ELSEVIER

Polymer 42 (2001) 8069-8074

polymer

www.elsevier.nl/locate/polymer

Slightly compatible polymer mixtures at equilibrium: phase composition, interfacial and diffusional properties

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Received 5 December 2000; received in revised form 2 April 2001; accepted 23 April 2001

Abstract

An approximate solution is presented to the phase equilibrium problem for the case of a partially miscible polymer solution or a binary heteropolymer blend. It is based on the Flory–Huggins theory and is valid for mixtures well into the phase-separated region. Analytical expressions are derived for the extent and composition of each of the two coexisting phases as a function of the component molecular size and interaction strength. These results are combined with Helfand's model to provide estimates for the interfacial tension and thickness and, therefore, a measure of the quality of the interfacial bonding in a polymer/polymer blend. They are also utilized in conjunction with a free volume theory approach for calculating the mutual diffusion coefficient of a penetrant, migrating through a polymer. © 2001 Published by Elsevier Science Ltd.

Keywords: Phase equilibrium; Polymer solutions; Polymer blends

1. Introduction

In both industry and nature, almost invariably, polymers are deliberately or accidentally mixed at various degrees with a multitude of solid and liquid substances. Among the latter ones, one may include plasticizers, processing aids, lubricants, antioxidants, contaminants, post-polymerization residues, fat and greases, other polymers, compatibilizers, humidity or other solvents existing in the environment. Irrespective of whether solvent adsorption is deliberate or accidental, or of whether its presence benefits (e.g. antidegrading action) or causes damage (e.g. environmental stress cracking), such an addition often has a big impact on polymer processability, mechanical strength, adhesion, toxicity and edibility. Evidently, it is of practical importance to be able to estimate readily the saturation limits of a particular solvent to a given polymer, at a given set of external conditions. This is in the focus of the present paper for the case where the liquid substrate, which may be a small-molecule solvent or a heteropolymer is slightly soluble and, therefore, *present in small amounts*. Of assistance to this task is the, by now mature, thermodynamic theory of polymers at phase equilibrium.

In this work, and for the special case of polymer/additive or polymer/polymer pairs, which are barely compatible, analytical estimates are provided for (1) the level of additive/contaminant that saturates a given polymer at a given temperature and (2) the phase distribution in such a system. Its closed form results circumvent the usual complexities and loss of physical clarity associated with solving the problem numerically. Subsequently, these results are implemented in estimating the interfacial properties and diffusivity of such a mixture. The treatment is based on the Flory–Huggins (FH) theory of polymer solutions [1], later extended to polymer/polymer blends by Scott and Tompa [2,3] and critically reviewed by Cowie [4].

Despite being over half a century old, FH theory is still a benchmark, and along with improvements, extensions and appropriate adaptations is in everyday use. It inspired several engineering models (e.g. Prausnitz-UNIFAC, Entropic-FV, GC-Flory, etc.), comprehensively reviewed by Tassios et al. [5], which predict polymer phase behavior of industrially relevant systems at various levels of success. It constitutes the basis of a recent study on pressure effects by Kumar [6]. It is the tool of analyzing multicomponent phase behavior [7–9] and small-angle neutron scattering results through which Higgins [10], Bates [11], Han [12], and more recently and prolifically, Graessley et al. [13,14] measured the thermodynamic interaction parameter, χ, and established qualitative trends and microstructural correlations pertaining to phase behavior and polymer miscibility.

