Statistical Thermodynamics of Preferential Sorption. 2

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ABSTRACT: The equation-of-state theory of polymer solutions developed by Flory (FPP theory) is applied to calculate the preferential adsorption coefficient (λ) and the total sorption potential (Y) of polymer–mixed solvent systems. The formulas deduced for λ and Y are compared with the ones obtained for these same magnitudes using the classical Flory–Huggins (FH) thermodynamic model. The dependence of polymer–solvent interaction parameters on concentration and the dependence of the liquid 1–liquid 2 interaction parameter (g_{12}) on solvent mixture composition are taken into account. In the FH theory, empirical ternary interaction parameters, g_T and χ_T, are usually added to describe λ and Y. In the FPP theory, thermodynamic quantities depend on the molecular characteristics and exchange interactions of all three components simultaneously and are thus ternary per se. The formulas of the FPP theory can be simplified to give results that are identical with those of the FH theory with ternary parameters. In practical applications, the ternary interaction parameters are usually taken proportional to g_{12}. The simplified results of the FPP theory show that the proportionality constants between g_T or χ_T and g_{12} contain as a major contribution the nonspecific effects arising from dissimilarities in molecular surface to volume ratio and in free volume between polymer and solvents.

Introduction

The theoretical description of preferential sorption in polymer–mixed solvent systems which has been most oftenly applied to interpret experimental results of the preferential adsorption coefficient, λ, is the one developed by Read.[1] This theory gives the variation of λ as a function of mixed-solvent composition in dilute polymer systems. To obtain λ Read wrote the Gibbs mixing function of the system, ΔG_M, according to the model of Flory and Huggins, but in an extended or modified version of it. In the simple Flory–Huggins expression, the interactional part of ΔG_M for the polymer–mixed solvent system is written in terms of binary interactions solvent 1–polymer, solvent 2–polymer, and solvent 1–solvent 2, each one represented by a constant binary interaction parameter.

Read extended this model to include the concentration dependence of each one of these binary interaction parameters and also to include a ternary interaction parameter χ_{123}. However, most authors who have applied Read's theory of λ to experimental results have not taken his χ_{123} into account.

Later, Pouchlý, Živný, and Šolc also developed a theory of λ[2,3] based on an extended Flory–Huggins model including explicitly a ternary interaction parameter, g_T, and taking into account the concentration dependence of interaction parameters. The application of the theory of Pouchlý, Živný, and Šolc has shown that both the ternary interaction parameter and the concentration dependence are very important factors for the proper interpretation of preferential adsorption phenomena as well as for the total sorption potential in polymer–mixed solvent systems.

The binary interaction parameters for the Gibbs function are g_{12}, g_{13}, and g_{23} (1 and 2 solvents, 3 polymer). These g_{ij}'s are in general not constant. g_{12} depends on the composition of the mixed solvent, and g_{13} and g_{23} depend on polymer concentration. Let us call φ_i the volume fraction of component i referred to the total volume of the ternary system ($\varphi_1 + \varphi_2 + \varphi_3 = 1$) and u_i the volume fraction referred to the volume occupied just by the liquid mixture ($u_1 + u_2 = 1$). The dependence of interaction parameters on concentration can be written $g_{12}(u_1)$, $g_{13}(u_3)$, and $g_{23}(u_3)$. In the ternary system only two composition variables are independent. Above, we have chosen them to be u_1 (composition of the liquid mixture) and u_3 (polymer concentration), where $u_i = \varphi_i/(1 - \varphi_3)$. The ternary interaction parameter, g_T, depends on both independent variables: $g_T(u_1,u_3)$.

In the limit of dilute polymer solution, the dependence on polymer concentration of the binary parameters g_{13} and g_{23} can be expressed by[4]

$$g^\circ_{i3} = \chi^\circ_{i3} + (\mathrm{d}g_{i3}/\mathrm{d}\varphi_3)^\circ \qquad (i = 1, 2) \tag{1}$$

where superscript zero is used throughout this paper to denote quantities in the limit $\varphi_3 \to 0$. The χ_{ij}'s are interaction parameters for the chemical potential and the g_{ij}'s for the Gibbs function.

In a parallel way one can write for the ternary parameter

$$g^\circ_T(u_1) = \chi^\circ_T(u_1) + (\partial g_T/\partial \varphi_3)^\circ \tag{2}$$

The ternary parameter or its dependence on concentration is not known beforehand and has to be adjusted to experimental results. The values thus obtained for $g^\circ_T(u_1)$ have been found to vary with u_1 in a manner that parallels the variation of $g_{12}(u_1)$ with u_1. This led Pouchlý and Patterson[5] to write as an adequate approximation

$$g^\circ_T = (\gamma/2)g_{12} \tag{3}$$

with γ a constant. Later, Pouchlý and Živný analyzed results of λ[6] and intrinsic viscosity[7] for a number of systems and introduced the approximations

$$g^\circ_T(u_1) = a_g g_{12}(u_1) \tag{4}$$

$$\chi^\circ_T(u_1) = a_\chi' g_{12}(u_1) \tag{5}$$

with a_g and a_χ' constants. (In fact, Pouchlý and Živný defined[7] a constant a_χ instead of a_χ' given by eq 5, but the relation between their a_χ and the present a_χ' is just $2a_\chi = a_\chi' + a_g$.) These authors showed that both approximations (eq 4 and 5) allow for a reasonable description of the experimental results of λ and $[\eta]$. Although these approximations provide information about the dependence of g°_T and of χ°_T on the mixed-solvent composition, they still maintain a_g and a_χ' as adjustable parameters whose values can be known only by comparison with experiment.

More recently, Figueruelo, Campos, and Celda[8] have found a new empirical correlation which is expressed by

$$g_T(u_1,u_3) = g_{13}(u_3)g_{23}(u_3)[g_{12}(u_1) + (\partial g_T/\partial \varphi_3)^\circ{}_{u_1}] \tag{6}$$

They have measured λ, $[\eta]$, and the second virial coefficient of poly(dimethylsiloxane) in methyl ethyl ketone + n-alkane mixtures and have found that the correlation expressed by eq 6 describes well their results and also results of other systems from the literature which they have also tested. The correlation of Figueruelo, Campos, and Celda has the virtue that, according to them, it allows for a

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prediction of the ternary parameter without any adjustable constant.

All the above developments have been conducted within the framework of the Flory–Huggins model for ΔG_M (either in its original form or in the modified or extended versions of it). The limitations of such a model to interpret thermodynamic properties of polymers in solution are already well-known. Flory[9] developed a new theory based on the principles of Prigogine and his school, which is more adequate to describe the thermodynamics of polymers in solution. Such a theory has been used to predict the variation of the interaction parameters χ_{i3} with polymer concentration, which in the theory is obtained as a consequence of the dissimilarities in free volume and in molecular surface to volume ratio or contact sites between polymer and solvents.

