Statistical Thermodynamics of Preferential Sorption

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ABSTRACT: The theory of polymer solutions developed by Flory and Patterson is used to calculate preferential and total sorption of macromolecules in mixed solvents. The coefficient of preferential adsorption is analyzed in terms of its dependence on parameters typical of the theory, such as molecular surface to volume ratios and free volume dissimilarity between polymer and solvents. Our theoretical results are compared with the ones from the simple Flory–Huggins theory. They are also compared with those obtained using an extended version of the Flory–Huggins theory which includes a phenomenological ternary interaction parameter. Based on this comparison, a partial interpretation is given for the molecular origin of such a ternary parameter.

The quasiternary systems formed by a polymer solute dissolved in a binary solvent mixture are encountered in many instances of polymer characterization.[1] When such systems are placed in osmotic equilibrium with the binary solvent, a redistribution of solvent molecules between the two phases spontaneously sets up, due to equilibration of the solvent chemical potentials. The resulting difference in solvent composition between the two phases at thermodynamic equilibrium is termed preferential or selective solvent sorption (solvation). For an isolated polymer coil immersed in a binary solvent medium, such osmotic equilibrium is established between the interior of the solvated coil and the mixture of pure solvents external to it. This purely osmotic contribution to preferential solvation is present in every system comprising a binary solvent. In highly polar systems, it has been found that a major contribution to the phenomenon of preferential solvation comes from the existence of specific strong interactions (hydrogen bonding, for example) between polymer segments and solvent molecules.[2-4] In the case of nonpolar or weakly polar systems, in which such strong interactions play a minor role, the phenomenon of preferential solvation has been interpreted by means of the Flory–Huggins lattice theory of polymer solutions. The statistical thermodynamic treatment of preferential solvation by means of the Flory–Huggins theory originates with the paper of Shultz and Flory[5] on polymer chain dimensions in mixed solvent media. Later, Read applied this same theory to give an explicit expression of the preferential adsorption coefficient λ.[6]

In the case of polymers in mixed solvents, the original Flory–Huggins theory has been extended by introducing a ternary interaction parameter χ_T.[7] A ternary term was first introduced by Read in his formulation of λ. Read pointed out[6] that this χ_T could be regarded, both mathematically and physically, as representing the change in the interaction between two solvent molecules, one of each kind, when both are in the vicinity of a polymer segment. Pouchlý et al.[8] have interpreted the necessity of introducing χ_T into the theory as being due to the effect of nonrandom mixing. In general, there is no theoretical scheme to calculate χ_T, and it has to be considered as an adjustable parameter. The original formulation has been thus extended to improve agreement with experiment, but at the expense of adding empiricism to the theory. Present studies of preferential sorption are based on this semiempirically extended Flory–Huggins theory.[9] The lattice model, however, suffers from basic deficiencies[10] which cannot be alleviated by extensions of the type mentioned.

The statistical thermodynamics of solutions composed of chain molecules is nowadays based on the theory formulated by Flory and co-workers[10] and by Patterson and co-workers,[11] which derive from the ideas advanced by Prigogine and his school.[12] This theory (to be designated as the FPP theory, for Flory, Prigogine, and Patterson) abandones the model of a rigid lattice for the solution and takes into account the differences in free volume between simple liquids and polymers, which give rise to such phenomena unforeseen by the Flory–Huggins theory (FH, from now on) as the excess volume and the existence of lower critical solution temperatures. In general, the thermodynamic properties of the polymer solution, according to the FPP theory, are the result of two main contributions besides the combinatorial one: a contribution from the contact energies between polymer segments and solvent molecules, and another one from the free volume dissimilarity between polymer chains and simple liquids. This last contribution is ignored in the FH theory. But the differences between both theories are not only contained in this free-volume dissimilarity contribution but, also, in the idea introduced with the FPP theory that the contact interactions take place on the molecular surfaces and depend, therefore, on the area exposed by the molecules and not on their volume, as is assumed in the FH theory. The contact interaction contribution in the FPP theory differs from the FH one in that it has an additional and important dependence on the molecular surface-to-volume ratios.