Of course, there has also been remarkable evolution; as it becomes apparent in a recent review by Economou [15],

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0032-3861/01/$ - see front matter © 2001 Published by Elsevier Science Ltd.
PII: S0032-3861(01)00294-4

phase equilibria calculations are increasingly based on an equation of state (EoS) approach, such as the Flory [16], Flory–Orwoll–Vrij [17,18], Patterson [19] or even the van der Waals [20] EoS, or on lattice fluid theories, such as the Born–Green–Yvon [21], Sanchez–Lacombe [15,18,22] or Panayotou–Vera [23]. These methods provide the advantage of explicitly accounting for energetic interactions among dissimilar molecules and for accommodating compressibility effects. On the other hand, Fredrickson and Bates conformational asymmetry theory [24] stresses the effect of non-local properties and molecular packing on miscibility, thus de-emphasizing energetic interactions. Freed and Dudowicz compressible lattice cluster theory [25,26] accommodates the presence of short chain branching and elucidates the relative contribution of both enthalpic and entropic effects. Presently, the theoretical study of polymer blend phase behavior is in the realm of lattice [27,28], off-lattice and hybrid [29] Monte Carlo simulations as well as molecular dynamics simulations [30].

2. Phase distribution

Let S and P be the components of a partially miscible binary mixture, of which one (say, P) may be a polymer and the other (S) a solvent or a smaller polymer. Let w_i be the overall mass fraction of component i in this phase-separated mixture ($w_S + w_P = 1$), ρ_i, its density and M_i, its molecular weight. Let f_i be volume fraction of the phase with the highest i-component concentration; again, $f_S + f_P = 1$. Within each of the two phases, a given precursor contributes with a volume fraction equal to v_{ij}, where the index ij signifies the i-component in the phase with most j (i.e. the portion of f_j that is i) and, therefore, $v_{ij} + v_{jj} = 1$.

The interrelationship between these various quantities that define the mixture quality may be established by a simple mass balance, which equates the two alternative ways of expressing the (externally controlled) component mass fraction ratio:

$$\frac{w_j}{w_i} = \frac{\rho_j(f_j v_{jj} + f_i v_{ji})}{\rho_i(f_j v_{ij} + f_i v_{ii})} \tag{1}$$

The volume fraction of each *phase* may then be calculated after some elementary algebra:

$$f_j = 1 - f_i = \frac{r + (1 - r)v_{ji}}{(1 + r)(1 - (v_{ji} + v_{ij}))} \tag{2}$$

where $r \equiv w_j\rho_i/w_i\rho_j$.

From this analysis, which is also valid in the absence of equilibrium, one sees that for a quantitative estimate of phase distribution in a mixture, the respective phase compositions should first be known.

3. Miscibility and individual phase composition at equilibrium

Microscopically, miscibility is aided by the entropy increase caused by mixing and, as a rule, is hindered by changes in enthalpy due to the unfavorable thermodynamic interactions which accompany intimate coexistence among dissimilar species [1]. A way of quantifying that latter factor is in terms of χ_{ij}, the thermodynamic interaction parameter whose dimensionless value is a positive measure of the incompatibility among the two constituents. For the case of non-polar components, and with no specific interactions present, χ_{ij} is a function of the individual solubilities, δ_i:

$$\chi_{ij} \approx \chi_{ij\mathrm{S}} + (V_i/RT)(\delta_i - \delta_j)^2 \approx A_{ij} + B_{ij}/T \tag{3}$$

Here, T is the temperature (in K), V_i ($=M_i/\rho_i$), the molecular volume of the i-component and R (=8.3 J/mol/K), the gas constant. $\chi_{ij\mathrm{S}}$ compensates for the lack of non-combinatorial entropy contributions in the FH treatment (≈0.34 in a polymer/solvent system), and A_{ij} and B_{ij} material parameters that depend on the nature of both i and j.