Using the framework of the new theory, Pouchlý and Patterson[10] derived the total sorption potential, Y, and verified that the contributions due to the dissimilarities in free volume and in contact sites between polymer and solvents allowed one to explain the experimental results of $[\eta]$ as a function of u_1. They also showed that the importance of those effects on $[\eta]$ is such that, when they are neglected in the Flory–Huggins model, a large ternary interaction parameter has to be introduced forcefully in order to approximate the experimental results.

The theory of λ using the same new thermodynamic formalism of Flory was derived by the present author[11] (paper 1). (The new Flory formalism was there abbreviated FPP, for Flory, Prigogine, and Patterson, and the classical Flory–Huggins formalism was abbreviated FH). The final equations obtained for λ in the FPP formalism[11] were rather complicated and, in order to ease their practical application, several approximations were introduced to obtain usable simpler expressions. In such simpler expressions the dissimilarities in free volume and in surface to volume ratio between polymer and solvents were approximately taken into account, but the dissimilarities between the solvents themselves were neglected, the same as Pouchlý and Patterson did in their theory of Y.[10] This is probably a reasonable approximation in most cases but, if necessary, it could be avoided by going back to the more complex complete equations of the theory.[11]

Some of the approximations contained in the simpler expressions of the FPP formalism for λ and Y have an important consequence. When they are introduced into the FPP expressions for the interaction parameters, these approximations are equivalent to neglecting the mixed-solvent composition dependence of g_{12} and to not properly taking into account the polymer concentration dependence of g_{i3}'s. The application of the simpler expressions of the FPP formalism for λ made to a number of systems[12-15] has met with difficulties in some cases. These difficulties can be attributed, to a large extent, to these effects of the approximations on the u_1 and φ_3 dependencies of interaction parameters.

It is possible to avoid such approximation by taking into account the dependence of g_{12} on mixed-solvent composition, $g_{12}(u_1)$, and by calculating the derivatives $(\partial g_{i3}/\partial \varphi_3)^\circ{}_{u_1}$ which express the polymer concentration dependencies of solvent–polymer interaction parameters. This task is the one we tackle in the present paper. We also apply the results to obtain new expressions for λ and Y which are still simple but which incorporate such $g_{12}(u_1)$ and $(\partial g_{i3}/\partial \varphi_3)^\circ{}_{u_1}$ dependencies of the interaction parameters. By so doing, we are able to compare the FPP expressions for λ and Y with the corresponding expressions based on the extended FH model.

This comparison finally allows us to establish a correspondence between the ternary parameter of the FH formalism and the parameters of the free volume and molecular surface to volume ratio dissimilarities in the FPP formalism.

The fundamental difference between the FH and the FPP formalisms in their description of a ternary system is that in the FH formalism the Gibbs mixing function, ΔG_M, is written as a sum of binary contributions (1–2, 1–3, 2–3) and needs an explicit introduction of ternary effects as an additional ad hoc term, while in the FPP formalism the terms of ΔG_M depend on the molecular characteristics and interactions of all the components simultaneously and are thus truly ternary per se.

The need of a ternary parameter has been justified sometimes as representing specific interactional effects[16] or some "gathering effect".[17] The present comparison between FH and FPP theories will show (more emphatically than before[10,11]) that g_T and χ_T also hide the free volume and molecular surface dissimilarity effects and that the contribution of such nonspecific effects to the ternary terms is large (in some systems they may be even the only effects accounted for by g_T and χ_T).

Theory

We shall use here the same terminology and symbols as in paper 1.[11] When referring to an equation in that paper we shall number it as eq In.

We start by splitting the Gibbs mixing function of the ternary system, ΔG_M, into its combinatorial, $-T\Delta S_{\text{comb}}$, and residual, G^R, parts (T is the absolute temperature):

$$\Delta G_M = -T\Delta S_{\text{comb}} + G^R \tag{7}$$

The combinatorial entropy is given by (eq I8)

$$\Delta S_{\text{comb}} = -R(n_1 \ln \phi_1 + n_2 \ln \phi_2 + n_3 \ln \phi_3) \tag{8}$$

where ϕ_i is the segment fraction or core volume fraction and n_i is amount of substance (R is the gas constant). The residual Gibbs function is composed of the heat of mixing, ΔH_M, and the residual entropy term, $-TS^R$:

$$G^R = \Delta H_M - TS^R \tag{9}$$

In the FPP theory, ΔH_M and S^R for a ternary system are given by eq I15 and I16, yielding the result for G^R:

$$\begin{aligned} G^R = {} & n_1 p_1{}^* V_1{}^* \{\tilde{U}(\tilde{T}) - \tilde{U}(\tilde{T}_1) - \tilde{T}_1[\tilde{S}(\tilde{T}) - \tilde{S}(\tilde{T}_1)]\} + \\ & n_2 p_2{}^* V_2{}^* \{\tilde{U}(\tilde{T}) - \tilde{U}(\tilde{T}_2) - \tilde{T}_2[\tilde{S}(\tilde{T}) - \tilde{S}(\tilde{T}_2)]\} + \\ & n_3 p_3{}^* V_3{}^* \{\tilde{U}(\tilde{T}) - \tilde{U}(\tilde{T}_3) - \tilde{T}_3[\tilde{S}(\tilde{T}) - \tilde{S}(\tilde{T}_3)]\} - \\ & (n_1\theta_2 V_1{}^* X_{12} + n_1\theta_3 V_1{}^* X_{13} + n_2\theta_3 V_2{}^* X_{23})\tilde{U}(\tilde{T}) \end{aligned} \tag{10}$$

Here, $p_i{}^*$, $V_i{}^*$, and $T_i{}^*$ are the reduction parameters of the pure components for pressure, molar volume, and temperature, respectively, and the tilde denotes reduced quantities, U being energy. The X_{ij}'s are binary exchange interaction parameters and the θ_i's are site fractions or molecular surface fractions.

The reduced temperature of the ternary system is given by (eq I19)

$$\begin{aligned} \tilde{T} = {} & (n_1 p_1{}^* V_1{}^* \tilde{T}_1 + n_2 p_2{}^* V_2{}^* \tilde{T}_2 + n_3 p_3{}^* V_3{}^* \tilde{T}_3) \times \\ & (n_1 p_1{}^* V_1{}^* + n_2 p_2{}^* V_2{}^* + n_3 p_3{}^* V_3{}^* - n_1\theta_2 V_1{}^* X_{12} - \\ & n_1\theta_3 V_1{}^* X_{13} - n_2\theta_3 V_2{}^* X_{23})^{-1} \end{aligned} \tag{11}$$

We see that $\tilde{T}$ depends on the reduction parameters of the three components and also on the three exchange interaction parameters X_{12}, X_{13}, and X_{23}, of all the possible binary interactions in the system. $\tilde{T}$ is a truly ternary magnitude. Due to this character of $\tilde{T}$, all the terms of G^R in eq 10 are also ternary, because they contain $\tilde{T}$ in $\tilde{U}(\tilde{T})$ or in $\tilde{S}(\tilde{T})$. There is no single term in eq 10 that could be considered binary.

