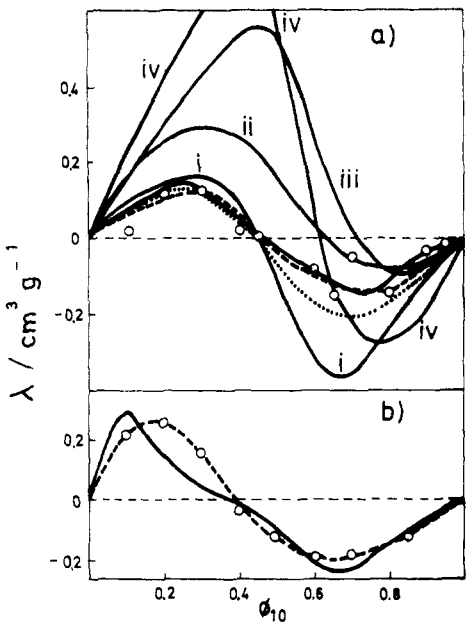

Figure 8. Dependence of preferential solvation coefficient (λ) on system composition for (a) ACN/CLB/PMMA ($\bar{M}_w$ = 237 000) [(○) experimental values; (– – –) smoothed curve to match experimental points, (—, no legend) calculated from binary parameters (···) and curve i, FPP theory,[19] and curves ii, iii and iv, FH theory][19] and (b) ACN/CTC/PMMA ($\bar{M}_w$ = 120 000) [(○) 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.

Acknowledgment. We are indebted to CAYCT for financial support (Project 2293/83) and to Prof. A. Horta (UNED, Madrid) for helpful comments.

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-

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Table I
Interaction Solvent/Polymer Parameters ($\chi_{i3}°$) and Potentials ($g_{i3}°$) for Diverse Ternary Systems

system	$\chi_{13}°$	$\chi_{23}°$	$g_{13}°$	$g_{23}°$
B/CH/PS (undetermined $\bar{M}_w$)	0.455[a]	0.510[a]	0.455[a]	0.715[a]
B/CH/PS ($\bar{M}_w$ = 117 000)	0.444[b]	0.530[b]	0.435[c]	0.749[c]
EA/CH/PS (mixed $\bar{M}_w$)	0.485[b]	0.530[b]	0.669[e]	0.735[d]
EA/CH/PS ($\bar{M}_w$ = 11 000)	0.485[b]	0.530[b]	0.659[c]	0.725[c]
HEP/MEK/PDMS (mixed $\bar{M}_w$)	0.430[f]	0.499[f]	0.520[g]	0.840[h]
HEP/MEK/PDMS ($\bar{M}_w$ = 125 000)	0.430[f]	0.499[f]	0.542[c]	0.853[c]
UND/MEK/PDMS ($\bar{M}_w$ = 125 000)	0.468[i]	0.499[i]	0.537[c]	0.797[c]
ACN/CLB/PMMA ($\bar{M}_w$ = 237 000)	0.508[j]	0.525[j]	0.769[c]	0.592[c]
ACN/CTC/PMMA ($\bar{M}_w$ = 120 000)	0.495[k]	0.510[k]	0.783[c]	0.508[c]

[a] From ref 16. [b] From ref 19 and 20. [c] From g^* (Table I ref 12) and K (Table II, this paper). [d] From $dg_{23}/d\phi_3 = 0.205$ and $\chi_{23}° = 0.530$. [e] From g^* and $g_{23}° = 0.735$ as calculated in footnote d. [f] From ref 21, 22. [g] From $dg_{13}/d\phi_3 = 0.09$ (see Table I in ref 12) and $\chi_{13}° = 0.430$. [h] From g^* and $g_{13}° = 0.520$ as calculated in footnote g. [i] From ref 13. [j] From ref 23. [k] From ref 24.

rameters and molecular magnitudes such as contact surfaces,[10] whereas in the latter, Y may be calculated from binary interaction parameters. The scarcity of general and reliable data in the FPP formalism and the neglect of ternary interaction parameters in the FH[5] one make Y evaluations generally difficult in the first and inadequate in the second. Of course, in the FH formalism as generalized by Pouchlý[11] for ternary systems Y is defined not only in terms of binary but also in terms of ternary interaction potentials. Because ternary interaction potentials and their derivatives with system composition are unknown, their evaluation from A_2 (and λ) experimental data and not the converse becomes the main task when Pouchlýs's formalism is applied to ternary systems.