The Hildebrand solubility parameter, δ, is equal to the square root of the cohesive energy density, i.e. the enthalpy of vaporization per unit volume. Another thermodynamic definition for δ [31] and its relationship to the surface tension, γ_i, for small molecule liquids [32] is given below:

$$\delta_i^2 = T(\partial P/\partial T)_{\rho_i} - P \approx 8\gamma_i(N_{\mathrm{Av}}/V_i)^{1/3} \tag{4}$$

where P is the pressure, ρ_i, the density of pure component i and N_{Av}, the Avogadro number (6×10^{23} molecules/gmol). Typically, $\delta^2 \sim 400$ MPa; for a solvent, $V_S \sim 10^2$ cc/gmol, while for a polymer, V_P is 2–4 orders of magnitude higher; γ_i for a high polymer is ~ 30 mJ/m^2, while for the corresponding oligomer can be 2–3 times smaller [33]. It has been experimentally established that for scores of polymer/solvent systems examined, as a rule, $-1 < \chi_{ij} < 2$ [34]; this demonstrates the limitations of Eq. (3), which does not accommodate negative χ values. On the other hand, χ values higher than two (pertinent in the case examined here) are possible based on δ difference calculations [31].

An alternative representation of the interaction among dissimilar species is in terms of χ'_{ij} (in gmol/cc), which is molecular size independent, and is defined as

$$\chi'_{ij} \equiv \chi_{ij}/V_i \tag{5}$$

Provided that the interaction intensity among species is independent of concentration, $\chi'_{ij} \approx \chi'_{ji}$. This, however, does not always hold with polymer/poor solvent mixtures [34,35] or with polymer/polymer blends [36].

Estimating v_{ij} may be accomplished by considering that at equilibrium, the chemical potential, μ, of a given component across the coexisting phases should stay the same:

$$\mu_{ii} = \mu_{ij} \tag{6}$$

The index *ij* signifies the *i*-component in the *j*-rich phase. It is reminded here that chemical potential is the incremental change in the free energy of mixing in a particular phase due to an infinitesimal *i*-component increase in this very phase. According to the FH theory, and for any *ij* index combination (i.e. SS, SP, PS, PP), the chemical potential may be compactly expressed as follows:

$$\mu_{ij} = RT[\ln(v_{ij}) + (1 - v_{ij})(1 - V_i/V_{k\neq i}) + (1 - v_{ij})^2 V_i \chi'_{ij}] \tag{7}$$

where index k may either be P or S, provided that it is not i. By equating the chemical potential of the i-component across the two phases $\mu_{ii} = \mu_{ij}$, one finds, for any ij-combination

$$\frac{1 - v_{ij}}{v_{ii}} = \frac{v_{ij}}{1 - v_{ji}} \approx \exp\left\{ -\left(1 - v_{ij} - v_{ji}\right)\left[1 - \frac{V_i}{V_j} + V_i\chi'_{ij}\left(1 - v_{ij} + v_{ji}\right)\right]\right\} \tag{8}$$

It is often the case that a pair of components constitutes a *barely compatibile* mixture. This may be either due to thermodynamic dissimilarity manifested by a high $|\delta_i - \delta_j|$ difference or large V_j values. In a usual χ (or T) versus v_i phase diagram, this translates into a convex (or concave) binodal coexistence curve that runs quite close to the $v_i = 0$ and $v_i = 1$ vertical axes. Consequently, v_{ij} and v_{ji} are small and, therefore, $f_i = 1 - f_j \to 1/(1 + r)$, irrespective on how balanced the initial w_js are. Then, it may be easily shown that, by neglecting v_{ij} and v_{ji} on the right-hand side of Eq. (8), this simplifies to

$$v_{ij}/(1 - v_{ji}) \approx \varepsilon_{ij} \equiv \exp\{-1 - V_i(\chi'_{ij} - 1/V_j)\} \tag{9}$$

Similarly, by equating the chemical potential of the j-component across the interface, or by simply rotating the indices i and j in Eqs. (8) and (9):

$$v_{ji}/(1 - v_{ij}) \approx \varepsilon_{ji} \equiv \exp\{-1 - V_j(\chi'_{ji} - 1/V_i)\} \tag{10}$$

By solving Eqs. (9) and (10) simultaneously, one finds that, for any ij-index combination ($i \neq j$),

$$v_{ij} = 1 - v_{jj} \approx \frac{\varepsilon_{ij}(1 - \varepsilon_{ji})}{1 - \varepsilon_{ij}\varepsilon_{ji}} \tag{11}$$