On the other hand, the G^{R} of the FH model (without g_{T}) is

$$G^{\mathrm{R}} = RT(n_1\varphi_2 g_{12} + n_1\varphi_3 g_{13} + n_2\varphi_3 g_{23}) + G^{\mathrm{R}'} \quad (12a)$$

with

$$G^{\mathrm{R}'} = RT[n_1 \ln (\varphi_1/\phi_1) + n_2 \ln (\varphi_2/\phi_2) + n_3 \ln (\varphi_3/\phi_3)] \quad (12b)$$

This $G^{\mathrm{R}'}$ arises because the FH model is defined in terms of volume fractions. The G^{R} of the FH model is a sum of binary terms. To destroy this additive character a ternary term is added:

$$G^{\mathrm{R}} = RT(n_1\varphi_2 g_{12} + n_1\varphi_3 g_{13} + n_2\varphi_3 g_{23} + n_1\varphi_2\varphi_3 g_{\mathrm{T}}) + G^{\mathrm{R}'} \quad (13)$$

No such additive character is present in G^{R} according to the FPP theory. All terms in eq 10 depend simultaneously on the properties of the three components and on their mutual interactions through $\tilde{T}$.

In order to show more clearly the lack of additivity in the FPP theory we try now to mimick the form of the FH expression eq 12 with the FPP eq 10. First we make $n_1 = 0$ in eq 10 and 11 to obtain $(G^{\mathrm{R}})_{23}$ for the pure solvent 2–polymer $(n_2 + n_3)$ binary solution, then $n_2 = 0$ $(\theta_2 = 0)$ to obtain $(G^{\mathrm{R}})_{13}$ for the pure solvent 1–polymer $(n_1 + n_3)$ binary solution, and then $n_3 = 0$ $(\theta_3 = 0)$ to obtain $(G^{\mathrm{R}})^\circ$ for the binary $(n_1 + n_2)$ liquid mixture without polymer. In each case we have to make n_1, n_2 (θ_2), or n_3 (θ_3) vanish not only in eq 10 but also in eq 11. That is, $(G^{\mathrm{R}})_{23}$ depends on a $\tilde{T}_{23}$ that is given by eq 11 with $n_1 = 0$, $(G^{\mathrm{R}})_{13}$ depends on a $\tilde{T}_{13}$ $(n_2 = 0, \theta_2 = 0$ in eq 11), and $(G^{\mathrm{R}})^\circ$ depends on a $\tilde{T}_0$ $(n_3 = 0, \theta_3 = 0$ in eq 11). Then

$$(G^{\mathrm{R}})^\circ = n_1 p_1^* V_1^* \{\tilde{U}(\tilde{T}_0) - \tilde{U}(\tilde{T}_1) - \tilde{T}_1[\tilde{S}(\tilde{T}_0) - \tilde{S}(\tilde{T}_1)]\} + n_2 p_2^* V_2^* \{\tilde{U}(\tilde{T}_0) - \tilde{U}(\tilde{T}_2) - \tilde{T}_2[\tilde{S}(\tilde{T}_0) - \tilde{S}(\tilde{T}_2)]\} - n_1\theta_{2(1)} V_1^* X_{12} \tilde{U}(\tilde{T}_0) \quad (14)$$

$$(G^{\mathrm{R}})_{13} = n_1 p_1^* V_1^* \{\tilde{U}(\tilde{T}_{13}) - \tilde{U}(\tilde{T}_1) - \tilde{T}_1[\tilde{S}(\tilde{T}_{13}) - \tilde{S}(\tilde{T}_1)]\} + n_3 p_3^* V_3^* \{\tilde{U}(\tilde{T}_{13}) - \tilde{U}(\tilde{T}_3) - \tilde{T}_3[\tilde{S}(\tilde{T}_{13}) - \tilde{S}(\tilde{T}_3)]\} - n_1\theta_{3(1)} V_1^* X_{13} \tilde{U}(\tilde{T}_{13}) \quad (15)$$

$$(G^{\mathrm{R}})_{23} = n_2 p_2^* V_2^* \{\tilde{U}(\tilde{T}_{23}) - \tilde{U}(\tilde{T}_2) - \tilde{T}_2[\tilde{S}(\tilde{T}_{23}) - \tilde{S}(\tilde{T}_2)]\} + n_3 p_3^* V_3^* \{\tilde{U}(\tilde{T}_{23}) - \tilde{U}(\tilde{T}_3) - \tilde{T}_3[\tilde{S}(\tilde{T}_{23}) - \tilde{S}(\tilde{T}_3)]\} - n_2\theta_{3(2)} V_2^* X_{23} \tilde{U}(\tilde{T}_{23}) \quad (16)$$

where the subscript $i(j)$ on concentration variables means concentration of i in the presence of only j as second component.

The common variable for the ternary system, $\tilde{T}$, is different from the variables of the binary ones $\tilde{T}_0$, $\tilde{T}_{13}$, and $\tilde{T}_{23}$, and thus the binary terms of eq 14–16 and the terms of eq 10 differ. The simultaneous presence of the three components and of their interactions is included in eq 10 and 11 and is not the result of just adding binary terms. This is an important advantage of the FPP formalism over the FH one.

Let us continue in our effort to mimick the FH expression and calculate now according to the FPP theory the binary interaction parameters g_{12}, g_{13}, and g_{23} and their concentration dependencies $\mathrm{d}g_{13}/\mathrm{d}\varphi_3$ and $\mathrm{d}g_{23}/\mathrm{d}\varphi_3$. To this end we equate each one of the FPP expressions for $(G^{\mathrm{R}})^\circ$, $(G^{\mathrm{R}})_{13}$, and $(G^{\mathrm{R}})_{23}$, eqs 14–16, to their corresponding expressions in the FH theory; namely, we make

$$(G^{\mathrm{R}})^\circ = RTn_1\varphi_{2(1)}g_{12} + (G^{\mathrm{R}'})^\circ \quad (17)$$

$$(G^{\mathrm{R}})_{13} = RTn_1\varphi_{3(1)}g_{13} + (G^{\mathrm{R}'})_{13} \quad (18)$$

$$(G^{\mathrm{R}})_{23} = RTn_2\varphi_{3(2)}g_{23} + (G^{\mathrm{R}'})_{23} \quad (19)$$

with $(G^{\mathrm{R}})^\circ$ given by eq 14, $(G^{\mathrm{R}})_{13}$ by eq 15, and $(G^{\mathrm{R}})_{23}$ by eq 16.

