3(\mathrm{d}g_{i3}/\mathrm{d}\phi_3) \qquad (7)$$

g_{i3}° and $\mathrm{d}g_{i3}/\mathrm{d}\phi_3$ being constants. The term $(s - 1 + g_{13}^\circ - sg_{23}^\circ)$ will then also be constant, with a value g^*

$$g^* = s - 1 + g_{13}^\circ + sg_{23}^\circ \qquad (8)$$

Because g_{13}° and/or g_{23}° is usually unknown, the constant g^* also remains as an unknown to be calculated either by approximate[10] or by exact methods, as shown later.

(c) $g_T^\circ(u_1)$ is the value of the $g_T(u_1, \phi_3)$ function at $\phi_3 = 0$. The functionality of $g_T(u_1, \phi_3)$ with u_1 and ϕ_3, when $\phi_3 \to 0$, can be expressed, as proposed by Pouchlý,[4] by

$$g_T(u_1,\phi_3) = a_0 + a_1u_1 + a_2u_1^2 + \ldots + a_nu_1^n + \phi_3(b_0 + b_1u_1 + b_2u_2^2 + \ldots b_mu_1^m) \qquad (9)$$

which may be arranged as

$$g_T(u_1,\phi_3) = g_T^\circ + \phi_3(\partial g_T/\partial\phi_3)_{u_1,\phi_3\to 0} \qquad (10)$$

where $g_{\mathrm{T}}^{\circ}(u_1)$ and $(\partial g_{\mathrm{T}}/\partial \phi_3)_{u_1,\phi_3\to 0}$ are polynomials in u_1 with n and m degrees, respectively.[6,8,13,14] The function $g_{\mathrm{T}}^{\circ}(u_1)$ in eq 4 remains then as an unknown to be calculated together with g^*, either by approximate or by exact methods.

(d) Finally, the partial derivative $(\partial g_{\mathrm{T}}/\partial u_1)_{\phi_3\to 0}$ can be written at polymer infinite dilution as $\mathrm{d}g_{\mathrm{T}}^{\circ}/\mathrm{d}u_1$, and it will be polynomial in u_1 with degree $n - 1$, easily evaluated if the function $g_{\mathrm{T}}^{\circ}(u_1)$ is known.

Analysis of Eq 6. In M_{33}, eq 6, g_{i3}° (i = 1, 2), the derivatives $\mathrm{d}g_{i3}/\mathrm{d}\phi_3$ (i = 1, 2), $g_{12}(\phi_{10})$, $g_{\mathrm{T}}(u_1)$, and the partial derivative $(\partial g_{\mathrm{T}}/\partial \phi_3)_{u_1,\phi_3\to 0}$ appear.

(a) With respect to g_{i3}° and $g_{12}(\phi_{10})$ the comments made above must be recalled.

(b) The derivatives $\mathrm{d}g_{i3}/\mathrm{d}\phi_3$ disappear in eq 6, since according to Koningsveld et al.[15,16]

$$\chi_{i3}(\phi_3) = g_{i3} - (1 - \phi_3)(\mathrm{d}g_{i3}/\mathrm{d}\phi_3) \tag{11}$$

which at polymer infinite dilution ($\phi_3 \to 0$) is transformed into

$$\chi_{i3}^{\circ} = g_{i3}^{\circ} - \mathrm{d}g_{i3}/\mathrm{d}\phi_3 \tag{12}$$

where all terms are constants. When $g_{i3}^{\circ} - \mathrm{d}g_{i3}/\mathrm{d}\phi_3$ given by the above equation is substituted into eq 6, it is transformed into

$$N_{33} = (1/2)(\phi_{10} + s\phi_{20}) - \chi_{13}^{\circ}\phi_{10} - s\chi_{23}^{\circ}\phi_{20} + (g_{12} - 2g_{\mathrm{T}} + (\partial g_{\mathrm{T}}/\partial \phi_3)_{u_1,\phi_3\to 0})\phi_{10}\phi_{20} \tag{13}$$

given in terms of solvent/polymer interaction parameters (χ_{i3}°), usually known or measurable.

(c) Finally, $g_{\mathrm{T}}^{\circ}(u_1)$ and $(\partial g_{\mathrm{T}}/\partial \phi_3)_{u_1,\phi_3\to 0}$ remain unknown.

Summary of the Analysis. From a phenomenological point of view, two magnitudes define the sorption equilibrium in tenary systems, total (Y) and preferential (λ) solvation coefficients. λ is a magnitude directly accessible through experiment, whereas Y is not, but is related with the experimental magnitude A_2 (second virial coefficient)[17,18] through

$$Y = V_1 A_2/\bar{v}_3^{\,2} \tag{14}$$

or indirectly related, through some excluded volume theory, with another experimental magnitude such as $[\eta]$ (intrinsic viscosity). On the other hand, according to the FH formalism, besides binary interaction parameters (potentials) usually known or measurable, three unknown functions (or parameters) are necessary to describe the above equilibrium, namely, the g^* parameter and the functions $g_{\mathrm{T}}^{\circ}(u_1)$ and $(\partial g_{\mathrm{T}}/\partial \phi_3)_{u_1,\phi_3\to 0}$. Because they are unknown, the main task, when intending to apply FH formalism, is their evaluations, FH formalism remaining then as a purely descriptive formalism. For the evaluation of the above unknowns, exact and approximate methods have been followed.

Evaluation of the Unknowns. The exact method, as proposed by Munk,[6] solves the differential equation in g_{T} defining λ (see eq 3–5), $g_{\mathrm{T}}^{\circ}(u_1)$ and g^* being respectively given by

$$g_{\mathrm{T}}^{\circ}(u_1) = g_{12}(\phi_{10}) + \frac{1}{\phi_{20}}\int_{\phi_{10}}^{1} \frac{\lambda(\phi_{10})}{\bar{v}_3} N_{11}\,\mathrm{d}\phi_{10} - \frac{1}{\phi_{10}}\int_{0}^{\phi_{10}} \frac{\lambda(\phi_{10})}{\bar{v}_3} N_{11}\,\mathrm{d}\phi_{10} \tag{15}$$

$$g^* = -\int_{0}^{1} \frac{\lambda(\phi_{10})}{\bar{v}_3} N_{11}\,\mathrm{d}\phi_{10} \tag{16}$$

Once $g_{\mathrm{T}}^{\circ}(u_1)$ and g^* are evaluated, the last unknown, $(\partial g_{\mathrm{T}}/\partial \phi_3)_{u_1,\phi_3\to 0}$, may be evaluated from A_2 data (see the substitutions in eq 2 of Y calculated from A_2 through eq 14 and of M_{ij}'s given by eq 4–6). Munk's method demands λ as a continuous function over the whole composition range.