In the previous paper of this series,[12] it was shown that both $g_T°$ (ternary interaction potential) and its derivative with polymer concentration $(\partial g_T/\partial\phi_3)_{u_1,\phi_3\to 0}$ can be exclusively defined in terms of binary interaction parameters, and as a consequence so can any property of the ternary system, as it was thoroughly tested by comparing calculated $\chi_T°$ (ternary interaction parameter) and λ (preferential sorption coefficient) with experimental ones. In this paper, the dependences of $g_T°$ and $(\partial g_T/\partial\phi_3)_{u_1,\phi_3\to 0}$ on binary interaction parameters are taken advantage of to predict Y (total sorption coefficient) values from data of the binary systems. Predicted Y values for the six ternary systems previously studied[12] are compared with experimental ones, and a critical analysis of the open question about the contribution of the preferential sorption to the total sorption is undertaken. Other possibilities of predicted Y values (or of predicted second virial coefficient, A_2, values) are also explored, as A_2 is evaluated from experimental data on preferential sorption coefficients.

Theory

Throughout the text, nomenclature, terminology, and abbreviations introduced in the previous paper[12] will be followed. Likewise, because total sorption coefficient (Y) is not directly accessible from experiment, it will be replaced by an experimental magnitude directly related to it, namely, by A_2 (second virial coefficient). From the usual approximate equation relating both magnitudes, $A_2 = (\bar{v}_3^2/V_1)Y$ and the Y definition according to the formalism as generalized by Pouchlý,[11] namely, $Y = (V_1/2RT)(M_{33} - M_{13}^2/M_{11})$, A_2 is given by

$$A_2 = \frac{\bar{v}_3^2}{2RT}\left(M_{33} - \frac{M_{13}^2}{M_{11}}\right) \tag{1}$$

where M_{ij}'s, the limits at polymer infinite dilution of the second derivatives of the Gibbs energy of mixing with respect to u_i and u_j, are not simple functions of system composition. They depend on binary (g_{ij}) and ternary (g_T) interaction potentials with system composition (see eq 4–6 in the previous paper[12]). In eq 1 the term M_{33} accounts for global sorption and the term M_{13}^2/M_{11} for preferential sorption; the former enhances polymer solubility whereas a positive value of the latter diminishes it. Substitution of M_{ij} values yields for A_2

$$A_2 = \frac{\bar{v}_3^2}{2V_1}\Bigg(\phi_{10} + s\phi_{20} - 2\chi_{13}°\phi_{10} - 2s\chi_{23}°\phi_{20} + 2\left(g_{12} - 2g_T° + \left(\frac{\partial g_T}{\partial\phi_3}\right)_{u_1,\phi_3\to 0}\right) - \left(s - 1 + g_{13}° - sg_{23}° + (\phi_{10} - \phi_{20})(g_{12} - g_T°) - \phi_{10}\phi_{20}\left(\frac{dg_{12}}{d\phi_{10}} - \frac{dg_T°}{du_1}\right)\right)^2 \Bigg/ \left(\frac{1}{\phi_{10}} + \frac{s}{\phi_{20}} - 2g_{12} + 2(\phi_{20} - \phi_{10})\frac{dg_{12}}{d\phi_{10}} + \phi_{10}\phi_{20}\frac{d^2g_{12}}{d\phi_{10}^2}\right)\Bigg) \tag{2}$$