By inspecting Eq. (11) or by considering the physics on which it is based, one realizes that $v_{ij} \approx \varepsilon_{ij}$. Its applicability presumes a mixture well into the phase-separated region. In terms of interaction parameter values, this translates to not merely

$$\chi'_{ij} > \chi'_{ij\,\mathrm{CRITICAL}} = \frac{1}{2}\left(\frac{1}{\sqrt{V_i}} + \frac{1}{\sqrt{V_j}}\right)^2 \tag{12}$$

but to a stronger repulsion among species; e.g. for $V_j \geq V_i$ and $v_{ij} < 5\%$:

$$\chi'_{ij} \geq 2/V_i + 1/V_j > \chi'_{ij\,\mathrm{CRITICAL}} \tag{13}$$

This last constraint, in conjunction with the v_{ij} expression (Eq. (11)), suggests that, for $\chi'_{ij} \approx \chi'_{ji}$,

$$\frac{v_{ij}}{v_{ji}} \approx \exp\left(\left(\frac{V_j}{V_i} - 1\right)\left(V_i\chi'_{ij} - 1 - \frac{V_i}{V_j}\right)\right) \geq \exp\left(\frac{V_j}{V_i} - 1\right) \geq 1 \tag{14}$$

For a polymer/solvent system (i/j = S/P), Eq. (14) correctly predicts that, eventually, the polymer leached in the solvent is negligible when compared to the solvent penetrating the polymer: $v_{\mathrm{SP}} \gg v_{\mathrm{PS}}$ [37]. And that, similarly, in a partially miscible polymer/polymer blend at equilibrium, where i/j = P1/P2 and $M_{\mathrm{P2}} > M_{\mathrm{P1}}$, there is more P1 presence in the P2-rich phase than the reverse, although this disparity in composition evens out as the molecular sizes approach each other.

For the approximate solution to the phase equilibrium problem presented here, one is most interested in establishing the *limits of validity*, given an error tolerance of

$$\Delta \equiv v_{ij}(\mathrm{FH})/v_{ij}(\mathrm{Apx}) - 1 \tag{15}$$

The ratio of the exact (FH) over the approximate (Apx) solution is obtained by dividing Eqs. (8) and (9):

$$\frac{v_{ij}(\mathrm{FH})}{v_{ij}(\mathrm{Apx})} \approx \exp\left\{\left(v_{ij} + v_{ji}\right) \times \left[1 - \frac{V_i}{V_j} + V_i\chi'_{ij}\left(1 - \left(v_{ij} - v_{ji}\right)\right)\right] - \left(v_{ij} - v_{ji}\right)\right\} \tag{16}$$

It is a matter of simple algebra to show that, e.g. for $\Delta \approx 10\%$ and a polymer/solvent system ($= i/j$), where both V_i/V_j and $v_{ji}/v_{ij} \to 0$, acceptable solutions should conform with

$$v_{ij} \leq \ln(1 + \Delta)/(2 + \chi_{ij}) \approx 1/(20 + 10\chi_{ij}) \tag{17}$$

while for a polymer/polymer blend of roughly equal size components, where both the V_i/V_j and v_{ji}/v_{ij} tend to unity:

$$v_{ij} \leq \ln(1 + \Delta)/(2\chi_{ij}) \approx 1/(20\chi_{ij}) \tag{18}$$

In that respect, Eq. (11) is the antipode, and complimentary of Flory's approximate solution to the phase equilibrium problem promulgated in Appendix XIII-A of Ref. [1], and valid only in the neighborhood of the critical point.