Several approximate methods have been proposed. Altena's method[8] assumes for both g_{T}° and $(\partial g_{\mathrm{T}}/\partial \phi_3)_{u_1,\phi_3\to 0}$ the same functionality degree in u_1, namely cubic expansions. From Y input values, calculated from $[\eta]$ experimental data through the Flory–Fox model,[9] Altena's method calculates the coefficients of both cubic polynomials by applying a computer program for the solution of a set of M (number input data) nonlinear equations (substitution in eq 2 of M_{ij}'s given by eq 4–6) with N unknowns ($M > N$). No further criticism on this method will appear in this paper, since, as the authors admitted, their g_{T}° and $(\partial g_{\mathrm{T}}/\partial \phi_3)_{u_1,\phi_3\to 0}$ calculated values did not reproduce those obtained by Munk's method,[6] probably due to the assumption of the cubic functionality of g_{T}° and $(\partial g_{\mathrm{T}}/\partial \phi_3)_{u_1,\phi_3\to 0}$ and to the use of indirect Y values (coming from the application of an excluded volume model).

Another approximate method is followed by Horta et al.,[19] who, from A_2 data and neglecting in Y preferential sorption effects as well as the $(\partial g_{\mathrm{T}}/\partial \phi_3)_{u_1,\phi_3\to 0}$ derivative, calculated g_{T}°, which, in turn, was applied to predict λ.

Also intending to reproduce λ's only from $g_{12}(\phi_{10})$ data or looking for a correlation between λ experimental data, Pouchlý[10] assumed that

$$g_{\mathrm{T}}^{\circ}(u_1) = a_g g_{12}(\phi_{10}) \tag{17}$$

a_g being a constant at any composition.

λ, defined by eq 3, is $g_{\mathrm{T}}^{\circ}(u_1)$ dependent through N_{13} (eq 5), but that dependence disappears when $g_{\mathrm{T}}^{\circ}(u_1)$ is substituted in eq 5 by its approximate value given by eq 17. The equation of a straight line is predicted upon rearranging terms in eq 3, after substitution of N_{11} given by eq 4 and the approximate N_{13}. From the intercept and slope the values of the constants g^* and $1 - a_g$ are evaluated, which, of course, may be used to recalculate λ.

In a further paper,[11] looking for correlations between $[\eta]$ data, Pouchlý assumes that

$$\chi_{\mathrm{T}}^{\circ}(u_1) = g_{\mathrm{T}}^{\circ}(u_1) - \frac{1}{2}\left(\frac{\partial g_{\mathrm{T}}}{\partial \phi_3}\right)_{u_1,\phi_3\to 0} = a_{\chi} g_{12}(\phi_{10}) \tag{18}$$

a_{χ} being a constant at any composition. The substitution of this assumption in eq 13 yields for N_{33} the following value:

$$N_{33} = (1/2)(\phi_{10} + \phi_{20}) - \chi_{13}\phi_{10} - s\chi_{23}\phi_{20} + g_{12}(1 - 2a_{\chi})\phi_{10}\phi_{20} \tag{19}$$

in which N_{33} no longer depends on $g_{\mathrm{T}}^{\circ}(u_1)$ and $(\partial g_{\mathrm{T}}/\partial \phi_3)_{u_1,\phi_3\to 0}$. The substitution in eq 2 of this new value together with the approximate N_{13} obtained by substitution in eq 5 of the approach 17 and with N_{11} given by eq 4 yields Y as a function of $g_{12}(\phi_{10})$. By the rearrangement of terms in the new defining Y equation, a linear correlation is predicted. From the intercept and the slope the magnitudes χ_{23}° and $(1 - 2a_{\chi})$ may respectively be evaluated if Y values are known. These can be calculated from experimental A_2 data through eq 14 or from $[\eta]$ values through any excluded volume model.

Results and Discussion

Of course, the direct verification of the above approaches shows experimental difficulties; among them and not the least is the availability of adequate experimental data. The calculations of g_{T} and its derivatives demand A_2 (or $[\eta]$) and λ measurements for the same polymer sample at the same temperature and over the whole composition range

Table I
Information Available on Interaction Potentials for Diverse Ternary Systems

system	$g_{13}°$	$g_{23}°$	$dg_{13}/d\phi_3$	$dg_{23}/d\phi_3$	$g_{13}°g_{23}°$	K^a	g^{*b}
B/CH/PS	0.455^c	0.715^c	0	0.205^c	0.325^c	0.33	−0.358
EA/CH/PS	0.662^e	0.727^d	0.171^f	0.205^c	$0.48^{d,e}$	0.48	−0.091
HEP/MEK/PDMS	0.52^h	0.84^i	0.09^g	0.34^j	$0.44^{h,i}$	0.46	−0.219
UND/MEK/PDMS						0.428	0.009
ACN/CLB/PMMA						0.455	−0.025
ACN/CTC/PMMA						0.398	0.050

[a] As evaluated from Figure 4. [b] As evaluated through eq 16.[6] [c] From ref 10. [d] Calculated through eq 12 from $\chi_{23}° = 0.522$[6] and $dg_{23}/d\phi_3 = 0.205$.[10] [e] From g^* with $g_{23}° = 0.727$ as calculated in footnote *d*. [f] Calculated through eq 12 from $\chi_{13}° = 0.491$[6] and $g_{13}° = 0.662$ as calculated in footnote *e*. [g] Assuming that $dg_{13}/d\phi_3 \approx d\chi_{13}/d\phi_3$[15] with $d\chi_{13}/d\phi_3 = 0.09$.[27] [h] Calculated through eq 12 from $\chi_{13}° = 0.430$[22] and $dg_{13}/d\phi_3 = 0.09$ as in footnote *g*. [i] *from* g^* with $g_{13}° = 0.52$ as calculated in footnote *h*. [j] Calculated through eq 12 from $\chi_{23}° = 0.499$[14] and $g_{23}°$ as calculated in footnote *i*.