Because $g_T°$ and $(\partial g_T/\partial\phi_3)_{u_1,\phi_3\to 0}$ are unknown, eq 2 is useless to evaluate A_2. The converse, however, holds true, so, through the above equation $(\partial g_T/\partial\phi_3)_{u_1,\phi_3\to 0}$ is evaluated from A_2 experimental data after $g_T°$ is evaluated from λ experimental data. To overcome the above difficulties, many approximations have been introduced in eq 2 in order to evaluate A_2 (or its related magnitude $\chi_{m3} \equiv$ interaction parameter solvent mixture/polymer); the reader should consult ref 13, where a critical analysis on the approaches most commonly followed is undertaken.

On the other hand, as it was previously shown,[12] $g_T°$ and $(\partial g_T/\partial\phi_3)_{u_1,\phi_3\to 0}$ may be defined in terms of binary parameters through

$$g_T° = \frac{g_{13}°g_{23}°}{1 - g_{13}°(dg_{23}/d\phi_3) - g_{23}°(dg_{13}/d\phi_3)}g_{12} \tag{3}$$

and

$$\left(\frac{\partial g_T}{\partial\phi_3}\right)_{u_1,\phi_3\to 0} = \frac{g_{13}°(dg_{23}/d\phi_3) + g_{23}°(dg_{13}/d\phi_3)}{1 - g_{13}°(dg_{23}/d\phi_3) - g_{23}°(dg_{13}/d\phi_3)}g_{12} \tag{4}$$

which, recalling Koningsveld's equation[14,15] at polymer infinite dilution, are respectively transformed into

$$g_T° = \frac{g_{13}°g_{23}°}{1 - 2g_{13}°g_{23}° + g_{13}°\chi_{23}° + g_{23}°\chi_{13}°}g_{12} \tag{5}$$

and

$$\left(\frac{\partial g_T}{\partial\phi_3}\right)_{u_1,\phi_3\to 0} = \frac{2g_{13}°g_{23}° - g_{13}°\chi_{23}° - g_{23}°\chi_{13}°}{1 - 2g_{13}°g_{23}° + g_{13}°\chi_{23}° + g_{23}°\chi_{13}°}g_{12} \tag{6}$$

Substitution of the above equations in eq 2 yields finally for A_2

$$A_2 = \frac{\bar{v}_3^2}{2V_1}\Bigg(\phi_{10} + s\phi_{20} - 2\chi_{13}^\circ\phi_{10} - 2s\chi_{23}^\circ\phi_{20} + \frac{(2 - 4g_{13}^\circ g_{23}^\circ)g_{12}\phi_{10}\phi_{20}}{1 - 2g_{13}^\circ g_{23}^\circ + g_{13}^\circ\chi_{23}^\circ + g_{23}^\circ\chi_{13}^\circ} - \Bigg\{\Bigg[s - 1 + g_{13}^\circ - sg_{23}^\circ + \frac{1 - 3g_{13}^\circ g_{23}^\circ + g_{13}^\circ\chi_{23}^\circ + g_{23}^\circ\chi_{13}^\circ}{1 - 2g_{13}^\circ g_{23}^\circ + g_{13}^\circ\chi_{23}^\circ + g_{23}^\circ\chi_{13}^\circ}g_{12}(\phi_{10} - \phi_{20}) - \phi_{10}\phi_{20}\frac{dg_{12}}{d\phi_{10}}\Bigg]\Bigg\}^2 \Bigg/ \Bigg\{\frac{1}{\phi_{10}} + \frac{s}{\phi_{20}} - 2g_{12} + 2(\phi_{20} - \phi_{10})\frac{dg_{12}}{d\phi_{10}} + \phi_{10}\phi_{20}\frac{d^2g_{12}}{d\phi_{10}^2}\Bigg\}\Bigg) \quad (7)$$

where A_2 is exclusively defined in terms of binary interaction parameters.