The FPP theory provides the current statistical thermodynamic interpretation of polymer solutions, and its use instead of the semiempirical extensions of the FH theory seems, therefore, preferable from a theoretical point of view. The first application of the FPP theory to polymers in mixed solvents was done, recently, by Pouchlý and Patterson,[13] who calculated intrinsic viscosities and heats of mixing to infinite dilution. They showed that the values predicted by the FPP and FH theories differ considerably from each other and that the FPP ones are in much better agreement with experiment. Changes in intrinsic viscosity with solvent composition are due to the expansion of the coil and reflect, therefore, the overall sorption of the binary solvent by the polymer. Pouchlý and Patterson neglected the influence of preferential solvation on total expansion and obtained the intrinsic viscosity in the single-liquid approximation, in which it is assumed that the binary solvent has the same composition inside and outside the polymer coils. Preferential solvation may be an important contribution to total sorption, and its influence cannot always be neglected. In fact, for liquid mixtures composed of a solvent and a precipitant, it has been found experimentally[14,15] that there is a correlation between the segment density inside the coil, which is governed by overall sorption, and the coefficient of preferential solvation λ. And, what is more important, λ can be measured

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directly by different experimental techniques, such as refractometry, light scattering, ultracentrifugation, density measurements, etc. and is, thus, a magnitude available for direct comparison with theory. The relevance of a proper theoretical calculation of λ is, therefore, great.

In the present paper, we develop the FPP theory of the preferential sorption coefficient λ. The presentation is organized as follows. In the Review of Thermodynamic Relationships section we review the general thermodynamic relationships (independent of any statistical model for the interactions) which relate preferential and overall sorption to the Gibbs function of mixing. Also, we calculate the contributions to these properties arising from the combinatorial entropy. In the next section we write the noncombinatorial Gibbs function according to the FPP theory, extending it to the case of ternary systems composed of two solvents and a polymer, and calculate its contribution to preferential and overall sorption. In the Discussion section we compare our results with the ones from the FH theory and discuss the relative importance of each one of the new contributions introduced by the FPP theory. We have not attempted to take into account the configurational restrictions imposed on the polymer chains by the excluded volume effect. In this sense, our results suffer from the same deficiency as the FH theory.

Review of Thermodynamic Relationships

The components in the quasiternary system will be denoted by the following subscripts: 1 and 2 for the solvents, 3 for the polymer. Superscript zero will mean that the superscripted magnitude is to be taken in the limit of vanishing polymer concentration. The preferential sorption coefficient λ is defined in terms of γ, the number of molecules of solvent 1 which are in excess inside the polymer coil, as:[16]

$$\lambda = (\bar{V}_1/M)\gamma \tag{1}$$

Here, V_i is molar volume, the bar denoting partial quantity in solution, and M is polymer molecular weight. The total sorption function, Y, which measures the solvent power of a given solvent mixture, is defined in terms of G_{el}, the Gibbs function of an isotropic elastic deformation of the swollen coil, as:[5]

$$Y = (V_1/RT)\upsilon_3^{-2}\,(\partial G_{\mathrm{el}}/\partial \upsilon)_{p,T} \tag{2}$$

where υ_3 is volume fraction of polymer inside a small, concentrated homogeneous volume element, υ, of the coil domain, and RT and p are thermal energy and pressure, respectively.

These preferential and total solvation quantities are to be calculated from the Gibbs function of mixing, ΔG_{M}, through the following relationships:[7]

$$\lambda = -\bar{v}_3{}^0 M_{13}/M_{11} \tag{3}$$

$$Y = (V_1/2RT)[M_{33} - M_{11}(\lambda/\bar{v}_3{}^0)^2] \tag{4}$$

where v_i is specific volume and the M_{ij}'s are second derivatives of ΔG_{M} introduced by Pouchlý et al.[7] The composition variables chosen are volume fractions, u_i, referred to a unit volume comprising just the binary solvent mixture free of polymer. Therefore, $u_1 + u_2 = 1$. The independent variables are u_1 and u_3. The M_{ij}'s are then defined by:

$$M_{ij} = \lim_{u_3 \to 0} \left(\frac{\partial}{\partial u_i}\right)_{u_j} \left(\frac{\partial}{\partial u_j}\right)_{u_i} G_u{}^* \tag{5}$$

where $G_u{}^*$ stands for (V being total volume)

$$G_u{}^* = (1 + u_3)\Delta G_{\mathrm{M}}/V - (RT/V_3)u_3 \ln \frac{u_3}{1 + u_3} \tag{6}$$

We can now split ΔG_{M} into its combinatorial and residual[10] contributions as follows:

$$\Delta G_{\mathrm{M}} = -T\Delta S_{\mathrm{comb}} + \Delta H_{\mathrm{M}} - TS^{\mathrm{R}} \tag{7}$$

where ΔS_{comb} and S^{R} are respectively the combinatorial and residual parts of the mixing entropy, and ΔH_{M} is the heat of mixing. For ΔS_{comb}, we take the usual form:[10]