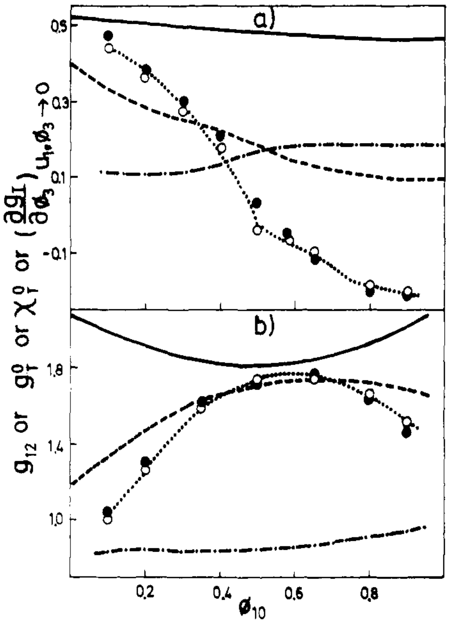

Figure 1. Dependences of g_{12} (—), $g_T°$ (– – –), $\chi_T°$ (– · –), and $(\partial g_T/\partial\phi_3)_{u_1,\phi_3\to 0}$ (···) on system composition for (a) B/CH/PS and (b) EA/CH/PS. (○) $\bar{M}_w = 372000$; (●) $\bar{M}_w = 35600$.

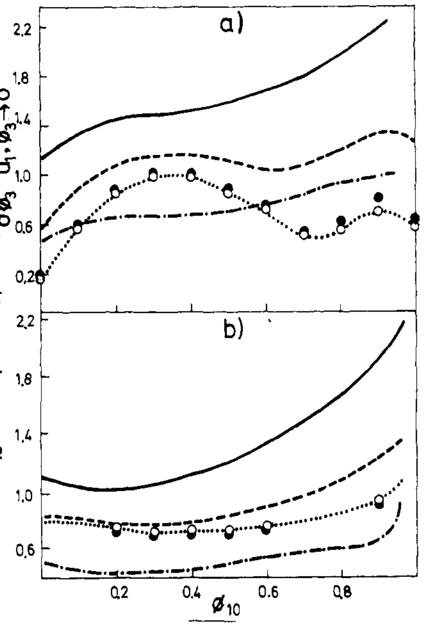

Figure 2. Dependences of g_{12} (—), $g_T°$ (– – –), $\chi_T°$ (– · –), and $(\partial g_T/\partial\phi_3)_{u_1,\phi_3\to 0}$ (···) on system composition for (a) HEP/MEK/PDMS, ((○) $\bar{M}_w = 125000$; (●) $\bar{M}_w = 80500$) and (b) UND/MEK/PDMS ((○) $\bar{M}_w = 125000$; (●) $\bar{M}_w = 150000$).

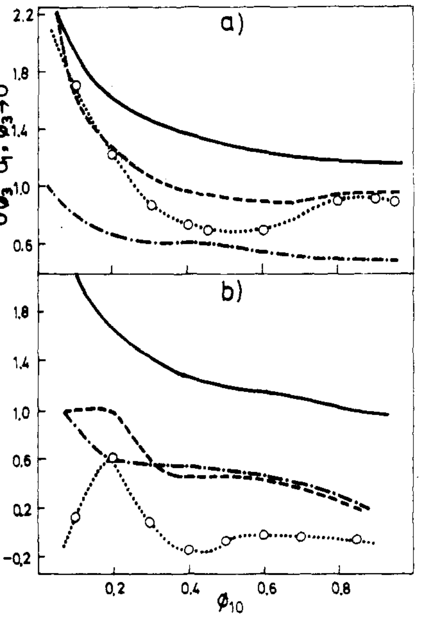

Figure 3. Dependences of g_{12} (—), $g_T°$ (– – –), $\chi_T°$ (– · –), and $(\partial g_T/\partial\phi_3)_{u_1,\phi_3\to 0}$ (···) on system composition for (a) ACN/CLB/PMMA ((○) $\bar{M}_w = 237000$) and (b) ACN/CTC/PMMA ((●) $\bar{M}_w = 120000$).

of the solvent mixture besides adequate χ_{ij} and $g_{12}(\phi_{10})$ values. As far as we know, few systems fulfill the above requirements. Horta et al. measured A_2 and λ for the same polymer sample over the whole composition range, as well as the function g_{12}, for the acetonitrile (ACN)/1-chloro-*n*-butane (CLB)/poly(methyl methacrylate) (PMMA) and ACN/carbon tetrachloride (CTC)/PMMA systems.[19-21] Similar information is also available for *n*-hexane (HEX)/butanone (MEK)/poly(dimethylsiloxane) (PDMS),[13] *n*-heptane (HEP)/MEK/PDMS,[13] and *n*-undecane (UND)/MEK/PDMS[14] systems. Munk et al.,[6,7] who pioneered the evaluation of g_T and its derivatives, used as test systems benzene (B)/cyclohexane (CH)/polystyrene (PS) and ethyl acetate (EA)/CH/PS. They measured A_2 and λ for both systems over the whole composition range; however, for the g_{12} functions they used tentative values in a first publication,[6] which were revised later in a second paper.[7]