4. Interfacial tension and thickness

These properties which indicate the quality of adhesion among heteropolymer surfaces control their fracture energy, slippage factor, speed of phase separation and phase morphology [33, 38]. Consequently, they are of importance in producing polymer/polymer blends of desirable mechanical, rheological, optical and barrier properties [39]. The interfacial thickness, a_I, and (the inverse of) the interfacial tension, γ_{ij}, are measures of heteropolymer bonding. For their approximate evaluation, the mean field model of Helfand and Sapse [40] may be adopted for of a blend of very long, asymmetric polymers, and for the case where the P1 rich phase is not entirely devoid of the P2 component. This theory, like a competing model by Roe [41], sometimes fails to reproduce the correct temperature dependence of $\gamma_{ij}(T)$; nevertheless, it is known to provide acceptable order of magnitude predictions:

$$\gamma_{ij} \approx \frac{2}{3}RT\sqrt{\chi'_{ij}}\left(\frac{B_j^2 + B_iB_j + B_i^2}{B_i + B_j}\right) \tag{19}$$

and

$$a_\mathrm{I} \approx [2(B_j^2 + B_i^2)/\chi'_{ij}]^{1/2} \tag{20}$$

where $\chi'_{ij} = \chi_{ij}/V_i$,

$$B_j = \left(\frac{\rho_j v_{jj}}{6m_j}\right)^{1/2} b_j \approx \left(\frac{\rho_j(1-\varepsilon_{ij})}{6m_j(1-\varepsilon_{ij}\varepsilon_{ji})}\right)^{1/2} b_j \tag{21}$$

and R is the gas constant (= 8.3 J/mol/K). ρ_j, M_j, and V_j are the density, molecular weight and molar volume of the j-polymer, while b_j, and m_j are correspondingly the length and molecular weight of the statistical segment of that same polymer; these quantities are related to the end-to-end distance of the macromolecule as follows [1]:

$$\langle R_j^2\rangle = (M_j/m_j)b_j^2 \tag{22}$$

Knowing the a_I value and the composition in the bulk of each phase, one may also obtain an idea on how the concentration profile evolves across the interface (i.e. at $-a_\mathrm{I}/2 \le z \le a_\mathrm{I}/2$ where $v_{ji} \le v_j(z) \le v_{jj}$) [42]:

$$v_j(z) \approx 0.5(v_{ji} + v_{jj}) + 0.5(v_{ji} - v_{jj})\tanh(2z/a_\mathrm{I}) \tag{23}$$

Consider a mildly incompatible polymer blend like, e.g. polystyrene/polymethyl-methacrylate (PS/PMMA) with each component having a molecular weight of $M_i \approx 10{,}000$ g/mol, i.e. being in the range where v_{ij} is close to but not equal to zero [43]. For both polymers, $\rho \approx 1.1$ g/cc, $b \approx 6.5$ Å and $m \approx 100$ g/mol; $\chi'_{ij} \approx 300\ \mathrm{mol/m^3}$ at 120°C [44]; then, $v_{ji} = v_{ij} \approx 0.95$ and that $B_i \approx B_\mathrm{j} \approx 2.7\times10^{-8}\ \mathrm{m^{-1/2}}$. It is therefore predicted that in this partially phase-separated mixture, $a_\mathrm{I} \approx 30$ Å and $\gamma_{ij} \approx 1.5\ \mathrm{mJ/m^2}$ (=dyn/cm), estimates which are matching quite close the experimental evidence [45].

It is therefore seen that a simple knowledge of the thermodynamic interaction between two constituents is, in principle, sufficient for predicting phase compositions and bonding quality. Conversely, if the thermodynamic interaction parameter is not known, yet, v_{ij} measurements are possible by sampling the individual phases, interfacial property estimation may be accomplished by eliminating χ'_{ij} from both Eqs. (19) and (20), and replacing it by

$$\chi'_{ij} \equiv \frac{\chi_{ij}}{V_i} \approx \frac{\rho_i}{M_i}\left(\ln\left(\frac{1}{v_{ij}}\right) - 1 + \frac{\rho_jM_i}{\rho_iM_j}\right) \tag{24}$$

Here also, there are several theoretical improvements in which the results of Section 3 may readily be incorporated. Most notably, Anastasiadis et al. [46] accounted for finite polymer molecular weight and reproduced the correct temperature dependence. Similar improvements were also made by Helfand et al. [47], and Tang and Freed [48]. Finally, Broseta et al. [49] and Ermoshkin and Semenov [50], examined the asymmetric case, of a binary mixture of heteropolymers with unequal length.