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

where the ϕ_i's are segment fractions or core volume fractions, and n_i denotes the amount of substance. The relationships

$$\begin{gathered} n_i/V = u_i/V_i(1 + u_3) \\ \phi_i = (u_i/\tilde{V}_i)/(u_1/\tilde{V}_1 + u_2/\tilde{V}_2 + u_3/\tilde{V}_3) \end{gathered} \tag{9}$$

allow us to write ΔS_{comb} in terms of the u_i variables. Here, $\tilde{V}_i$ means reduced molar volume (reduced quantities are introduced in extenso in the following section). The combinatorial entropy is most commonly defined in terms of volume fractions rather than segment fractions. If required, ϕ_i can be easily converted into volume fraction simply by taking equal value for all the $\tilde{V}_i$'s in eq 9.

Substituting ΔG_{M} of eq 7 into eq 6 yields for $G_u{}^*$

$$G_u{}^* = RT\left[\frac{u_1}{V_1}\ln \phi_1 + \frac{u_2}{V_2}\ln \phi_2 + \frac{u_3}{V_3}\ln\left(\phi_3\frac{1 + u_3}{u_3}\right)\right] + g \tag{10}$$

where we have introduced the symbol g to denote the contributions to $G_u{}^*$ arising from ΔH_{M} and S^{R}:

$$g \equiv (\Delta H_{\mathrm{M}} - TS^{\mathrm{R}})(1 + u_3)/V \tag{11}$$

These contributions are the ones calculated here using the FPP theory.

Substituting $G_u{}^*$ into eq 5 gives for the M_{ij}'s required to calculate λ and Y:

$$M_{11} = \left(\frac{\partial^2 g}{\partial u_1{}^2}\right)^0 + \frac{RT}{V_1 u_{10} u_{20}}\left\{l u_{10} + u_{20} + \frac{u_{10}u_{20}(1 - \tilde{l})}{u_{10} + \tilde{l}u_{20}}\left[(1 - \tilde{l})\frac{u_{10} + l u_{20}}{u_{10} + \tilde{l}u_{20}} - 2(1 - l)\right]\right\} \tag{12}$$

$$M_{13} = \left(\frac{\partial^2 g}{\partial u_1\,\partial u_3}\right)^0 + \frac{RT}{V_1}\left\{\frac{\tilde{V}_1}{\tilde{V}_3}\frac{l - 1}{u_{10} + \tilde{l}u_{20}} + \frac{\tilde{l} - 1}{u_{10} + \tilde{l}u_{20}}\left[\frac{V_1}{V_3} - \frac{\tilde{V}_1}{\tilde{V}_3}\frac{u_{10} + l u_{20}}{u_{10} + \tilde{l}u_{20}}\right]\right\} \tag{13}$$

$$M_{33} = \left(\frac{\partial^2 g}{\partial u_3{}^2}\right)^0 + \frac{RT}{V_1}\left\{\left(\frac{\tilde{V}_1}{\tilde{V}_3}\right)^2 \frac{u_{10} + l u_{20}}{(u_{10} + \tilde{l}u_{20})^2} + 2\frac{V_1}{V_3}\left[1 - \frac{\tilde{V}_1}{\tilde{V}_3}\frac{1}{u_{10} + \tilde{l}u_{20}}\right]\right\} \tag{14}$$

the u_{i0}'s being volume fractions for the solvent mixture in the absence of polymer, $l = V_1/V_2$, and $\tilde{l} = \tilde{V}_1/\tilde{V}_2$.

To proceed in the calculation of λ and Y we require the function g.

Preferential and Total Sorption

We take now the problem of finding g according to the FPP theory. The formulation of this theory given by Patterson and Delmas[11] can be easily extended to the case of ternary systems. The resulting heat of mixing and residual entropy are:

$$\Delta H_M = n_1U_1^*[\tilde{U}(\tilde{T}) - \tilde{U}(\tilde{T}_1)] + n_2U_2^*[\tilde{U}(\tilde{T}) - \tilde{U}(\tilde{T}_2)] + n_3U_3^*[\tilde{U}(\tilde{T}) - \tilde{U}(\tilde{T}_3)] - (n_1\theta_2V_1^*X_{12} + n_1\theta_3V_1^*X_{13} + n_2\theta_3V_2^*X_{23})\tilde{U}(\tilde{T}) \quad (15)$$

$$S^{\mathrm{R}} = n_1S_1^*[\tilde{S}(\tilde{T}) - \tilde{S}(\tilde{T}_1)] + n_2S_2^*[\tilde{S}(\tilde{T}) - \tilde{S}(\tilde{T}_2)] + n_3S_3^*[\tilde{S}(\tilde{T}) - \tilde{S}(\tilde{T}_3)] \quad (16)$$