From the g_{ij}'s obtained in this way we calculate the limiting values $g^\circ{}_{i3}$ and also the derivatives $(\mathrm{d}g_{i3}/d\varphi_3)^\circ{}_{u_1}$. The results, after some mathematics, are as follows:

$$g^\circ{}_{i3} = \frac{p_i^* V_i^*}{RT}\,\frac{\tilde{V}_i}{\tilde{V}_3}\left\{\frac{p_3^*}{p_i^*}\{\tilde{U}(\tilde{T}_i) - \tilde{U}(\tilde{T}_3) - \tilde{T}_3[\tilde{S}(\tilde{T}_i) - \tilde{S}(\tilde{T}_3)]\} - \tilde{U}(\tilde{T}_i)\frac{X_{i3}}{p_i^*}\,\frac{s_3}{s_i}\right\} + \left(1 - \frac{\tilde{V}_i}{\tilde{V}_3}\right) - \frac{V_i}{V_3}\ln\left(\frac{\tilde{V}_3}{\tilde{V}_i}\right) \qquad (i = 1, 2) \quad (20)$$

with s_i the number of contact sites per segment, and

$$\left(\frac{\mathrm{d}g_{i3}}{\mathrm{d}\varphi_3}\right)^\circ = g^\circ{}_{i3} + \frac{p_i^* V_i^*}{RT}\left(\frac{\tilde{V}_i}{\tilde{V}_3}\right)^2 \tilde{U}(\tilde{T}_i)\left\{\frac{X_{i3}}{p_i^*}\left(\frac{s_3}{s_i}\right)^2 - \frac{1}{2}\,\frac{\tilde{T}_i\tilde{C}_p(\tilde{T}_i)}{\tilde{U}(\tilde{T}_i)}\left[\frac{p_3^*}{p_i^*}\left(\frac{T_i^*}{T_3^*} - 1\right) + \frac{X_{i3}}{p_i^*}\,\frac{s_3}{s_i}\right]^2\right\} - \frac{1}{2}\left[1 - \left(\frac{\tilde{V}_i}{\tilde{V}_3}\right)^2\right] + \frac{V_i}{V_3}\left(1 - \frac{\tilde{V}_i}{\tilde{V}_3}\right) \qquad (i = 1, 2) \quad (21)$$

with $\tilde{C}_p$ reduced molar heat capacity.

In the case of g_{12} we calculate the product $u_{10}u_{20}g_{12}$, which is more useful in the formulas of λ and Y. Here, u_{i0} means volume fraction in the binary liquid mixture free of polymer. From eq 17 we get

$$\frac{V_1}{RT}\left(\frac{G^{\mathrm{R}}}{V}\right)^\circ = u_{10}u_{20}g_{12} + \frac{V_1}{RT}\left(\frac{G^{\mathrm{R}'}}{V}\right)^\circ \quad (22)$$

and substituting from eq 14

$$u_{10}u_{20}g_{12} = u_{10}\frac{p_1^* V_1^*}{RT}\{\tilde{U}(\tilde{T}_0) - \tilde{U}(\tilde{T}_1) - \tilde{T}_1[\tilde{S}(\tilde{T}_0) - \tilde{S}(\tilde{T}_1)]\} + lu_{20}\frac{p_2^* V_2^*}{RT}\{\tilde{U}(\tilde{T}_0) - \tilde{U}(\tilde{T}_2) - \tilde{T}_2[\tilde{S}(\tilde{T}_0) - \tilde{S}(\tilde{T}_2)]\} - u_{10}\theta_{20}\frac{V_1^* X_{12}}{RT}\tilde{U}(\tilde{T}_0) - \frac{V_1}{RT}\left(\frac{G^{\mathrm{R}'}}{V}\right)^\circ \quad (23)$$

where $l = V_1/V_2$.

Having identified $g^\circ{}_{13}$, $g^\circ{}_{23}$, $(\mathrm{d}g_{13}/\mathrm{d}\varphi_3)^\circ$, $(\mathrm{d}g_{23}/\mathrm{d}\varphi_3)^\circ$, and $u_{10}u_{20}g_{12}$ in the FPP theory, let us turn now to the calculation of λ and Y.

According to thermodynamic theory,[2,3] λ and Y are given by

$$\lambda = -\bar{v}_3{}^\circ(M_{13}/M_{11}) \quad (24)$$

$$Y = \frac{V_1}{2RT}\left[M_{33} - M_{11}\left(\frac{\lambda}{\bar{v}_3{}^\circ}\right)^2\right] \quad (25)$$

where the M_{ij}'s are second derivatives of the Gibbs function with respect to u_i and u_j, which can be found defined in I ($\bar{v}$ is the specific volume). Each M_{ij} has a contribution from the combinatorial part of ΔG_{M} and a contribution from the residual part. The expressions for the combinatorial terms of M_{11}, M_{13}, and M_{33} are given in eq I12–14. The residual terms, $M_{ij}{}^{\mathrm{R}}$, are

$$M_{11}{}^{\mathrm{R}} = (\partial^2 g/\partial u_1{}^2)^\circ \quad (26)$$

$$M_{13}{}^{\mathrm{R}} = (\partial^2 g/\partial u_1 \partial u_3)^\circ \quad (27)$$

$$M_{33}{}^{\mathrm{R}} = (\partial^2 g/\partial u_3{}^2)^\circ \quad (28)$$

with g the residual Gibbs function per unit volume of the liquid mixture:

$$g = (G^{\mathrm{R}}/V)(1 + u_3) \quad (29)$$

We can rewrite

$$M_{11}{}^{\mathrm{R}} = \frac{\partial^2}{\partial u_{10}{}^2}\left(\frac{G^{\mathrm{R}}}{V}\right)^{\circ} \tag{30}$$

$$M_{13}{}^{\mathrm{R}} = \frac{\partial}{\partial u_{10}}\left(\frac{\partial g}{\partial u_3}\right)^{\circ} \tag{31}$$

and using eq 22

$$M_{11}{}^{\mathrm{R}} = \frac{RT}{V_1}\frac{\partial^2}{\partial u_{10}{}^2}\left[(u_{10}u_{20}g_{12}) + \frac{V_1}{RT}\left(\frac{G^{\mathrm{R}\prime}}{V}\right)^{\circ}\right] \tag{32}$$

with $u_{10}u_{20}g_{12}$ having the meaning given in eq 23.