5. Diffusivity

Estimates may also be made for D_SP, the mutual diffusion coefficient in a partially miscible system, where P may be a high polymer (taken as the fixed frame of reference) and S a smaller molecular size penetrant. In applications ranging from the food and pharmaceutical industry to physiology [51], this property, in conjunction with Fick's second law of diffusion and the appropriate boundary conditions, is used in modeling adsorption or desorption of liquid moieties from polymers and elastomers [52]. For a polymer of plate or sheet geometry, for example, this may be accomplished by solving Eq. (25) for the J_SP flux of the penetrant or its evolving concentration, $v_\mathrm{SP}(t,x)$, as a function of time, t, and plate thickness, x:

$$\frac{\partial v_\mathrm{SP}}{\partial t} = \frac{1}{\rho_\mathrm{S}}\frac{\partial J_\mathrm{SP}}{\partial x} = \frac{\partial}{\partial x}\left(\frac{D_\mathrm{SP}}{1-v_\mathrm{SP}}\frac{\partial v_\mathrm{SP}}{\partial x}\right) \tag{25}$$

Diffusivity depends on the ever present self-diffusion due to thermally induced molecular mobility, D_self, but also on the 'distance' from the point of saturation [53]:

$$\frac{D_\mathrm{SP}}{1-v_\mathrm{SP}} = \frac{D_\mathrm{self}}{RT}\frac{\partial\mu_\mathrm{SP}}{\partial\ln(v_\mathrm{SP})} \tag{26}$$

Via Eq. (7), this translates to

$$\frac{D_\mathrm{SP}}{1-v_\mathrm{SP}} = D_\mathrm{self}\left(\frac{V_\mathrm{S}}{V_\mathrm{P}} + (1-v_\mathrm{SP})\left(1 - \frac{V_\mathrm{S}}{V_\mathrm{P}} - 2\chi'_\mathrm{SP}V_\mathrm{S}v_\mathrm{SP}\right)\right) \tag{27}$$

The thermodynamic self-diffusion coefficient is an increasing function of $\mathrm{f_{SP}}$, the fractional free volume available, which is assumed equal to be the weighted average of the individual f_i [54]:

$$D_\mathrm{self} = D_0\exp\left(\frac{-B}{\mathrm{f_{SP}}}\right) = D_0\exp\left(\frac{-B}{v_\mathrm{SP}\mathrm{f_S} + v_\mathrm{PP}\mathrm{f_P}}\right) \tag{28}$$

In this model, which was later perfected, albeit at a considerable loss of simplicity [55,56], D_0 and B are constants that depend on the size and shape of the penetrant and B is a measure of the free volume required for an incremental S move. $\mathrm{f_i} \approx \mathrm{f}_{ig} + \alpha_{if}(\mathrm{T} - \mathrm{T}_{ig})$ and, as a rule, $\mathrm{f_S} > \mathrm{f_P}$. The subscript g signifies a property at the glass transition and α_f is the free volume thermal expansion coefficient. Within the context of this work, and with the help of Eq. (11), the self-diffusion coefficient at equilibrium may be expressed as follows:

$$D_\mathrm{self} \approx D_0 \exp\left(\frac{-B(1 - \varepsilon_\mathrm{SP}\varepsilon_\mathrm{PS})}{(1 - \varepsilon_\mathrm{PS})\varepsilon_\mathrm{SP} f_\mathrm{S} + (1 - \varepsilon_\mathrm{SP}) f_\mathrm{P}} \right) \tag{29}$$