Here, U_i^* and S_i^* are molar reduction parameters of the pure components for energy and entropy, respectively; they are related to the reduction parameters for pressure (p_i^*), molar volume (V_i^*), and temperature (T_i^*) through

$$U_i^* = p_i^*V_i^* \qquad S_i^* = p_i^*V_i^*/T_i^* \quad (17)$$

The X_{ij}'s are binary exchange interaction parameters and the θ_i's are site or surface fractions in the ternary system. They are given in terms of the segment fractions, or core volume fractions, ϕ_i, as:

$$\theta_i = \phi_is_i/(\phi_1s_1 + \phi_2s_2 + \phi_3s_3) \quad (18)$$

where s_i is the number of contact sites per segment; s_i measures the molecular surface to volume ratio, an important parameter of the FPP theory. The tilde in eq 15 and 16 denotes reduced quantities. The reduced temperature, $\tilde{T}$, is given by:

$$\tilde{T} = (n_1U_1^*\tilde{T}_1 + n_2U_2^*\tilde{T}_2 + n_3U_3^*\tilde{T}_3)/(n_1U_1^* + n_2U_2^* + n_3U_3^* - n_1\theta_2V_1^*X_{12} - n_1\theta_3V_1^*X_{13} - n_2\theta_3V_2^*X_{23}) \quad (19)$$

In order to obtain the residual Gibbs function g, we rewrite eq 15, 16, 18, and 19, in terms of the composition variables u_i, using the following direct equivalences:

$$\phi_i = n_iV_i^*/nV^* \qquad n_iV_i^* = n_iV_i/\tilde{V}_i \qquad n_iV_i = u_iV/(1 + u_3) \quad (20)$$

and obtain for g:

$$g = u_1\frac{p_1^*}{\tilde{V}_1}\{\tilde{U}(\tilde{T}) - \tilde{U}(\tilde{T}_1) - \tilde{T}_1[\tilde{S}(\tilde{T}) - \tilde{S}(\tilde{T}_1)]\} + u_2\frac{p_2^*}{\tilde{V}_2}\{\tilde{U}(\tilde{T}) - \tilde{U}(\tilde{T}_2) - \tilde{T}_2[\tilde{S}(\tilde{T}) - \tilde{S}(\tilde{T}_2)]\} + u_3\frac{p_3^*}{\tilde{V}_3}\{\tilde{U}(\tilde{T}) - \tilde{U}(\tilde{T}_3) - \tilde{T}_3[\tilde{S}(\tilde{T}) - \tilde{S}(\tilde{T}_3)]\} - \left(u_1\theta_2\frac{X_{12}}{\tilde{V}_1} + u_1\theta_3\frac{X_{13}}{\tilde{V}_1} + u_2\theta_3\frac{X_{23}}{\tilde{V}_2}\right)\tilde{U}(\tilde{T}) \quad (21)$$

This form of g is to be derivated twice with respect to volume fractions (u_i) in order to calculate λ and Y. These derivatives are considered now.

It is possible to write a general form common to the three second derivatives of g required for λ and Y. By making use of the thermodynamic relationships

$$\partial\tilde{U}/\partial\tilde{T} = \tilde{C}_{\mathrm{p}} \qquad \partial\tilde{S}/\partial\tilde{T} = \tilde{C}_{\mathrm{p}}/\tilde{T} \quad (22)$$