Subsequently, the verification of Horta's approach on the one hand and Pouchlý's, on the other is attempted. As test systems, the above PMMA and PS systems are chosen. Only two PDMS systems are studied, namely, the *n*-heptane and *n*-undecane ones. In Figures 1–3, g_{12}, $g_T°$, $(\partial g_T/\partial\phi_3)_{u_1,\phi_3\to 0}$, and $\chi_T°$ functions for the above systems are represented, and in Table I their $(g_{13}° - sg_{23}°)$ values (evaluated from g^*) are gathered. $g_T°$, as evaluated by Munk's method (eq 15) should be polymer molecular weight dependent through the dependences of λ and $g_{i3}°$ on polymer molecular mass. However, in the PS[6,7] and PDMS[13,14,22] systems, no clear dependence of λ on molecular weight was experimentally observed, at least in the measured range of molecular weights. Because of that, single $g_T°(u_1)$ functions represented in Figures 1 and 2 were evaluated from the single smoothed λ curves depicted through the diverse λ experimental data, as Munk et al.[6,7] and Pouchlý et al.[10] did before. $(\partial g_T/\partial \phi_3)_{u_1,\phi_3\to 0}$ evaluation through Munk's method demands $g_T°$ and A_2 data. Although $g_T°$ dependence on molecular mass has been omitted as mentioned above and given that A_2 is more sensitive to polymer molecular weight than λ, for an example, in Figures 1 and 2 $(\partial g_T/\partial \phi_3)_{u_1,\phi_3\to 0}$ values for diverse molecular weights have been represented. However, in order not to excessively crowd the figures, only one smoothed $(\partial g_T/\partial \phi_3)_{u_1,\phi_0\to 0}$ function corresponding to a single molecular weight has been represented. $(\partial g_T/\partial \phi_3)_{u_1,\phi_3\to 0}$ smoothed functions are for a polymer with $\bar{M}_w = 125000$ in both PDMS systems and $\bar{M}_w = 372000$ in both PS systems. Those $(\partial g_T/\partial \phi_3)_{u_1,\phi_3\to 0}$ smoothed functions were used together with $g_T°$ ones to evaluate $\chi_T°$ functions as defined by Pouchlý (eq 18), also represented in the figures.

The g_{12} functions depicted in Figures 1–3 are those measured by Horta et al. for the PMMA systems at 25 °C[19,20] and by Campos et al.[13,14] for the PDMS systems at 20 °C, whereas g_{12} for the B/CH system is the one reported by Pouchlý,[10] very close to that proposed by Munk.[6,7] The g_{12} function as proposed by Munk[6,7] for the EA/CH/PS system does not proceed from direct measurements at 20.0 °C but from indirect data. In order to ascertain the reliability of the g_{12} function used by Munk, its measurement by light scattering at 20.0 °C was undertaken[20] in this laboratory. The equation

$$g_{12} = 1.810 + 0.0249(\phi_{10} - \phi_{20}) + 0.306(\phi_{10} - \phi_{20})^2$$

reproduced the obtained data with a standard deviation of 0.6%, and it is the one represented in Figure 1.

$g_T°$, $(\partial g_T/\partial \phi_3)_{u_1,\phi_3\to 0}$, and $\chi_T°$ for the PMMA systems proceed from λ and A_2 data for a polymer with $\bar{M}_w = 237000$ in the ACN/CLB/PMMA[19] system and $\bar{M}_w = 120000$ in the ACN/CTC/PMMA[21] one. The λ smoothed curves used for $g_T°$ evaluation are those reported by Campos et al.[13,14] for the PDMS systems, by Pouchlý,[10] collecting diverse experimental data, for the B/CH/PS system, and by Munk et al.[6] for the EA/CH/CP system. A_2 used data for $(\partial g_T/\partial \phi_3)_{u_1,\phi_3\to 0}$, and $\chi_T°$ evaluations were those given by Campos et al.[13,14,22] for PDMS systems and by Munk et al.[6] for PS.

In all the systems, represented values in Figures 1–3 clearly show the inadequacy of Horta's approach. $(\partial g_T/\partial \phi_3)_{u_1,\phi_3\to 0}$ values are about the same order of magnitude as $g_T°$ ones; therefore the former cannot be neglected. The introduction of both functions is necessary for plausible interpretation of experimental data, as was pointed out by Munk et al.[6,7] and quantitatively demonstrated by Campos et al.[14]

On the other hand, except for the EA/CH/PS system and minor deviations occurring in other systems in certain narrow composition ranges, similar trends seem to be followed by $g_T°$, $\chi_T°$, and g_{12}, so both of Pouchlý's assumptions, as expressed by eq 17 and 18, seem then to hold as a general rule. From the relationship between $\chi_T°$ and $(\partial g_T/\partial \phi_3)_{u_1,\phi_3\to 0}$ in eq 18, when both of Pouchlý's assumptions are obeyed the more general correlation

$$g_T° = K\left(g_{12} + \left(\frac{\partial g_T}{\partial \phi_3}\right)_{u_1,\phi_3\to 0}\right) \tag{20}$$

must also hold, with $K = a_g/(1 + 2a_g - 2a_\chi)$ being a constant. In Figure 4, the above equation, represented as plots of $g_T°/(g_{12} + (\partial g_T/\partial \phi_3)_{u_1,\phi_3\to 0})$ vs. ϕ_{10}, is tested for the six systems studied so far in this paper. A fair constancy over the whole composition range in the quotient $g_T°/(g_{12} + (\partial g_T/\partial \phi_3)_{u_1,\phi_3\to 0})$ obtains in all systems, even EA/CH/PS, which, as mentioned above, does not completely obey Pouchlý's first assumption. Obtained K values for the six systems are gathered in Table I.

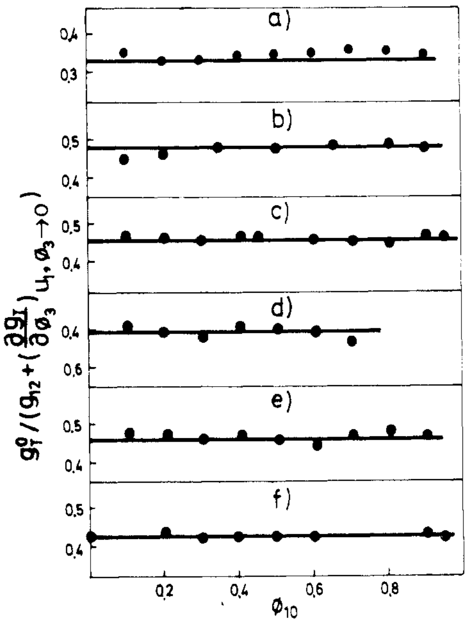

Figure 4. Dependence of $g_T°/(g_{12} + (\partial g_T/\partial \phi_3)_{u_1,\phi_3\to 0})$ on system composition for (a) B/CH/PS, (b) EA/CH/PS, (c) ACN/CLB/PMMA, (d) ACN/CTC/PMMA, (e) HEP/MEK/PDMS, and (f) UND/MEK/PDMS.