Eq. (23) may then be rewritten as follows:

$$\frac{D_\mathrm{SP}}{D_\mathrm{self}} \approx \left(\frac{1 - \varepsilon_\mathrm{SP}}{1 - \varepsilon_\mathrm{SP}\varepsilon_\mathrm{PS}} \right) \left\{ \frac{V_\mathrm{S}}{V_\mathrm{P}} + \left(\frac{1 - \varepsilon_\mathrm{SP}}{1 - \varepsilon_\mathrm{SP}\varepsilon_\mathrm{PS}} \right) \times \left(1 - \frac{V_\mathrm{S}}{V_\mathrm{P}} - 2\chi'_\mathrm{SP} V_\mathrm{S} \frac{\varepsilon_\mathrm{SP}(1 - \varepsilon_\mathrm{PS})}{1 - \varepsilon_\mathrm{SP}\varepsilon_\mathrm{PS}} \right) \right\} \tag{30}$$

In the case that the molecular size of the migrating penetrant is insignificant in comparison with that of the polymer host, $(\rho_\mathrm{P} M_\mathrm{S})/(\rho_\mathrm{S} M_\mathrm{P}) = V_\mathrm{S}/V_\mathrm{P} \rightarrow 0$ and $\varepsilon_\mathrm{SP} \gg \varepsilon_\mathrm{PS} \rightarrow 0$, Eq. (30) simplifies somewhat. It may then be expressed in terms of polymer composition:

$$D_\mathrm{SP} \approx D_0 (1 - v_\mathrm{SP})^2 \{1 + 2v_\mathrm{SP}[1 + \ln(v_\mathrm{SP})]\} \exp\left(\frac{-B}{v_\mathrm{SP}\mathrm{f_S} + (1 - v_\mathrm{SP})\mathrm{f_P}} \right) \tag{31}$$

which is a form of importance when attempting to solve Eq. (25) numerically. Alternatively, and since $v_\mathrm{SP} \approx \exp - (1 + \chi_\mathrm{SP})$, Eq. (31) may be used for an approximate D_SP estimate at a given temperature, provided the thermodynamic interaction parameter and the individual $\mathrm{f_i}$ are known; evidently, such an estimate is destined to be in the lower limit of the D_SP variation since it presumes v_SP close to saturation.

6. Conclusions

The results presented here may be of assistance in a series of practical situations, like optimizing additive incorporation, predicting plastics degradation in hostile environments, improving adhesive strength, assessing substance migration from packaging to foodstuff (or the reverse) or possible contamination levels during post-use polymer recycling, etc. They refer to binary mixtures but they may also serve as a guide for multicomponent ones. This is because in our case of marginal miscibility, the limited extent of individual additive participation should not severely affect each other's presence in the mostly P host. Consequently, it is reasonable to expect that the fraction of S_i, one of several poor solvents ($i = 1,2,3,\ldots$), is proportional to $\sim\exp\{-1 - \mathrm{V}_{\mathrm{S}i}(\chi'_{\mathrm{S}i\mathrm{P}} - 1/\mathrm{V_P})\}$.

The reliability of these estimates is, of course, subject to the limitations of the physical model from which they were derived (Sections 1 and 3, and p. 166 in Ref. [7]) and the accuracy of the physico-chemical data introduced in this model. Even when these prerequisites are fulfilled, they provide an upper limit for the penetrant concentration within the polymer (or of the polymer within the surrounding solvent) since they presume equilibrium conditions which may not always be feasible due to component mingling at inadequate proportions, imperfect mechanical mixing or, in the case passive presence of a polymer in a solvent laden environment, mutual exposure of short duration.

Acknowledgements

This work was partially funded by US grant NSF-DMR-9212668 and EU project FAIR-CT98-4318, for which the authors are grateful.

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