where $\tilde{C}_{\mathrm{p}}$ is reduced molar heat capacity, we arrive at

$$\frac{\partial}{\partial u_l}\frac{\partial}{\partial u_k}g = -\tilde{U}(\tilde{T})\frac{\partial^2}{\partial u_l\partial u_k}\left(u_1\theta_2\frac{X_{12}}{\tilde{V}_1} + u_1\theta_3\frac{X_{13}}{\tilde{V}_1} + u_2\theta_3\frac{X_{23}}{\tilde{V}_2}\right) - \tilde{C}_{\mathrm{p}}(\tilde{T})\left(u_1\frac{p_1^*}{\tilde{V}_1}\tilde{T}_1 + u_2\frac{p_2^*}{\tilde{V}_2}\tilde{T}_2 + u_3\frac{p_3^*}{\tilde{V}_3}\tilde{T}_3\right)^{-1} \times \left\{\frac{p_k^*}{\tilde{V}_k}\tilde{T}_k - \delta_{k1}\frac{p_2^*}{\tilde{V}_2}\tilde{T}_2 - \tilde{T}\left[\frac{p_k^*}{\tilde{V}_k} - \delta_{k1}\frac{p_2^*}{\tilde{V}_2} - \frac{\partial}{\partial u_k} \times \left(u_1\theta_2\frac{X_{12}}{\tilde{V}_1} + u_1\theta_3\frac{X_{13}}{\tilde{V}_1} + u_2\theta_3\frac{X_{23}}{\tilde{V}_2}\right)\right]\right\} \times \left\{\frac{p_l^*}{\tilde{V}_l}\tilde{T}_l - \delta_{l1}\frac{p_2^*}{\tilde{V}_2}\tilde{T}_2 - \tilde{T}\left[\frac{p_l^*}{\tilde{V}_l} - \delta_{l1}\frac{p_2^*}{\tilde{V}_2} - \frac{\partial}{\partial u_l}\left(u_1\theta_2\frac{X_{12}}{\tilde{V}_1} + u_1\theta_3\frac{X_{13}}{\tilde{V}_1} + u_2\theta_3\frac{X_{23}}{\tilde{V}_2}\right)\right]\right\} \quad (23)$$

δ_{ij} being the Kronecker delta. Performing now the derivatives indicated in this general expression and going to the limit of vanishing polymer concentration ($u_3 \rightarrow 0$), prescribed for the M_{ij}'s, we finally obtain:

$$\left(\frac{\partial^2 g}{\partial u_1^2}\right)^0 = -2[-\tilde{U}(\tilde{T}_0)]\frac{S_1S_2^2}{S_0^3}\xi_{12} - \frac{\tilde{C}_{\mathrm{p}}(\tilde{T}_0)A_0^2}{u_{10}\pi_1^*\tilde{T}_1 + u_{20}\pi_2^*\tilde{T}_2} \quad (24)$$

$$\left(\frac{\partial^2 g}{\partial u_3^2}\right)^0 = -2[-\tilde{U}(\tilde{T}_0)]\frac{S_3^2}{S_0^2} \times \left(\theta_{10}\xi_{13} + \theta_{20}\xi_{23} - \frac{S_2}{S_0}\theta_{10}\theta_{20}\xi_{12}\right) - \frac{\tilde{C}_{\mathrm{p}}(\tilde{T}_0)A_3^2}{u_{10}\pi_1^*\tilde{T}_1 + u_{20}\pi_2^*\tilde{T}_2} \quad (25)$$

$$\left(\frac{\partial^2 g}{\partial u_1\,\partial u_3}\right)^0 = [-\tilde{U}(\tilde{T}_0)]\frac{S_3S_2}{S_0^2} \times \left[\xi_{13} - \frac{S_1}{S_2}\xi_{23} + \xi_{12}(\theta_{10} - \theta_{20})\right] - \frac{\tilde{C}_{\mathrm{p}}(\tilde{T}_0)A_0A_3}{u_{10}\pi_1^*\tilde{T}_1 + u_{20}\pi_2^*\tilde{T}_2} \quad (26)$$

Here, $S_i = s_i/\tilde{V}_i$, $\xi_{ij} = X_{ij}/\tilde{V}_i$, the volume and site fractions u_{i0}, θ_{i0} refer to the mixture of solvents free of polymer, $\tilde{T}_0$ is the value of $\tilde{T}$ defined in eq 19 when $u_3 = \theta_3 = 0$, and $S_0 = u_{10}S_1 + u_{20}S_2$. The symbols A_0 and A_3 stand for:

$$A_0 = \pi_1^*(\tilde{T}_1 - \tilde{T}_0) - \pi_2^*(\tilde{T}_2 - \tilde{T}_0) - \tilde{T}_0\frac{S_2}{S_1}\xi_{12}\left(\frac{S_1}{S_0}\theta_{10} - \frac{S_1}{S_2}\theta_{20}\right) \quad (27)$$

$$A_3 = \pi_3^*(\tilde{T}_3 - \tilde{T}_0) - \tilde{T}_0\frac{S_3}{S_1}\left(\xi_{12}\theta_{10}\theta_{20} - \xi_{13}\theta_{10} - \frac{S_1}{S_2}\xi_{23}\theta_{20}\right) \quad (28)$$

where $\pi_i^* = p_i^*/\tilde{V}_i$.

Introducing these expressions into eq 12–14 we get the M_{ij}'s required for the calculation of λ and Y according to eq 3 and 4. Therefore, the formulation of the FPP theory for preferential and total sorption is contained in eq 3, 4, 12–14, and 24–28.