A detailed analysis of those K values shows that they are very close to those in the product $g_{13}°g_{23}°$, which are also gathered in Table I for those systems where separate values of $g_{13}°$ and $g_{23}°$ are known. This surprising behavior seems to indicate that there is certain information enclosed in K; therefore its empirical character should be put aside. $g_T°$ seems then to be defined by

$$g_T° = g_{13}°g_{23}°\left(g_{12} + \left(\frac{\partial g_T}{\partial \phi_3}\right)_{u_1,\phi_3\to 0}\right) \tag{21}$$

Looking for an explanation to that general (universal?) behavior, we had to resort to the underlying ideas in the creation of g_T, as introduced by Pouchlý in his formalism.[10] g_T is introduced by Pouchlý in the FH formalism so as to take into account the possible dependences of the binary parameters on the third component in the ternary phase. The following analysis tries to rationalize those dependeces. It must be certainly pointed out that the treatment leaves unchanged each one of the terms contributing to the mixing Gibbs energy, as originally defined in eq 1, and it only intends to qualify the possible contributions of the binary parameters to the ternary one.

The value of the g_{i3} parameter, which in the absence of the j third component ($i = 1,2$; $j \neq i$) depends solely on polymer concentration, $g_{i3}(\phi_3)$, will adopt in its presence a new "perturbed" value $g_{i3}(\phi_3,\phi_j)$. Similarly, the binary $g_{12}(\phi_{10})$ parameter through the presence of polymer will be transformed into the "perturbed" $g_{12}(\phi_1,\phi_3)$. Let us call α, β, and γ the "perturbations" suffered by the binary parameters in the presence of the third component in the ternary phase, in such a way that

$$g_{13}(\phi_3,\phi_2) = g_{13}(\phi_3) + \alpha$$
$$g_{23}(\phi_3,\phi_1) = g_{23}(\phi_3) + \beta$$
$$g_{12}(\phi_1,\phi_3) = g_{12}(\phi_{10}) + \gamma \tag{22}$$

where the functions $g_{i3}(\phi_3)$, defined in eq 7, display similar functionalities with ϕ_3 to that followed by $g_T(\phi_1,\phi_3)$ (see eq 10).

On the other hand, it is generally admitted that g_T is mainly created at the expense of g_{12},[10,23] which seems to indicate that the deviations occurring in g_{i3} parameters due to the presence of the j component are minimal. In other words, in a first approach, at least in dilute polymer solutions, let us assume that $\alpha \simeq 0$, $\beta \simeq 0$, and $\gamma \simeq \gamma^\circ$ ($\gamma^\circ \equiv \gamma_{\phi_3\to 0}$), since even at $\phi_3 \to 0$ there is a ternary phase and therefore γ, which is the perturbation suffered by g_{12} in the immediate vicinity of the chain, does not vanish as neither does the ternary phase.

By generalizing Pouchlý's first approach, $g_T{}^\circ(u_1) \sim g_{12}(\phi_{10})$, at any composition of the ternary mixture and assuming that $g_T(u_1,\phi_3)$ is proportional not only to g_{12} but also to g_{13} and g_{23}, one obtains the following equation:

$$g_T(u_1,\phi_3) \sim g_{12}(\phi_1,\phi_3)g_{13}(\phi_2,\phi_3)g_{23}(\phi_1,\phi_3) \qquad (23)$$

Assuming that the proportionality constant of the above equation is unity, substituting the resulting $g_T(u_1,\phi_3)$ function in the expression defining the mixing Gibbs energy (eq 1), and recalling the definition of $g_{i3}(\phi_3)$, as given by eq 7, we obtain the following values for M_{13} and M_{33}:

$$\frac{M_{13}V_1}{RT} = \left(s - 1 - (\phi_{10} - \phi_{20})g_{12} - \phi_{10}\phi_{20}\frac{\mathrm{d}g_{12}}{\mathrm{d}\phi_{10}} + g_{13}{}^\circ - sg_{23}{}^\circ\right) + (\phi_{20} - \phi_{10})\left(g_{13}{}^\circ g_{23}{}^\circ(g_{12} + \gamma^\circ) + \phi_{10}\phi_{20}\frac{\mathrm{d}g_{12}}{\mathrm{d}\phi_{10}} + g_{13}{}^\circ g_{23}{}^\circ\left(\frac{\partial\gamma^\circ}{\partial u_1}\right)_{\phi_3\to 0}\right) \qquad (24)$$

$$\frac{M_{33}V_1}{2RT} = \frac{1}{2}(\phi_{10} - \phi_{20}) - \left(g_{13}{}^\circ - \frac{\mathrm{d}g_{13}}{\mathrm{d}\phi_3}\right)\phi_{10} - s\left(g_{23}{}^\circ - \frac{\mathrm{d}g_{23}}{\mathrm{d}\phi_3}\right)\phi_{20} + g_{12}\phi_{10}\phi_{20} - 2(g_{13}{}^\circ g_{23}{}^\circ(g_{12} + \gamma^\circ))\phi_{10}\phi_{20} + \left((g_{12} + \gamma^\circ) \times \left(g_{23}{}^\circ\frac{\mathrm{d}g_{13}}{\mathrm{d}\phi_3} + g_{13}{}^\circ\frac{\mathrm{d}g_{23}}{\mathrm{d}\phi_3}\right) + g_{13}{}^\circ g_{23}{}^\circ\left(\frac{\partial\gamma^\circ}{\partial\phi_3}\right)_{\phi_3\to 0}\right)\phi_{10}\phi_{20} \qquad (25)$$