Results and Discussion

Before the validity of eq 7 to predict A_2 values is tested, some general comments on its applicability may be worthwhile. The application of eq 7 demands, besides knowledge of g_{12}, data on g_{13}°, g_{23}°, χ_{13}°, and χ_{23}° or, as an alternative, on g_{13}°, g_{23}°, $dg_{13}/d\phi_3$, and $dg_{23}/d\phi_3$ or, as the last possibility, on χ_{13}°, χ_{23}°, $dg_{13}/d\phi_3$, and $dg_{23}/d\phi_3$, if Koningsveld's equation is recalled. Whereas χ_{i3}° data is usually available or easily evaluated from experiment, data on g_{i3}° and/or $dg_{i3}/d\phi_3$ is very scarce in the literature,[16] and its determination is not a simple experimental task.[17,18] Fortunately, as it has been thoroughly shown in the previous paper,[12] g_{13}° and g_{23}° are related through the integral g^* and through the constant K

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

therefore making it possible from g^* and K values to evaluate both interaction potentials. That is one of the most rewarding accomplishments of our assumptions.

As test systems, those studied in the previous paper,[12] namely, benzene/cyclohexane/polystyrene (B/CH/PS), ethyl acetate/cyclohexane/polystyrene (EA/CH/PS), *n*-heptane/butanone/poly(dimethylsiloxane) (HEP/MEK/PDMS), *n*-undecane/butanone/poly(dimethylsiloxane) (UND/MEK/PDMS), acetonitrile/1-chloro-*n*-butane/poly(methyl methacrylate) (ACH/CLB/PMMA), and acetonitrile/carbon tetrachloride/poly(methyl methacrylate), ACN/CTC/PMMA, have again been chosen here. Regarding the source of their interaction potentials, they may be grouped in three categories. The first is exclusively occupied with B/CH/PS, both g_{13}° and g_{23}° being literature values. EA/CH/PS and HEP/MEK/PDMS are enclosed in the second group. In this group, one of the g_{13}° values is obtained from literature, g_{23}° in the EA/CH/PS system and g_{13}° in the PDMS system, and the other g_{13}° value has been calculated from g^* integrals. Finally, in the third group are those systems for which no bibliographic g_{i3}° value is known. Both g_{i3}°'s are, then, calculated from g^* and K values. In Table I, χ_{i3}° and g_{i3}° values for the above systems are gathered, whereas g_{12} functions were depicted in Figures 1–3 in a previous paper.[12]

In Figures 1–3, calculated through eq 7, A_2 values are compared with experimental ones. A_2 is molecular weight dependent through the dependences of χ_{13}° and g_{13}° on polymer molecular mass. As above said, χ_{i3}° and g_{i3}° for the B/CH/PS system are literature data, as g_{i3}° values for the EA/CH/PS and HEP/MEK/PDMS systems, although partially, are as well. Unfortunately, however, the molecular weights of the polymers corresponding to those χ_{i3}° and g_{i3}° values were omitted in the respective literature references. In these systems, it seems no conclusion can be derived from the comparison between calculated