Discussion

Let us discuss now the significance of each one of the contributions to λ and Y present in the above equations and also compare them with the corresponding Flory–Huggins expressions. The two important effects of free volume dissimilarity between solvents and polymer and of their difference in molecular surface-to-volume ratios are contained in $(\partial^2 g/\partial u_i\,\partial u_j)^0$. Both effects are typical of the FPP theory of solutions and are ignored in the FH theory, as we recalled before. The molecular surface-to-volume ratios are expressed in the S_i factors and the free volume dissimilarities in the difference of reduced temperatures (mainly $\tilde{T}_3 - \tilde{T}_0$).

Our results for λ and Y can be cast in the classical form corresponding to the FH theory if we introduce in eq 24–28 the following simplifications. We make all terms in $\tilde{C}_p$ vanish, neglecting thus all the contributions from free-volume dissimilarities. We also neglect all differences in surface-to-volume ratios, that is, we make $S_1 = S_2 = S_3$. As a consequence, the site fractions θ_{i0} become identical with volume fractions u_{i0}. We further assume $\tilde{T}_0 = \tilde{T}_1 = \tilde{T}_2$ and define interaction parameters, ϵ_{ij}, by:

$$\epsilon_{ij} = -\tilde{U}(\tilde{T}_i)V_i\xi_{ij}/RT \tag{29}$$

Then, also using volume fractions for the combinatorial terms, we reduce eq 12–14 and 24–28 to the following simple expressions:

$$\lambda = -\bar{v}_3{}^0\frac{l - 1 + \epsilon_{13} - l\epsilon_{23} + \epsilon_{12}(u_{10} - u_{20})}{lu_{10} + u_{20} - 2\epsilon_{12}u_{10}u_{20}}u_{10}u_{20} \tag{30}$$

$$Y = \tfrac{1}{2}(lu_{10} + u_{20} - 2\epsilon_{12}u_{10}u_{20})^{-1}[l - 2l\epsilon_{13}u_{10} - 2l\epsilon_{23}u_{20} + u_{10}u_{20}(2\epsilon_{12}\epsilon_{13} + 2l\epsilon_{12}\epsilon_{23} + 2l\epsilon_{13}\epsilon_{23} - \epsilon_{12}{}^2 - \epsilon_{13}{}^2 - l^2\epsilon_{23}{}^2)] \tag{31}$$

If we identify the ϵ_{ij}'s with the classical FH interaction parameters χ_{ij}, then eq 30 and 31 coincide with the expressions of λ due to Read[6] (without ternary parameters) and of Y due to Shultz and Flory,[5] respectively. Making use of the relationship $\tilde{U} = U/U^* = U/p^*V^*$, we have for ϵ_{ij}:

$$\epsilon_{ij} = -(U_i/RT)X_{ij}/p_i^* \tag{32}$$

which we recognize as the contact interaction term in the formulation of χ_{ij} by the FPP theory.[17] An additional term of the form $(C_{pi}/2R)(1 - T_i^*/T_j^*)^2$ is included also in the FPP theory of χ_{ij} but is out of the scope of the FH one. Therefore, our equations, when properly simplified in the manner described above, include correctly the FH results for λ and Y, as a particular case.

In order to make our theoretical results useful for interpretation of experimental data, it is convenient to simplify somewhat the general expressions obtained and find a form more amenable to calculation. The simplification should not be as drastic as the one leading to the classical FH results (eq 30 and 31) but, rather, it should retain the features of surface-to-volume and free-volume differences which are important when the polymer is compared with the liquids comprising the binary solvent. As a first approximation, the differences between the two solvents may be neglected (in the presence of the polymer), leading then to the following set of useful simplifications:[13] $\tilde{V}_1 = \tilde{V}_2$, $p_1^* = p_2^*$, $S_1 = S_2$, $\tilde{T}_1 = \tilde{T}_2$. Reduced quantities depending on $\tilde{T}_0$ may also be expanded around T_1, disregarding products of interaction parameters ξ_{ij}, and retaining only the terms linear in $\tilde{T}_0 - \tilde{T}_1$.[13] The preferential adsorption coefficient then simplifies to:

$$\lambda = -\bar{v}_3{}^0\frac{\tilde{V}_1}{\tilde{V}_3}\frac{l - 1 + s(\epsilon_{13} - l\epsilon_{23}) + (s - \alpha)\epsilon_{12}(u_{10} - u_{20})}{lu_{10} + u_{20} - 2\epsilon_{12}u_{10}u_{20}}u_{10}u_{20} \tag{33}$$

where $s = s_3/s_1$, and

$$\alpha = \{\tilde{T}_1\tilde{C}_p(\tilde{T}_1)/[-\tilde{U}(\tilde{T}_1)]\}(p_3^*/p_1^*)(1 - T_1^*/T_3^*) \tag{34}$$