A comparison of eq 24 with eq 5 allows us to establish the following equalities:

$$g_T{}^\circ = g_{13}{}^\circ g_{23}{}^\circ(g_{12}(\phi_{10}) + \gamma^\circ)$$
$$\left(\frac{\partial g_T}{\partial u_1}\right)_{\phi_3\to 0} = g_{13}{}^\circ g_{23}{}^\circ\left(\frac{\mathrm{d}g_{12}}{\mathrm{d}\phi_{10}} + \left(\frac{\partial\gamma^\circ}{\partial u_1}\right)_{\phi_3\to 0}\right) \qquad (26)$$

both consistent between them. Similarly, the comparison of eq 25 with eq 6 yields again eq 26 and

$$\left(\frac{\partial g_T}{\partial\phi_3}\right)_{u_1,\phi_3\to 0} = (g_{12}(\phi_{10}) + \gamma^\circ) \times \left(g_{23}{}^\circ\frac{\mathrm{d}g_{13}}{\mathrm{d}\phi_3} + g_{13}{}^\circ\frac{\mathrm{d}g_{23}}{\mathrm{d}\phi_3}\right) + g_{13}{}^\circ g_{23}{}^\circ\left(\frac{\partial\gamma^\circ}{\partial\phi_3}\right)_{\phi_3\to 0} \qquad (27)$$

this last equation also being consistent with eq 26.

Equation 26 is coincident with the one empirically found (eq 21), whose validity was thoroughly discussed before, if

$$\gamma^\circ = (\partial g_T/\partial\phi_3)_{u_1,\phi_3\to 0} \qquad (28)$$

which is in accordance with the widespread idea that g_T proceeds from g_{12}. So, Bohdanecký[24] specifically points out that g_T is "the parameter representing the 1–2 interaction of solvent molecules in the vicinity of the polymer segment" and Pouchlý et al.[10,25] defines the difference ($g_{12} - g_T$) as an "effective g_{12}". Hereupon an equivalence must exist between γ, which takes into account the g_{12} variations in the presence of ϕ_3, and the term accounting for the g_T changes with ϕ_3, namely $(\partial g_T/\partial\phi_3)_{u_1,\phi_3\to 0}$.

Finally, from $g_T(\phi_1,\phi_3) = g_T{}^\circ(u_1) + \phi_3(\partial g_T/\partial\phi_3)_{u_1,\phi_3\to 0}$, as stated in eq 10, and the fact that $g_T{}^\circ(u_1)$ and $(\partial g_T/\partial\phi_3)_{u_1,\phi_3\to 0}$ are polynomials in u_1 with n and m degrees, respectively, that is, both independent of ϕ_3 at polymer infinite dilution and therefore so is γ°, eq 27 is transformed into

$$\left(\frac{\partial g_T}{\partial\phi_3}\right)_{u_1,\phi_3\to 0} = \left(g_{12}(\phi_{10}) + \left(\frac{\partial g_T}{\partial\phi_3}\right)_{u_1,\phi_3\to 0}\right)\left(g_{13}{}^\circ\frac{\mathrm{d}g_{23}}{\mathrm{d}\phi_3} + g_{23}{}^\circ\frac{\mathrm{d}g_{13}}{\mathrm{d}\phi_3}\right) \qquad (29)$$

The value of the adjusting parameter $(\partial g_T/\partial\phi_3)_{u_1,\phi_3\to 0}$ can then be defined in terms of binary interaction parameters by

$$\left(\frac{\partial g_T}{\partial\phi_3}\right)_{u_1,\phi_3\to 0} = g_{12}(\phi_{10})\left(g_{23}{}^\circ\frac{\mathrm{d}g_{13}}{\mathrm{d}\phi_3} + g_{13}{}^\circ\frac{\mathrm{d}g_{23}}{\mathrm{d}\phi_3}\right)\Bigg/\left(1 - g_{13}{}^\circ\frac{\mathrm{d}g_{13}}{\mathrm{d}\phi_3} - g_{23}{}^\circ\frac{\mathrm{d}g_{23}}{\mathrm{d}\phi_3}\right) \qquad (30)$$

Similarly, substitution of the $(\partial g_T/\partial\phi_3)_{u_1,\phi_3\to 0}$ value in eq 21, or in eq 26 with the γ value given by eq 28, also allows us to define the other adjustable function, $g_T{}^\circ(u_1)$, as an exclusive function of binary parameters through

$$g_T{}^\circ(u_1) = g_{12}(\phi_{10})g_{13}{}^\circ g_{23}{}^\circ\Bigg/\left(1 - g_{23}{}^\circ\frac{\mathrm{d}g_{13}}{\mathrm{d}\phi_3} - g_{13}{}^\circ\frac{\mathrm{d}g_{23}}{\mathrm{d}\phi_3}\right) \qquad (31)$$

Defining in short

$$\delta \equiv g_{13}{}^\circ\frac{\mathrm{d}g_{23}}{\mathrm{d}\phi_3} + g_{23}{}^\circ\frac{\mathrm{d}g_{13}}{\mathrm{d}\phi_3}$$

eq 30 and 31 are respectively transformed into

$$\left(\frac{\partial g_T}{\partial\phi_3}\right)_{u_1,\phi_3\to 0} = \frac{\delta}{1 - \delta}g_{12}(\phi_{10}) \qquad (32)$$

$$g_T{}^\circ(u_1) = \frac{g_{13}{}^\circ g_{23}{}^\circ}{1 - \delta}g_{12}(\phi_{10}) \qquad (33)$$

and $\chi_T{}^\circ(u_1)$ can also be defined in terms of binary parameters through

$$\chi_T{}^\circ(u_1) = \frac{g_{13}{}^\circ g_{23}{}^\circ - \delta/2}{1 - \delta}g_{12}(\phi_{10}) \qquad (34)$$

recalling the $\chi_T{}^\circ$ definition in eq 18. Both 33 and 34 agree with both Pouchlý's assumptions (eq 17 and 18, respectively); therefore the proportionality constant a_g and a_χ lose their empirical character and their values may be predicted from data of the binary systems. In the following, for brevity, the validity of eq 32–34 is only tested with calculated $\chi_T{}^\circ(u_1)$ values since in $\chi_T{}^\circ(u_1)$ are enclosed both $g_T{}^\circ(u_1)$ and $(\partial g_T/\partial\phi_3)_{u_1,\phi_3\to 0}$. The evaluation of $\chi_T{}^\circ(u_1)$, or $g_T{}^\circ(u_1)$, or $(\partial g_T/\partial\phi_3)_{u_1,\phi_3\to 0}$ demands known values for the following parameters of the binary systems: $g_{13}{}^\circ$, $g_{23}{}^\circ$, $\mathrm{d}g_{13}/\mathrm{d}\phi_3$, $\mathrm{d}g_{23}/\mathrm{d}\phi_3$ (all of them enclosed in δ), and $g_{12}(\phi_{10})$. $g_{12}(\phi_{10})$ functions for all the systems studied so far in this paper are depicted in Figure 1. The remaining data for