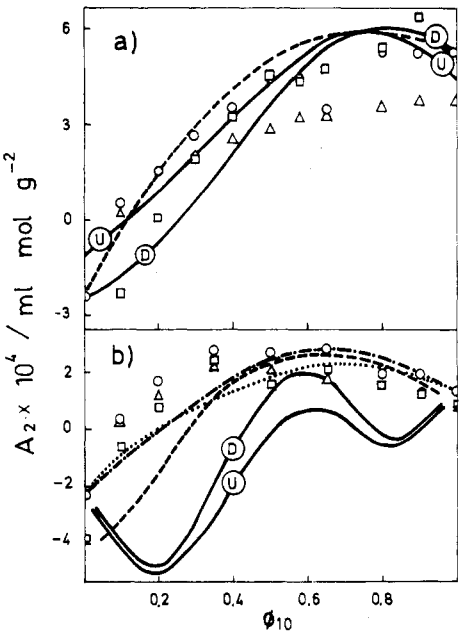

Figure 1. Experimental (points)[19] and calculated (curves) second virial coefficients, A_2, as a function of solvent mixture composition, ϕ_{10}, in (a) B/CH/PS and (b) EA/CH/PS systems: (—) calculated from eq 7 with g_{i3}° in Table I for a polymer sample with undetermined or mixed molecular weight (indicated by a circled U) and for a sample with $\bar{M}_w$ = 117 000 (indicated by a circled D); (– – –) calculated with eq 12 for B/CH/PS and with eq 11 for the remaining systems; (···) calculated from eq 12 with g_{i3}° in Table II; (–·–) calculated with eq 13. $\bar{M}_w$ = 372 000 (△); $\bar{M}_w$ = 117 000 (○); $\bar{M}_w$ = 35 600 (□).

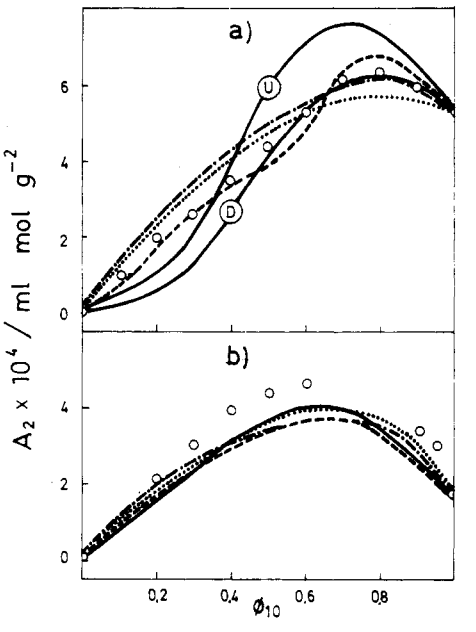

Figure 2. Experimental (points)[13,21,22] and calculated (curves) of second virial coefficients, A_2, as a function of solvent mixture composition, ϕ_{10}, in (a) HEP/MEK/PDMS ($\bar{M}_w$ = 125 000) and (b) UND/MEK/PDMS ($\bar{M}_w$ = 125 000) systems: (—) calculated from eq 7 with g_{i3}° in Table I for a polymer sample with mixed molecular weight (indicated by a circled U), and for a sample with $\bar{M}_w$ = 125 000 (indicated by a circled D). The remaining symbols for curves as in Figure 1.

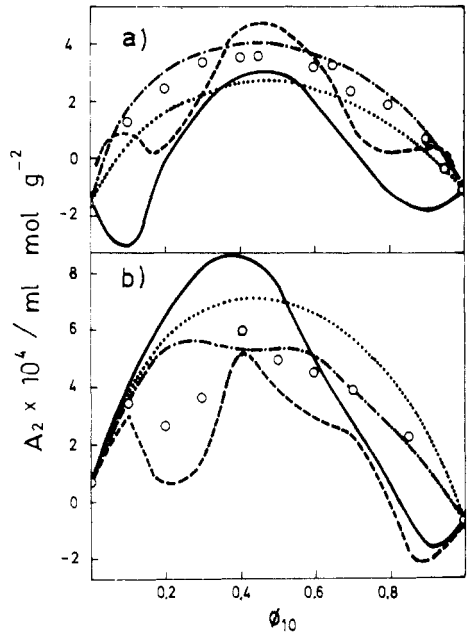

Figure 3. Experimental (points)[23,24] and calculated (curves) of second virial coefficients, A_2, as a function of solvent mixture composition, ϕ_{10}, in (a) ACN/CLB/PMMA ($\bar{M}_w$ = 237 000) and (b) ACN/CTC/PMMA ($\bar{M}_w$ = 120 000) systems: (—) calculated from eq 7 with $g_{i3}°$ in Table I. The remaining symbols for curves as in Figure 1.