Equation 33 differs from the classical FH eq 30 in the appearance of the following: the factor s containing surface-to-volume ratios, the free-volume dissimilarity term α, and $\tilde{V}_1/\tilde{V}_3$. Equation 33 reduces to eq 30 if $s = 1$, $\alpha = 0$, and $\tilde{V}_1/\tilde{V}_3 = 1$. For a particular polymer–binary solvent system, s can be calculated from the known geometry of the different molecules. For the same system, α can be calculated from the reduction parameters p_1^*, p_3^*, T_1^*, T_2^* and the solvent thermal expansion coefficient α_1:

$$\tilde{T}_1\tilde{C}_p(\tilde{T}_1)/[-\tilde{U}(\tilde{T}_1)] = \alpha_1 T \tag{35}$$

As an example of the relative importance of s and α, we give their values for the extensively studied system polystyrene–benzene–cyclohexane (PS–BZ–CH), which are: $s = 0.48$; $\alpha = 0.13$ (at 25 °C).[18] As we see, s differs appreciably from unity in this system, so that the influence of the difference in surface-to-volume ratio between polymer and solvents, which is not taken into account by the FH theory, is important in the preferential solvation phenomenon. The value of α in this same system is small compared to s but is still by no means negligible. To ignore this contribution from free volume dissimilarity may introduce a relevant error, especially if the temperature is high, since α is an increasing function of temperature (through $\alpha_1 T$). It should be noted that the factor $s - \alpha$ appears in the term containing $u_{10} - u_{20}$. This term is the one responsible for the inversion in λ observed in many systems,[9,19] because $u_{10} - u_{20}$ is the only term changing sign with varying solvent composition. Since the appearance of inversion is favored by a large value of the term in $u_{10} - u_{20}$,[20] both s and α are important in locating such an inversion point in λ, when it occurs.

Regarding the overall sorption, the same simplifications used for λ yield for $\Delta Y = Y - u_{10}Y_1 - u_{20}Y_2$:

$$\Delta Y = \tfrac{1}{2}(\tilde{V}_1/\tilde{V}_3)^2(lu_{10} + u_{20} - 2\epsilon_{12}u_{10}u_{20})^{-1}\{-(l - 1)^2 + 2\epsilon_{12}[(s^2 - \alpha' - s\alpha)(lu_{10} + u_{20}) - (l - 1)(s - \alpha)(u_{10} - u_{20})] - 2(l - 1)s(\epsilon_{13} - l\epsilon_{23}) - \epsilon_{12}{}^2[4(s^2 - \alpha' - s\alpha)u_{10}u_{20} + (s - \alpha)^2(u_{10} - u_{20})^2] - s^2(\epsilon_{13} - l\epsilon_{23})^2 - 2s(s - \alpha)\epsilon_{12}(\epsilon_{13} - l\epsilon_{23})(u_{10} - u_{20})\}u_{10}u_{20} \tag{36}$$

where $\alpha' = \alpha p_3^*/p_1^*$. This expression reduces to the one obtained previously by Pouchlý and Patterson[13] if we neglect terms containing the differences $\epsilon_{13} - l\epsilon_{23}$, $u_{10} - u_{20}$, or $l - 1$. The contribution to the total ΔY of the terms thus neglected is as important as the contribution from the terms retained, as we have verified by calculating ΔY for the example system PS–BZ–CH. However, Pouchlý has argued[21] that the single-liquid approximation to ΔY of ref 13 should be superior to the complete eq 36, because the terms arising from preferential sorption diminish ΔY too much. As pointed out by Yamamoto and White,[22] two effects contribute in determining the solvent power of a mixed solvent: one is the effect of a mean potential acting throughout the polymer region, and the other is the effect of short-range forces acting between the polymer segments and the solvent coating adjacent to them. The "results of these effects may cancel out, and the simple average of the solvent power of individual solvents may indeed give a good approximation of the solvent power of a mixed solvent".[22] An argument similar to this is used by Pouchlý in his preference for the single-liquid approximation for ΔY.[21]