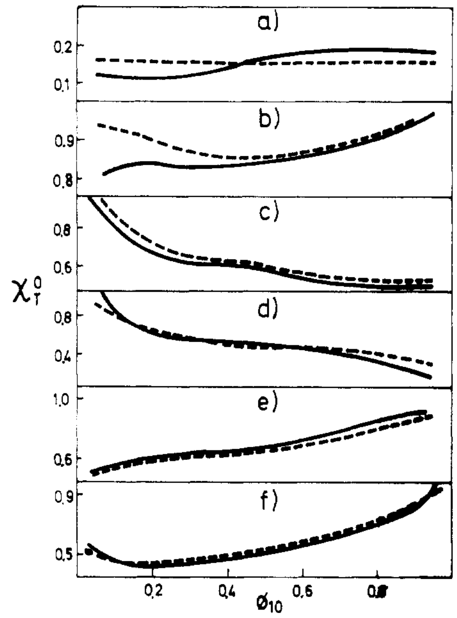

Figure 5. Variations with system composition of calculated binary parameters (---) and experimental (—) ternary interaction parameter ($\chi_T°$) for the same systems as in Figure 4.

those systems for which separate $g_{13}°$ and $g_{23}°$ values are known are also gathered in Table I. For UND/MEK/PDMS,[14] ACN/CLB/PMMA,[19] and ACN/CTC/PMMA[21] systems only separate data for $\chi_{13}°$ and $\chi_{23}°$ are known. These systems obey eq 20 (see Figure 4) with K values gathered in Table I. Under the assumption that the physical significance of K also holds for these systems, from $K = g_{13}°g_{23}°$ and $g^* = (s - 1 + g_{13}° - sg_{23}°)$, also gathered in Table I, separate values for $g_{13}°$ and $g_{23}°$ can be obtained. Once these are known, the remaining unknown $\mathrm{d}g_{i3}/\mathrm{d}\phi_3$ ($i = 1, 2$) parameters can be evaluated through Koningsveld's equation,[15] from $g_{i3}°$ and $\chi_{i3}°$ known values. The following data sets were obtained in that way for the above systems. UND/MEK/PDMS system: $\chi_{13}° = 0.468$,[14] $\chi_{23}° = 0.499$,[14] $g_{13}° = 0.537$, $g_{23}° = 0.797$, $\mathrm{d}g_{13}/\mathrm{d}\phi_3 = 0.069$, and $\mathrm{d}g_{23}/\mathrm{d}\phi_3 = 0.298$. ACN/CLB/PMMA system: $\chi_{13}° = 0.508$,[19] $\chi_{23}° = 0.525$,[19] $g_{13}° = 0.769$, $g_{23}° = 0.592$, $\mathrm{d}g_{13}/\mathrm{d}\phi_3 = 0.261$, and $\mathrm{d}g_{23}/\mathrm{d}\phi_3 = 0.067$. ACN/CTC/PMMA system: $\chi_{13}° = 0.495$,[21] $\chi_{23}° = 0.510$,[21] $g_{13}° = 0.783$, $g_{23}° = 0.508$, $\mathrm{d}g_{13}/\mathrm{d}\phi_3 = 0.288$, and $\mathrm{d}g_{23}/\mathrm{d}\phi_3 = -0.002$. Even though the above results for both PMMA systems proceed from independent measurements, it is rewarding that there is consistence between both calculated $g_{13}°$ values, the small difference between them probably arising from different molecular weights of the studied PMMA samples, $\bar{M}_w = 237000$ in the ACN/CLB/PMMA system and $\bar{M}_w = 120000$ in the ACN/CTC/PMMA one.

In Figure 5 $\chi_T°(u_1)$ values calculated through eq 34 are compared with experimental values, which already were depicted in Figures 1–3. As can be seen, calculated $\chi_T°(u_1)$ values fairly fit experimental ones. The importance of this behavior should be stressed, since if the ternary parameters can already be calculated from the binary ones, any property of the ternary system may be predicted from data of the binary systems. As an example, the validity of the $g_T°(u_1)$ evaluation from binary parameters is used advantageously for the prediction of a property of the ternary system such as the preferential solvation parameter, λ, whose prediction is uncertain even through the FPP formalism.[19,26]

λ through the FH formalism generalized by Pouchlý is defined by eq 3. The substitution in that equation of the $g_T°(u_1)$ value given by eq 32, recalling that, as stated in

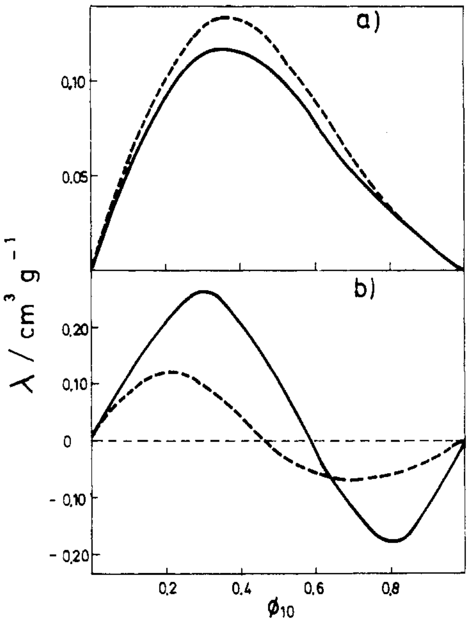

Figure 6. Variations with system composition of calculated (—) and experimental (---) preferential solvation coefficient (λ) for (a) B/CH/PS and (b) EA/CH/PS systems.