A_2 values for an undetermined molecular weight and the experimental ones measured at a given molecular weight. In order to overcome the above uncertainties, $g_{i3}°$ values for the above systems and for a specified polymer molecular weight have been evaluated from g^* and K values, and these are also gathered in Table I. Predicted A_2 values with these new $g_{i3}°$'s have been depicted in Figures 1 and 2 too.

In spite of the complexity of the lengthy eq 7, A_2 values calculated from it compare fairly well with experimental ones, as Figures 1–3 show. At this point, an objection, however, can be raised against the followed procedure to predict A_2. Individual $g_{13}°$ and $g_{23}°$ values are obtained at once from g^* and K values. Whereas g^* proceeds from λ data, K proceeds from $g_T°$ and $(\partial g_T/\partial\phi_3)_{u_1,\phi_3\to 0}$ values, which in turn come from λ and A_2 experimental data. In other words, it seems that in a certain sense, a two-way road was taken, since from A_2 experimental data are calculated $g_{i3}°$'s, which, in turn, are used to predict A_2 values. However, in that apparent two-way road our assumptions[12] had to be obeyed, that is to say that the adjustable parameters $g_T°$ and $(\partial g_T/\partial\phi_3)_{u_1,\phi_3\to 0}$ were able to be defined in terms of binary interaction parameters. Of course, the similarity between experimental and predicted A_2 values is an additional test supporting our formalism once again. Moreover, at least in two or three of the studied systems, the above objection could be avoided. So, CH is a common component in the two PS systems studied, as MEK is in both PDMS ones or ACN in the two PMM's. That means, using the PS systems as an example, that $g_{23}°$ could be evaluated from g^* and K values (λ and A_2 experimental data) for, e.g., the B/CH/PS system. This $g_{23}°$ value together with g^* for the EA/CH/PS would then allow us to evaluate $g_{13}°$ for this last system without resorting to the K value and in no way at all to the A_2 experimental values. Similarly, $g_{13}°$ for the B/CH/PS system can be evaluated from its g^* and $g_{23}°$ for EA/CH/PS. $g_{i3}°$ values evaluated in this way are $g_{13}°$ (EA/CH/PS) = 0.684, as obtained from its g^* value and $g_{23}°$ for the B/CH/PS system and $g_{13}°$-(B/CH/PS) = 0.417, from its g^* and $g_{23}°$ for EA/CH/PS. Both values are very close indeed to those evaluated at once from g^* and K values (see Table I), an additional proof of our assumption's correctness.

In fact, the particular casuistry above considered may be extended to those systems in which an inversion in λ occurs, A_2 evaluation being possible only from λ data when even $g_{i3}°$ parameters are unknown.

Let us call ϕ_{10}^{i} the solvent mixture composition at the inversion point. At that composition $\lambda = 0$ and the preferential sorption term in $A_2 M_{13}^2/M_{11} = 0$, therefore $M_{13}(\phi_{10}^{i}) = 0$. Moreover, it is a well-established fact that the inversion in λ is accompanied by a maximum in the total sorption (or in A_2), even when $s \neq 1$.[21,23,25] The application of the condition of the maximum to the total sorption term, taking into account that $M_{13}(\phi_{10}^{i}) = 0$, yields $d[M_{33}(\phi_{10}^{i})]/d\phi_{10} = 0$. From the definitions of M_{13} and M_{33}, the above two conditions at the inversion point, assuming that $(dg_T°/du_1) \approx (dg_T°/d\phi_{10})$, may be written as

$$M_{13}(\phi_{10}^{i}) = (s - 1 + g_{13}° - sg_{23}°) + \frac{d(g_T°\phi_{10}\phi_{20})}{d\phi_{10}} - \frac{d(g_{12}\phi_{10}\phi_{20})}{d\phi_{10}} = 0 \quad (8)$$

and

$$\frac{dM_{33}(\phi_{10}^{i})}{d\phi_{10}} = \frac{1}{2}(1 - s) - \chi_{13}° + s\chi_{23}° + \frac{d}{d\phi_{10}}\left(\left(g_{12} - 2g_T° + \left(\frac{\partial g_T}{\partial\phi_3}\right)_{u_1,\phi_3\to 0}\right)\phi_{10}\phi_{20}\right) = 0 \quad (9)$$