We now calculate $(\partial g/\partial u_3)^{\circ}$ needed in eq 31. Substituting G^{R} by its expression given in eq 10 into eq 29 and performing the derivative with respect to u_3, we get in the limit $\varphi_3 \to 0$

$$\left(\frac{\partial g}{\partial u_3}\right)^{\circ} = \frac{1}{\tilde{V}_3}\Bigg\{p_3{}^*\{\tilde{U}(\tilde{T}_0) - \tilde{U}(\tilde{T}_3) - \tilde{T}_3[\tilde{S}(\tilde{T}_0) - \tilde{S}(\tilde{T}_3)]\} - \tilde{U}(\tilde{T}_0)\frac{s_3}{s_0{}'}\left(u_{10}X_{13} + \tilde{l}u_{20}X_{23} - u_{10}u_{20}\tilde{l}\frac{s_2}{s_0{}'}X_{12}\right)\Bigg\} \tag{33}$$

where $\tilde{l} = \tilde{V}_1/\tilde{V}_2$ and $s_0{}' = u_{10}s_1 + \tilde{l}u_{20}s_2$. Obviously, if we now apply the derivative $\partial/\partial u_{10}$ to eq 33, we obtain the same expression given in I for $(\partial^2 g/\partial u_1\partial u_3)^{\circ}$, namely, eq I26.[11]

The second derivative $(\partial^2 g/\partial u_3{}^2)^{\circ}$ needed in eq 28 was already obtained in I, but it was then slightly misprinted (eq I25[11]). We give it here again:

$$\left(\frac{\partial^2 g}{\partial u_3{}^2}\right)^{\circ} = 2\tilde{U}(\tilde{T}_0)\frac{s_3{}^2}{s_0{}'^2}\frac{\tilde{V}_1}{\tilde{V}_3{}^2}\left[u_{10}X_{13} + \tilde{l}u_{20}X_{23} - \frac{s_2}{s_0{}'}\tilde{l}u_{10}u_{20}X_{12}\right] - \frac{\tilde{C}_p(\tilde{T}_0)A_3{}^2}{u_{10}(p_1{}^*/\tilde{V}_1)\tilde{T}_1 + u_{20}(p_2{}^*/\tilde{V}_2)\tilde{T}_2} \tag{34}$$

with A_3 defined in eq I28.

Let us compare now these expressions of the FPP theory with the ones of the FH formalism. Using the FH eq 12 for ΔG_{M} it is obtained

$$M_{11}{}^{\mathrm{R}} = \frac{RT}{V_1}\frac{\partial^2}{\partial u_{10}{}^2}\left[u_{10}u_{20}g_{12} + \frac{V_1}{RT}\left(\frac{G^{\mathrm{R}\prime}}{V}\right)^{\circ}\right] \tag{35}$$

$$\begin{aligned} M_{13}{}^{\mathrm{R}} &= \frac{RT}{V_1}\frac{\partial}{\partial u_{10}}\left[u_{10}g^{\circ}{}_{13} + lu_{20}g^{\circ}{}_{23} - u_{10}u_{20}g_{12} - (u_{10} + lu_{20})\left(1 - \frac{\tilde{V}_1/\tilde{V}_3}{u_{10} + \tilde{l}u_{20}}\right) - \frac{V_1}{V_3}\ln\left(\frac{\tilde{V}_1/\tilde{V}_3}{u_{10} + \tilde{l}u_{20}}\right)\right] \\ &= \frac{RT}{V_1}\left\{g^{\circ}{}_{13} - lg^{\circ}{}_{23} - \frac{\partial}{\partial u_{10}}(u_{10}u_{20}g_{12}) + (l - 1) \times \left(1 - \frac{\tilde{V}_1/\tilde{V}_3}{u_{10} + \tilde{l}u_{20}}\right) - \frac{\tilde{l} - 1}{u_{10} + \tilde{l}u_{20}}\left[\frac{V_1}{V_3} - \frac{\tilde{V}_1}{\tilde{V}_3}\frac{u_{10} + lu_{20}}{u_{10} + \tilde{l}u_{20}}\right]\right\} \end{aligned} \tag{36}$$

$$M_{33}{}^{\mathrm{R}} = 2\frac{RT}{V_1}\left\{u_{10}u_{20}g_{12} - (u_{10}\chi^{\circ}{}_{13} + lu_{20}\chi^{\circ}{}_{23}) + \frac{u_{10} + lu_{20}}{2}\left[1 - \left(\frac{\tilde{V}_1/\tilde{V}_3}{u_{10} + \tilde{l}u_{20}}\right)^2\right] - \frac{V_1}{V_3}\left(1 - \frac{\tilde{V}_1/\tilde{V}_3}{u_{10} + \tilde{l}u_{20}}\right)\right\} \tag{37}$$

Table I

Factor f in $g_{12}{}^{\mathrm{eff}} = fg_{12}$ for Preferential and Total Sorption[a]

theory	f in M_{13} (λ)	in M_{33} (Y)
FPP		
set A of approximations	$(\tilde{V}_1/\tilde{V}_3)(s - \alpha)$	$(\tilde{V}_1/\tilde{V}_3)^2(s^2 - s\alpha - \alpha')$
FH		
ternary parameter approximated by eq 4 and 5[6,7]	$1 - a_g$	$1 - a_g - a_{\chi}{}'$
ternary parameter approximated by eq 6[8]	$1 - g^{\circ}{}_{13}g^{\circ}{}_{23}/(1 - \kappa)$	$1 - (2g^{\circ}{}_{13}g^{\circ}{}_{23} - \kappa)/(1 - \kappa)$

[a] κ defined in eq 60.

Equation 35 for $M_{11}{}^{\mathrm{R}}$ is the same as eq 32. Therefore, $M_{11}{}^{\mathrm{R}}$ has the same form in the FPP and FH formalisms. If g_{12} is substituted by its empirical value and its composition dependence is taken into account in one of the formalisms (FH), so can be done in the other (FPP). Therefore, M_{11} is the same in the FH and FPP theories when in both the empirical values of g_{12} and of its derivatives with respect to solvent mixture composition are used.

Let us consider now $M_{13}{}^{\mathrm{R}}$ or equivalently $(\partial g/\partial u_3)^{\circ}$ (eq 31). In the FPP theory $(\partial g/\partial u_3)^{\circ}$ is given by eq 33. In the FH theory it is given by (eq 31 and 36) $(\partial g/\partial u_3)^{\circ} = (RT/V_1)(u_{10}g^{\circ}{}_{13} + lu_{20}g^{\circ}{}_{23} - u_{10}u_{20}g_{12} - ...)$. To see whether these two expressions for $(\partial g/\partial u_3)^{\circ}$ are equivalent or not and what are their differences, if any, we can use our formulas for g_{12}, $g^{\circ}{}_{13}$, and $g^{\circ}{}_{23}$, according to the FPP theory, eq 20 and 23, and substitute them above to obtain $(RT/V_1)(u_{10}g^{\circ}{}_{13} + lu_{20}g^{\circ}{}_{23} - u_{10}u_{20}g_{12} - ...)$ according to the FPP theory. Comparing the result with eq 33 for $(\partial g/\partial u_3)^{\circ}$, we can see that both look alike but are not equal.