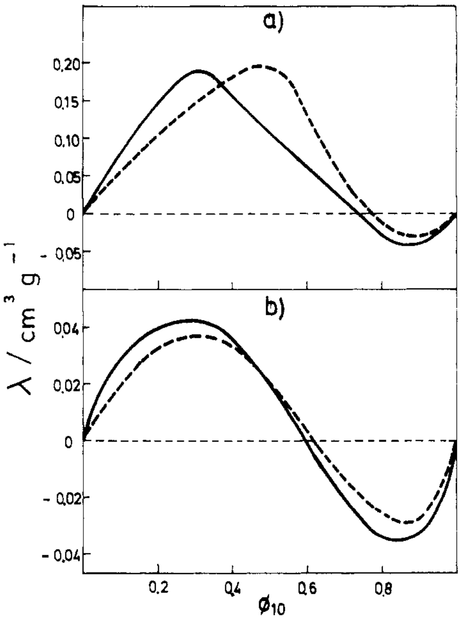

Figure 7. Variations with system composition of calculated (—) and experimental (---) preferential solvation coefficient (λ) for (a) HEP/MEK/PDMS and (b) UND/MEK/PDMS systems.

the theoretical part, $(\partial g_T/\partial u_1)_{\phi_3\to 0} = \mathrm{d}g_T°/\mathrm{d}u_1$ and taking into account Koningsveld's equation at polymer infinite dilution, allows us to define λ exclusively in terms of binary parameters as

$$\lambda = -\frac{\bar{v}_3}{N_{11}}\left((s - 1 + g_{13}° - sg_{23}°) + \frac{1 - 3g_{13}°g_{23}° + g_{13}°\chi_{23}° + g_{23}°\chi_{13}°}{1 - 2g_{13}°g_{23}° + g_{13}°\chi_{23}° + g_{23}°\chi_{13}°}\left(g_{12}(\phi_{10} - \phi_{20}) - \phi_{10}\phi_{20}\frac{\mathrm{d}g_{12}}{\mathrm{d}\phi_{10}}\right)\right)$$

In Figures 6–8 λ values predicted through the above equation are compared to experimental ones. Except for the EA/CH/PS system, which also shows deviations on the calculated $\chi_T°(u_1)$ function, the calculated λ values

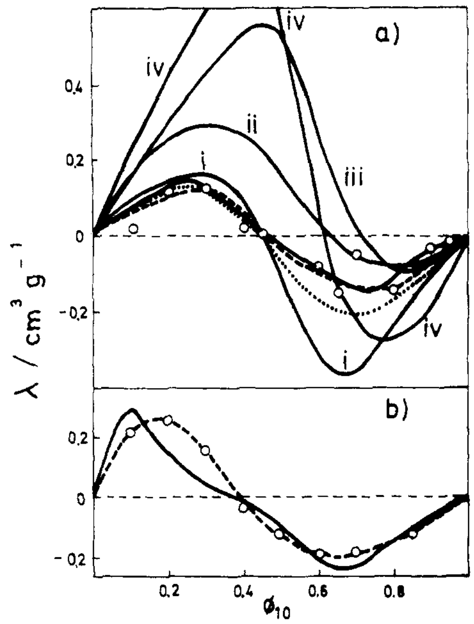

Figure 8. Dependence of preferential solvation coefficient (λ) on system composition for (a) ACN/CLB/PMMA ($\bar{M}_w$ = 237000) [(○) experimental values; (---) smoothed curve to match experimental points, (—, no legend) calculated from binary parameters (···) and curve i, FPP theory,[19] and curves ii, iii and iv, FH theory][19] and (b) ACN/CTC/PMMA ($\bar{M}_w$ = 120000) [(○) experimental values; (---) smoothed curve to match experimental points, (–) calculated from binary parameters].

reproduce the experimental ones fairly well. Perhaps the validity of predicted λ's is better stressed in Figure 8, in which λ values predicted through the FH and FPP formalisms have also been represented as a comparison.

In conclusion, in a similar way any other equilibrium property of the ternary system, such as the second virial coefficient (A_2), total solvation parameter (Y), or even a transport property such as the intrinsic viscosity ([η]), through some excluded theory, can be predicted from the interaction parameters of the respective binary systems. Moreover, if any of those magnitudes (or λ) is experimentally known, the remaining ones can be predicted from the experimental data of the former. A further paper will illustrate these statements.

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Registry No. PS (homopolymer), 9003-53-6; PMMA (homopolymer), 9011-14-7.

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Predictability of Properties in Ternary Solvent (1)/Solvent (2)/Polymer (3) Systems from Interaction Parameters of the Binary Systems. 2. Evaluation of Total Sorption Parameters and Related Magnitudes

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ABSTRACT: Starting from the correlation $g_T^\circ = K\,(g_{12} + (\partial g_T/\partial \phi_3)_{u_1,\phi_3\to 0})$ holding for ternary solvent (1)/solvent (2)/polymer (3) systems and from the physical significance of K, namely, $K = g_{13}^\circ g_{23}^\circ$, equations allowing the prediction of total sorption coefficients (Y) or its related magnitudes and second virial coefficients (A_2), either from binary interaction parameters (χ_{ij}) and potentials (g_{ij}) or from data on preferential sorption coefficients (λ), have been derived. Second virial coefficients evaluated from data of the binary systems are compared with experimental ones for two polystyrene, two poly(methyl methacrylate), and two poly(dimethylsiloxane) ternary systems, and the contribution of preferential sorption to total sorption is discussed.

Introduction

The evaluation of the total sorption parameter, Y, in ternary solvent (1)/solvent (2)/polymer (3) systems has usually been undertaken following Flory–Prigogine–Patterson (FPP)[1-4] or Flory–Huggins (FH) formalisms.[5-9] In the former, Y is defined in terms of equation state pa-