The substitutions in the above equation of $(\partial g_T/\partial\phi_3)_{u_1,\phi_3\to 0}$ and $d(g_T°\phi_{10}\phi_{20})/d\phi_{10}$, deduced respectively from the correlation $g_T° = K(g_{12} + (\partial g_T/\partial\phi_3)_{u_1,\phi_3\to 0})$ and from eq 8, yield

$$1/K = \chi_{13}° - s\chi_{23}° + (1 - s)/2/\left(-g^* + (\phi_{20}^{i} - \phi_{10}^{i})g_{12}(\phi_{10}^{i}) + \phi_{20}^{i}\phi_{10}^{i}\frac{dg_{12}(\phi_{10}^{i})}{d\phi_{10}}\right) + 2 \quad (10)$$

which allows the evaluation of K from $\chi_{i3}°$, $g_{12}(\phi_{10})$, and g^* data.

With λ data over the whole composition range of the binary solvent mixture, ϕ_{10}^{i} becomes known and $g_T°$ and g^* can be evaluated by the Munk's method,[19,20] and therefore K and M_{33} can also be calculated. With this in mind, from $\lambda = -\bar{v}_3 M_{13}/M_{11}$, eq 1 is finally transformed into

$$A_2 = \frac{\bar{v}_3^2}{2V_1}\left(\phi_{10} + s\phi_{20} - 2\chi_{13}°\phi_{10} - 2s\chi_{23}°\phi_{20} + \{(2\chi_{13}° - 2s\chi_{23}° - 1 + s)g_T°\}\Big/\left\{-g^* + (\phi_{20}^{i} - \phi_{10}^{i})g_{12}(\phi_{10}^{i}) + \phi_{20}^{i}\phi_{10}^{i}\frac{dg_{12}(\phi_{10}^{i})}{d\phi_{10}}\right\}\right) - \frac{\lambda_2}{2RT}M_{11} \quad (11)$$

which allows A_2 to be calculated from λ experimental data and the interaction parameters of the binary systems, $\chi_{13}°$, $\chi_{23}°$, and $g_{12}(\phi_{10})$. A_2 values predicted through the above equation have also been represented in Figures 1–3, always for a fixed molecular weight. No significative differences between these A_2 values and those calculated from the binary interaction parameters through eq 7 are observed.

Perhaps A_2 values calculated from λ experimental data better reflect the experimental λ fluctuations. At this point, the open question of preferential sorption contribution to total sorption deserves some comments. So, whereas from a phenomenological point of view, FPP formalism[2,23] completely ignores preferential sorption contribution to total sorption, in the FH formalism, as generalized by Pouchlý,[11] a term accounting for preferential sorption (M_{13}^2/M_{11} in eq 1) is specifically stated in the Y definition. Of course, the absence or presence of a preferential sorption term in Y has to do with the Y thermodynamic definition itself, which, on the other hand, is related to the structure of the ternary phase depicted by the model or even with what part of the system is considered as the ternary phase. A detailed introduction of the above points is beyond the scope of this paper and can be found in ref 26. Returning to Y (or A_2) evaluation, throughout this paper the preferential sorption term has always been taken into account. If it is neglected, eq 7 and 11 defining A_2 are simplified and respectively transformed into