To obtain an easier comparison between them we have to resort to the same kind of approximations used in I, namely,[11] to neglect dissimilarities in free volume and in molecular surface to volume ratio between both solvents[18] and to expand quantities depending on $\tilde{T}_0$ in powers of the small difference $\tilde{T}_0 - \tilde{T}_1$, retaining only linear terms and neglecting products of interaction parameters X_{ij}. This set of approximations we call *set A* for further reference. Then, using such a set A of approximations, $(\partial g/\partial u_3)^{\circ}$ and $g^{\circ}{}_{13}$, $g^{\circ}{}_{23}$, and g_{12} simplify to

$$\left(\frac{\partial g}{\partial u_3}\right)^{\circ} = \frac{1}{\tilde{V}_3}\left\{p_3{}^*\{\tilde{U}(\tilde{T}_1) - \tilde{U}(\tilde{T}_3) - \tilde{T}_3[\tilde{S}(\tilde{T}_1) - \tilde{S}(\tilde{T}_3)]\} - \tilde{U}(\tilde{T}_1)\frac{s_3}{s_1}\left\{u_{10}X_{13} + u_{20}X_{23} - u_{10}u_{20}X_{12}\left[1 + \frac{s_1}{s_3}\frac{p_3{}^*}{p_1{}^*}\frac{\tilde{T}_1\tilde{C}_p(\tilde{T}_1)}{\tilde{U}(\tilde{T}_1)}\left(1 - \frac{T_1{}^*}{T_3{}^*}\right)\right]\right\}\right\} \tag{38}$$

$$g^{\circ}{}_{i3} = \frac{p_1{}^*V_i{}^*}{RT}\frac{\tilde{V}_1}{\tilde{V}_3}\left\{\frac{p_3{}^*}{p_1{}^*}\{\tilde{U}(\tilde{T}_1) - \tilde{U}(\tilde{T}_3) - \tilde{T}_3[\tilde{S}(\tilde{T}_1) - \tilde{S}(\tilde{T}_3)]\} - \tilde{U}(\tilde{T}_1)\frac{s_3}{s_1}\frac{X_{i3}}{p_1{}^*}\right\} + 1 - \frac{\tilde{V}_1}{\tilde{V}_3} + \frac{V_i}{V_3}\ln\left(\frac{\tilde{V}_1}{\tilde{V}_3}\right) \qquad (i = 1, 2) \tag{39}$$

$$g_{12} = -\frac{p_1{}^*V_1{}^*}{RT}\tilde{U}(\tilde{T}_1)\frac{X_{12}}{p_1{}^*} \tag{40}$$

Therefore, comparing eq 38–40, we find that, under the set A of approximations

$$\left(\frac{\partial g}{\partial u_3}\right)^{\circ} = \frac{RT}{V_1}\left\{u_{10}g^{\circ}{}_{13} + lu_{20}g^{\circ}{}_{23} - u_{10}u_{20}g_{12}\frac{\tilde{V}_1}{\tilde{V}_3}\left[\frac{s_3}{s_1} + \frac{p_3{}^*}{p_1{}^*}\,\frac{\tilde{T}_1\tilde{C}_p(\tilde{T}_1)}{\tilde{U}(\tilde{T}_1)}\left(1 - \frac{T_1{}^*}{T_3{}^*}\right)\right] - (u_{10} + lu_{20})\left(1 - \frac{\tilde{V}_1}{\tilde{V}_3}\right) - \frac{V_1}{V_3}\ln\left(\frac{\tilde{V}_1}{\tilde{V}_3}\right)\right\} \quad (41)$$

In I we simplified notation by calling[11]

$$s = s_3/s_1 \quad (42)$$

$$\alpha = \frac{\tilde{T}_1\tilde{C}_p(\tilde{T}_1)}{[-\tilde{U}(\tilde{T}_1)]}\,\frac{p_3{}^*}{p_1{}^*}\left(1 - \frac{T_1{}^*}{T_3{}^*}\right) \quad (43)$$

According to such definitions, eq 41 now reads

$$\left(\frac{\partial g}{\partial u_3}\right)^{\circ} = \frac{RT}{V_1}\left[u_{10}g^{\circ}{}_{13} + lu_{20}g^{\circ}{}_{23} - u_{10}u_{20}g_{12}\frac{\tilde{V}_1}{\tilde{V}_3}(s - \alpha) - (u_{10} + lu_{20})\left(1 - \frac{\tilde{V}_1}{\tilde{V}_3}\right) - \frac{V_1}{V_3}\ln\left(\frac{\tilde{V}_1}{\tilde{V}_3}\right)\right] \quad (44)$$

And substituting into eq 31 we finally obtain for $M_{13}{}^{\mathrm{R}}$ according to the FPP theory under the set A of approximations:

$$M_{13}{}^{\mathrm{R}} = \frac{RT}{V_1}\left[g^{\circ}{}_{13} - lg^{\circ}{}_{23} - \frac{\tilde{V}_1}{\tilde{V}_3}(s - \alpha)\frac{\partial}{\partial u_{10}}(u_{10}u_{20}g_{12}) + (l - 1)\left(1 - \frac{\tilde{V}_1}{\tilde{V}_3}\right)\right] \quad (45)$$

This is the same expression as in the FH formalism, eq 36 with $\tilde{l} = 1$, except for the factor $(\tilde{V}_1/\tilde{V}_3)(s - \alpha)$. Now, in both formalisms we can substitute the interaction parameters for their empirical values; i.e., we can use experimental results of $g^{\circ}{}_{13}$, $g^{\circ}{}_{23}$, and g_{12} (obtained in their respective binary systems) to compute $M_{13}{}^{\mathrm{R}}$. Then both formalisms, FH and FPP, are equivalent, except for the fact that the influence of the $(\partial/\partial u_{10})(u_{10}u_{20}g_{12})$ term is modified by the factor $(\tilde{V}_1/\tilde{V}_3)(s - \alpha)$ in the FPP theory.

Let us now consider $M_{33}{}^{\mathrm{R}}$ or $(\partial^2 g/\partial u_3{}^2)^{\circ}$. In the FPP theory $(\partial^2 g/\partial u_3{}^2)^{\circ}$ is given by eq 34. In the FH theory it is given by eq 37. Again, we use the expressions of $\chi^{\circ}{}_{13}$, $\chi^{\circ}{}_{23}$, and g_{12}, given by the FPP theory (eq 1, 20, 21, and 23), and substitute them into eq 37, thus obtaining $(RT/V_1)[u_{10}u_{20}g_{12} - (u_{10}\chi^{\circ}{}_{13} + lu_{20}\chi^{\circ}{}_{23}) + ...]$ according to the FPP theory. Comparing the result with eq 34 for $(\partial^2 g/\partial u_3{}^2)^{\circ}$, we can see here also that they are similar expressions, but they are not equal. Resorting again to the set A of approximations in order to advance further in the comparison of both expressions, we get for $(\partial^2 g/\partial u_3{}^2)^{\circ}$, $\chi^{\circ}{}_{13}$, and $\chi^{\circ}{}_{23}$