Our theoretical results will be compared now with the extended FH theory which introduces a ternary interaction parameter χ_T. This comparison will allow us to interpret, in part, the molecular origin of χ_T. The expression obtained for λ when χ_T is included in the FH theory (neglecting for simplicity the concentration dependence of the χ_{ij}'s) is identical with 30, but with the FH χ_{ij}'s in place of the ϵ_{ij}'s, except for the ϵ_{12} in the numerator which is to be replaced by $\chi_{12} - \chi_T$.[9] When the resulting expression is compared with our λ of eq 33, we find the following formal correlation: the χ_T parameter in the extended FH theory corresponds to the factor $(\tilde{V}_1/\tilde{V}_3)(s - \alpha)$ in the FPP theory, since both χ_T and $s - \alpha$ affect the $u_{10} - u_{20}$ term of λ. The influence of the ternary parameter χ_T is to decrease the contribution from χ_{12}, leading to an effective $\chi_{12}^{\text{eff}} = \chi_{12} - \chi_T$ smaller than χ_{12}. The same influence is exerted by the factor $s - \alpha$ which leads to an effective $\epsilon_{12}^{\text{eff}} = \epsilon_{12}(s - \alpha)$ smaller than ϵ_{12} because $s - \alpha < 1$.[23] The terms s and α as multiplication factors for ϵ_{12} depend on the characteristics of the polymer and reflect its influence on the 1–2 interactions between unlike solvent molecules. The phenomenological parameter χ_T has to be introduced, then, to incorporate in a semiempirical way the effect caused in such interactions by the presence of the polymer. An s smaller than unity and the negative contribution from α in $\epsilon_{12}(s - \alpha)\tilde{V}_1/\tilde{V}_3$ are equivalent to introducing a ternary χ_T. This represents a partial molecular interpretation of such a phenomenological parameter.

Support for the identification of s and α as contributions included in χ_T comes from a comparison between λ and ΔY. As noted by Máša et al.,[24] the decrease of influence of the 1–2 terms due to ternary interactions is almost two times lower in the case of λ than in the case of Y. This is taken into account in the extended FH theory where the χ_T parameter enters in the form of $\chi_{12} - \chi_T$ in λ and in the form of $\chi_{12} - 2\chi_T$ in Y. Now, we can explain this need of a contribution from χ_T higher in Y than in λ by noting that the terms in ϵ_{12} in eq 36 contain the factor $(\tilde{V}_1/\tilde{V}_3)^2(s^2 - \alpha' - s\alpha)$, while the term in ϵ_{12} in eq 33 contains only the factor $(\tilde{V}_1/\tilde{V}_3)(s - \alpha)$, the former being smaller than the latter. For the example system PS–BZ–CH, we have $(\tilde{V}_1/\tilde{V}_3)^2(s^2 - \alpha' - s\alpha) = 0.07$ and $(\tilde{V}_1/\tilde{V}_3)(s - \alpha) = 0.39$, which explains why the so-called ternary interactions have a larger influence on total swelling than in preferential sorption.

Other contributions to the ternary parameter besides those represented by s and α may be present. Any attempt to generalize the theory to include additional contributions should first recognize that several simplifications are contained in the present formulation of λ. For example, we have neglected the exchange interaction entropy term Q_{ij}, introduced by Flory.[25] For detailed agreement of theoretical results with experiment, the introduction of this entropic contribution may be required. Also, the assumption of random mixing of segments, inherent in the FPP theory, has not been avoided. Recent versions of the FPP which incorporate nonrandom mixing effects may be relevant.[26] Within the framework of the FH theory, Pouchlý et al.[8] have incorporated nonrandom mixing effects due to the formation of association complexes by the components of the system.

An important limitation of our theory is the neglect of excluded volume. Yamamoto and White[22] considered excluded volume in their calculation of the Θ temperature of polymers in mixed solvents. A similar incorporation of excluded volume into the FPP theory of λ would be an important step forward in the understanding of preferential solvation.

Application of our theory to certain experimental systems may need the use of the complete eq 24–28, since the approximations leading to the simpler eq 33 may not always be justified. In particular, if the solvents in the mixture have different reduction parameters, as is the case if one of the solvents is an oligomeric liquid,[27] then $\tilde{T}_1 \neq \tilde{T}_2$, and the full equations have to be considered.

We have not mentioned the molecular weight dependence of λ. According to Dondos and Benoit[28] and to Read,[6] λ varies with M as $\lambda = \lambda_\infty + AM^{-1/2}$. The thermodynamic formulas we have used to derive λ consider only terms of the lowest order in the density of polymer segments inside the coil. They do not include, therefore, contributions of the type $AM^{-1/2}$ which arise from higher order terms.[29] Our expressions correspond, then, to λ_∞.

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