$$A_2 = \frac{\bar{v}_3^2}{2V_1}\left(\phi_{10} + s\phi_{20} - 2\chi_{13}^\circ\phi_{10} - 2s\chi_{23}^\circ\phi_{20} + \frac{2 - 4g_{13}^\circ g_{23}^\circ}{1 - 2g_{13}^\circ g_{23}^\circ + g_{13}^\circ\chi_{23}^\circ + g_{23}^\circ\chi_{13}^\circ}g_{12}\phi_{10}\phi_{20}\right) \quad (12)$$

and

$$A_2 = \frac{\bar{v}_3^2}{2V_1}\left(\phi_{10} + s\phi_{20} - 2\chi_{13}^\circ\phi_{10} - 2s\chi_{23}^\circ\phi_{20} + \{(2\chi_{13}^\circ - 2s\chi_{23}^\circ - 1 + s)g_T^\circ\} \Big/ \left\{-g^* + (\phi_{23}^{\,i} - \phi_{10}^{\,i})g_{12}(\phi_{10}^{\,i}) + \phi_{20}^{\,i}\phi_{10}^{\,i}\frac{dg_{12}(\phi_{10}^{\,i})}{d\phi_{10}}\right\}\right) \quad (13)$$

Whereas the last equation is immediately applicable, some details prior to the application of the former must be cleared up. The omission of the preferential sorption term in Y does not affect the way in which the adjustable parameters g_T° and $(\partial g_T/\partial\phi_3)_{u_1,\phi_3\to 0}$ are evaluated from A_2 and λ experimental data (Munk's method[19]), but, however, it affects the numerical values obtained for $(\partial g_T/\partial\phi_3)_{u_1,\phi_3\to 0}$. Similarly, whereas our previous findings hold with independence of the λ contribution to Y, i.e., $g_T^\circ(g_{12} + (\partial g_T/\partial\phi_3)_{u_1,\phi_3\to 0})$ remaining constant along the whole composition range of the binary solvent mixture, K values obtained when the preferential sorption term is omitted obviously differ from those evaluated when the contribution is taken into account. In Table II, K values obtained with and without the λ contribution are gathered for comparison, the difference between both sets of K data being negligible. g_{i3}° values obtained from g^* and the new K values (no λ contribution) are also enclosed in Table II. As can be seen, these new g_{i3}° are very close to those gathered in Table I, which were evaluated considering preferential sorption contributions to Y. Because of the small difference between both g_{i3}° data sets, the evaluation and use of the new g_{i3}° values intend to keep the formal aspect, notwithstanding the practical side.

Table II
K Values Evaluated with and without the Preferential Sorption Contribution to Total Sorption and Binary Interaction Parameters Calculated from the Latter K's

system	with λ K	without λ K	g_{13}°	g_{23}°
B/CH/PS ($\bar{M}_w$ = 117 000)	0.326	0.368	0.467	0.788
EA/CH/PS ($\bar{M}_w$ = 117 000)	0.478	0.477	0.659	0.724
HEP/MEK/PDMS ($\bar{M}_w$ = 125 000)	0.460	0.473	0.551	0.859
UND/MEK/PDMS ($\bar{M}_w$ = 125 000)	0.428	0.430	0.538	0.799
ACN/CLB/PMMA ($\bar{M}_w$ = 237 000)	0.455	0.462	0.772	0.598
ACN/CTC/PMMA ($\bar{M}_w$ = 120 000)	0.398	0.419	0.793	0.528

In Figures 1–3, A_2 values calculated through eq 12 with g_{i3}° values of Table II and from eq 13 are depicted. As the figures clearly show and as a final conclusion, it seems that, at least in the systems here studied, A_2 values calculated either from binary parameters or from λ data when preferential sorption contributions to Y are omitted are closer to experimental ones (surprisingly close in some systems) than those evaluated when λ contributions are considered.

Acknowledgment. We are indebted to CAYCT for financial support (Project 2293/83).

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

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