$$\left(\frac{\partial^2 g}{\partial u_3{}^2}\right)^{\circ} = 2\frac{\tilde{V}_1}{\tilde{V}_3{}^2}\tilde{U}(\tilde{T}_1)\left\{u_{10}\left\{s^2X_{13} - \frac{\alpha}{2}\left[p_3{}^*\left(\frac{T_1{}^*}{T_3{}^*} - 1\right) + 2sX_{13}\right]\right\} + u_{20}\left\{s^2X_{23} - \frac{\alpha}{2}\left[p_3{}^*\left(\frac{T_1{}^*}{T_3{}^*} - 1\right) + 2sX_{23}\right]\right\} - u_{10}u_{20}X_{12}\left[s^2 - \alpha\left(\frac{p_3{}^*}{p_1{}^*} + s\right)\right]\right\} \quad (46)$$

$$\chi^{\circ}{}_{i3} = -\frac{p_1{}^*V_i{}^*}{RT}\left(\frac{\tilde{V}_1}{\tilde{V}_3}\right)^2\tilde{U}(\tilde{T}_1) \times \left\{s^2\frac{X_{i3}}{p_1{}^*} - \frac{\alpha}{2}\left[\frac{p_3{}^*}{p_1{}^*}\left(\frac{T_1{}^*}{T_3{}^*} - 1\right) + 2s\frac{X_{i3}}{p_1{}^*}\right]\right\} + \frac{1}{2}\left[1 - \left(\frac{\tilde{V}_1}{\tilde{V}_3}\right)^2\right] - \frac{V_i}{V_3}\left(1 - \frac{\tilde{V}_1}{\tilde{V}_3}\right) \qquad (i = 1, 2) \quad (47)$$

Comparing eq 40, 46, and 47, we realize that, under the set A of approximations, the FPP theory gives

$$\left(\frac{\partial^2 g}{\partial u_3{}^2}\right)^{\circ} = -2\frac{RT}{V_1}\left\{u_{10}\chi^{\circ}{}_{13} + lu_{20}\chi^{\circ}{}_{23} - \left(\frac{\tilde{V}_1}{\tilde{V}_3}\right)^2(s^2 - \alpha' - s\alpha)u_{10}u_{20}g_{12} - \frac{u_{10} + lu_{20}}{2}\left[1 - \left(\frac{V_1}{V_3}\right)^2\right] + \frac{V_1}{V_3}\left(1 - \frac{V_1}{V_3}\right)\right\} \quad (48)$$

where we have used α' with the same meaning as in I:[11]

$$\alpha' = \alpha(p_3{}^*/p_1{}^*) \quad (49)$$

Therefore, comparing eq 37 (with $\tilde{l} = 1$) and 48, we can see that the FPP theory, under the set A of approximations, gives for $M_{33}{}^{\mathrm{R}}$ the same result as the FH formalism, except for the factor $(\tilde{V}_1/\tilde{V}_3)^2(s^2 - \alpha' - s\alpha)$ modifying the influence of the $u_{10}u_{20}g_{12}$ term.

Adding now the combinatorial part of the M_{ij},[11] we get the final results of the FPP theory under the set A of approximations. In summary, they are

$$M_{11} = \frac{RT}{V_1}\,\frac{lu_{10} + u_{20} + u_{10}u_{20}\dfrac{\partial^2}{\partial u_{10}{}^2}(u_{10}u_{20}g_{12})}{u_{10}u_{20}} \quad (50)$$

$$M_{13} = \frac{RT}{V_1}\left[l - 1 + g^{\circ}{}_{13} - lg^{\circ}{}_{23} - \frac{\tilde{V}_1}{\tilde{V}_3}(s - \alpha)\frac{\partial}{\partial u_{10}}(u_{10}u_{20}g_{12})\right] \quad (51)$$

$$M_{33} = 2\frac{RT}{V_1}\left[\frac{u_{10} + lu_{20}}{2} - (u_{10}\chi^{\circ}{}_{13} + lu_{20}\chi^{\circ}{}_{23}) + \left(\frac{\tilde{V}_1}{\tilde{V}_3}\right)^2(s^2 - \alpha' - s\alpha)u_{10}u_{20}g_{12}\right] \quad (52)$$

Ternary Parameter

In our comparison of the FPP and FH expressions we have made use of eq 12 for G^{R} in the FH model. Let us consider the contribution of the ternary parameter explicitly by using eq 13 and compare the role of such a parameter with the results of the FPP theory.

The ternary parameter does not appear in M_{11}, so that eq 50 is also valid with G^{R} given by eq 13. Let us see now M_{13} and M_{33}. The corresponding expressions in the extended FH theory can be written as

$$M_{13} = \frac{RT}{V_1}\left\{l - 1 + g^{\circ}{}_{13} - lg^{\circ}{}_{23} - \left(\frac{\partial}{\partial u_1}[u_1u_2(g_{12} - g_{\mathrm{T}})]\right)^{\circ}\right\} \quad (53)$$

$$M_{33} = 2\frac{RT}{V_1}\left[\frac{u_{10} + lu_{20}}{2} - (u_{10}\chi^{\circ}{}_{13} + lu_{20}\chi^{\circ}{}_{23}) + u_{10}u_{20}(g_{12} - g_{\mathrm{T}} - \chi_{\mathrm{T}})^{\circ}\right] \quad (54)$$

Table II
Values of f in $g_{12}^{\text{eff}} = fg_{12}$ for Preferential and Total Sorption[a,b]

polymer	mixed solvent	λ: $1 - a_g$	λ: $1 - \frac{g^\circ_{13}g^\circ_{23}}{1-\kappa}$	λ: $\frac{\tilde{V}_1}{\tilde{V}_3}(s-\alpha)$[c]	Y: $1 - a_g - a_\chi'$	Y: $1 - \frac{2g^\circ_{13}g^\circ_{23} - \kappa}{1-\kappa}$	Y: $\left(\frac{\tilde{V}_1}{\tilde{V}_3}\right)^2(s^2 - s\alpha - \alpha')$[c]
PIB	C_6H_6 + c-C_6H_{12}			0.55	0.23		0.26
PS	C_6H_6 + c-C_6H_{12}	0.22–0.76	0.64	0.41	0.17–0.25	0.39	0.08
PS	C_6H_6 + n-C_7H_{16}	0.66	0.46	0.43		−0.08	0.08
PS	EtOAc + c-C_6H_{12}		0.35			0.05	
PDMS	n-C_7H_{16} + MEK	0.27	0.42	0.61		0.16	0.37
PDMS	n-$C_{11}H_23_4$ + MEK	0.34	0.41	0.62		0.14	0.39
PMMA	CH_3CN + BuCl		0.42	0.41		0.11	0.03
PMMA	CH_3CN + CCl_4		0.53	0.44		0.24	0.11

[a] Empirical values of a_g and a_χ' obtained in ref 6–8 from experimental data of λ and Y. [b] Empirical values of g°_{13}, g°_{23}, $(\mathrm{d}g_{13}/\mathrm{d}\varphi_3)^\circ$, and $(\mathrm{d}g_{23}/\mathrm{d}\varphi_3)^\circ$ obtained in ref 8 from experimental data. [c] Theoretical values calculated from the molecular characteristics of the pure components. p_1^*, p_3^*, T_1^*, T_3^*, $\tilde{V}_1$, $\tilde{V}_3$, α_1, and s (geometrical value) taken from ref 14 and 19–25.

We now use the correlation of g_T and χ_T suggested by the experimental results of λ and Y. First, we use the type of approximations of Pouchlý and Živný[6,7] expressed here by eq 4 and 5. Substitution of these equations into eq 53 and 54 yields

$$M_{13} = \frac{RT}{V_1}\left[l - 1 + g^\circ_{13} - lg^\circ_{23} - (1 - a_g)\frac{\partial}{\partial u_{10}}(u_{10}u_{20}g_{12})\right] \quad (55)$$

$$M_{33} = 2\frac{RT}{V_1}\left[\frac{u_{10} + lu_{20}}{2} - (u_{10}\chi^\circ_{13} + lu_{20}\chi^\circ_{23}) + (1 - a_g - a_\chi')u_{10}u_{20}g_{12}\right] \quad (56)$$

Let us consider now the correlation of Figueruelo, Campos, and Celda, expressed by eq 6. From such a correlation these authors deduce[8]

$$g^\circ_T = g_{12}g^\circ_{13}g^\circ_{23}(1 - \kappa)^{-1} \quad (57)$$

$$\left(\frac{\partial g_T}{\partial u_1}\right)^\circ = \frac{\mathrm{d}g_{12}}{\mathrm{d}u_{10}}g^\circ_{13}g^\circ_{23}(1 - \kappa)^{-1} \quad (58)$$

$$\left(\frac{\partial g_T}{\partial \varphi_3}\right)^\circ_{u_1} = g_{12}\kappa(1 - \kappa)^{-1} \quad (59)$$

with

$$\kappa = g^\circ_{13}\left(\frac{\mathrm{d}g_{23}}{\mathrm{d}\varphi_3}\right)^\circ + g^\circ_{23}\left(\frac{\mathrm{d}g_{13}}{\mathrm{d}\varphi_3}\right)^\circ \quad (60)$$

We substitute now eq 57–59 into eq 53 and 54 and obtain

$$M_{13} = \frac{RT}{V_1}\left[l - 1 + g^\circ_{13} - lg^\circ_{23} - \left(1 - \frac{g^\circ_{13}g^\circ_{23}}{1 - \kappa}\right)\frac{\partial}{\partial u_{10}}(u_{10}u_{20}g_{12})\right] \quad (61)$$

$$M_{33} = 2\frac{RT}{V_1}\left[\frac{u_{10} + lu_{20}}{2} - (u_{10}\chi^\circ_{13} + lu_{20}\chi^\circ_{23}) + \left(1 - \frac{2g^\circ_{13}g^\circ_{23} - \kappa}{1 - \kappa}\right)u_{10}u_{20}g_{12}\right] \quad (62)$$

Comparing these results derived from the correlation of Figueruelo, Campos, and Celda, eq 61 and 62, with the results derived from the assumptions of Pouchlý and Živný, eq 55 and 56, we see that both are entirely equivalent in the sense that no new terms containing additional dependencies of λ or Y on solvent composition are introduced with the ternary parameter in either case.

The role of such a ternary parameter is to reduce the effect of g_{12}. Instead of g_{12}, in M_{13} and in M_{33} an effective g_{12}^{eff} is used, such that

$$g_{12}^{\text{eff}}(u_{10}) = fg_{12}(u_{10}) \quad (63)$$

where f is a constant factor. f is equal to $1 - a_g$ in M_{13} and to $1 - a_g - a_\chi'$ in M_{33} when the type of assumptions (eq 4 and 5) proposed by Pouchlý and Živný are used. f is equal to $1 - g^\circ_{13}g^\circ_{23}(1 - \kappa)^{-1}$ in M_{13} and to $1 - (2g^\circ_{13}g^\circ_{23} - \kappa)(1 - \kappa)^{-1}$ in M_{33} when the correlation (eq 6) of Figueruelo, Campos, and Celda is used.

If we now look back at the expressions deduced in the FPP theory under the set A of approximations, eq 51 and 52, we see that they are of the same form. In such eq 51 and 52 of the FPP theory, the influence of g_{12} is also reduced by a constant factor f, which is $(\tilde{V}_1/\tilde{V}_3)(s - \alpha)$ in M_{13} and $(\tilde{V}_1/\tilde{V}_3)^2(s^2 - s\alpha - \alpha')$ in M_{33}.

The different forms of the factor f are compared in Table I. The main consequence from the comparison between the results of the FPP and FH theories is that the factor f always contains the effects of dissimilarities in free volume and in molecular surface to volume ratio between polymer and solvents. Even if the system is nonpolar and no other effects are present, these dissimilarities introduce a nonunity f, which in the FH theory is understood as due to a ternary interaction parameter.

If in addition to the effect of these dissimilarities, other effects such as polar or specific interactions are present in the system, they can also contribute to f, but their additional contribution should be difficult to interpret in terms of ternary interaction parameters unless the permanent contributions from s, α, and α' are first recognized.

To stress the idea that these nonspecific contributions of free volume and molecular surface are in fact contained in g°_T and χ°_T, we compare now the numerical values that are calculated for the factor f using the ternary parameter of the FH theory and the values predicted for f by the FPP theory under the set A of approximations. The results are shown in Table II.

As we can see, the values of f given by the ternary parameter g°_T using λ data range around f = 0.3–0.6, in relative agreement with the range of values predicted by the FPP theory for $f = (\tilde{V}_1/\tilde{V}_3)(s - \alpha)$. The values of f obtained from the ternary parameter χ°_T using Y data are smaller (f = 0.1–0.3), also in relative accordance with the values of the FPP theory for $(\tilde{V}_1/\tilde{V}_3)^2(s^2 - s\alpha - \alpha')$. At any rate, $(\tilde{V}_1/\tilde{V}_3)(s - \alpha)$ and especially $(\tilde{V}_1/\tilde{V}_3)^2(s^2 - s\alpha - \alpha')$

deviate substantially from unity, so that the effects of free volume and contact site dissimilarities included in g°_T and in χ°_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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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 $(\partial g_T/\partial\phi_3)_{u_1,\phi_3\to 0}$, 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, $g_T^\circ = K(g_{12} + (\partial g_T/\partial\phi_3)_{u_1,\phi_3\to 0})$. 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, $K = g_{13}^\circ g_{23}^\circ$ and both g_T° and its derivative $(\partial g_T/\partial\phi_3)_{u_1,\phi_3\to 0}$ 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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