Thermodynamics of Polymer Compatibility in Ternary Systems

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ABSTRACT: A numerical procedure is described for calculating phase diagrams in ternary systems containing one solvent and two polymers; calculations are based on the Flory-Huggins theory. Particular attention is given to the effect of asymmetry (the interaction between the solvent and the first polymer is different from that between the solvent and the second polymer) and to the effect of differences in polymer molecular weight. Phase diagrams are presented for a variety of typical cases. The calculations confirm Patterson's suggestion that the difference between two polymer-solvent interactions, not the absolute values, affects greatly the compatibility and that the binodal curve is a closed loop when the interaction between the two polymers is extremely small. Also presented are calculated limiting miscibilities as a function of interaction parameters.

The Flory–Huggins theory of 1942 is still widely used to represent the thermodynamic properties of polymer solutions, although a better theory based on free volume has been suggested by Prigogine[2a] and revised and extended by Flory.[2b] However, for many practical purposes the added complexity of calculation corresponding to the new theory does not warrant its use for polymer compatibility at this time, especially because of insufficient experimental data required to determine the necessary parameters.

Application of Flory-Huggins theory to polymer compatibility has been made by Scott[3] and by Tompa[4] for symmetrical systems, *i.e.*, for systems where the Flory interaction parameters between solvent and polymers, χ_{1s} and χ_{2s}, are equal. In this work we consider systems that are not symmetric.

The conclusion drawn from Scott's analysis agrees fairly well with the experimental findings of Dobry and Boyer-Kawenoki[5] that if two high polymers are incompatible in one solvent, they are generally incompatible in all other solvents. Berek *et al.*,[6] in their study of the phase relations in the system of polystyrene-polypropylene-toluene, calculated the binodal curve by assuming symmetry and found that the theoretical curve agreed quite well with the experimental results; similar agreement was obtained by Bristow[7] for the system rubber-poly(methyl methacrylate)-benzene. These results are not surprising since the solvents used in these systems were all equally good solvents for both polymers in the system, *i.e.*, $\chi_{1s} \approx \chi_{2s}$ as indicated by nearly horizontal tie lines. On the other hand, Hugelin and Dondos[8] concluded in their investigation of the compatibility of polystyrene and poly(methyl methacrylate) in different solvents that, in order to achieve maximum compatibility for two polymers, the solvent must have comparable affinities for each of them. In other words, if the interaction of the solvent with one polymer is different from that with the other, the polymers become less miscible, contrary to Scott's prediction. This solvent effect on polymer compatibility has been recognized by many investigators. For example, Bank *et al.*[9] found that polystyrene-poly(vinyl methyl ether) mixtures are incompatible in trichloroethylene but compatible in toluene. In the study of threshold points of polystyrene-poly(methyl methacrylate) mixtures, Kern[10] observed benzene and chlorobenzene are among the best solvents whereas ethyl acetate is relatively poor. Patterson[11] has noticed such effect on cloud points in very dilute ternary systems. This led him to reexamine Scott's treatment by calculating the spinodals; he showed that a small difference in polymer-solvent interactions appears to have a marked effect on polymer compatibility. Spinodals, however, while simpler to calculate, reveal only the general trend of phase separation; only the binodal curve gives details of equilibrium relationships between two phases.

Because of recent advances in high-speed computer techniques and numerical methods, calculation of the binodal curve of a ternary polymer solution is no longer a major obstacle. The purpose of this paper is to present a method of computation for phase equilibrium in polymer solution based on the Flory-Huggins theory and to show how interaction parameters and molecular weights affect polymer compatibility.

Method of Computation

The Flory–Huggins expression for the Gibbs energy of mixing for a system of two polymers and one solvent is

$$\Delta G^{\mathrm{M}}/RT = n_1 \ln \phi_1 + n_2 \ln \phi_2 + n_s \ln \phi_s + (\chi_{12}\phi_1\phi_2 + \chi_{1s}\phi_1\phi_s + \chi_{2s}\phi_2\phi_s)(m_1n_1 + m_2n_2 + m_sn_s) \tag{1}$$

where n_i is the number of moles of ith component in the mixture; ϕ_i is the volume fraction of ith component; χ_{ij} is the Flory interaction parameter; and m_i is the ratio of the molar volume of i to that of a reference component. Subscripts 1 and 2 denote polymers 1 and 2 and s denotes the solvent. The chemical potentials as given by Tompa[12] were obtained by differentiation of the Gibbs energy of mixing with respect to n_i

$$\Delta\mu_s/RT = \ln \phi_s + [1 - (1/m_1)]\phi_1 + [1 - (1/m_2)]\phi_2 + \chi_s(\phi_1 + \phi_2)^2 + \chi_1\phi_1^2 + \chi_2\phi_2^2 \tag{2}$$

$$\Delta\mu_1/RT = \ln \phi_1 + [1 - (m_1/m_2)]\phi_2 + (1 - m_1)\phi_s + m_1[\chi_1(\phi_2 + \phi_s)^2 + \chi_2\phi_2^2 + \chi_s\phi_s^2] \tag{3}$$

$$\Delta\mu_2/RT = \ln \phi_2 + [1 - (m_2/m_1)]\phi_1 + (1 - m_2)\phi_s + m_2[\chi_2(\phi_1 + \phi_s)^2 + \chi_1\phi_1^2 + \chi_s\phi_s^2] \tag{4}$$

where

$$\chi_1 = (1/2)(\chi_{1s} + \chi_{12} - \chi_{2s}), \text{etc.} \tag{5}$$

and where m_1 and m_2 are the molar volume ratios of the polymers to the reference volume V_0. In this work we take V_0 as the molar liquid volume of solvent; thus, m_s is equal to unity and

$$\begin{aligned} m_1 &= V_1/V_s \\ m_2 &= V_2/V_s \end{aligned} \tag{6}$$

At equilibrium the chemical potential of each component must be the same in both phases

$$\begin{aligned} \Delta\mu_1'(\phi_1',\phi_2',\phi_s') &= \Delta\mu_1''(\phi_1'',\phi_2'',\phi_s'') \\ \Delta\mu_2'(\phi_1',\phi_2',\phi_s') &= \Delta\mu_2''(\phi_1'',\phi_2'',\phi_s'') \\ \Delta\mu_s'(\phi_1',\phi_2',\phi_s') &= \Delta\mu_S''(\phi_1'',\phi_2'',\phi_s'') \end{aligned} \tag{7}$$

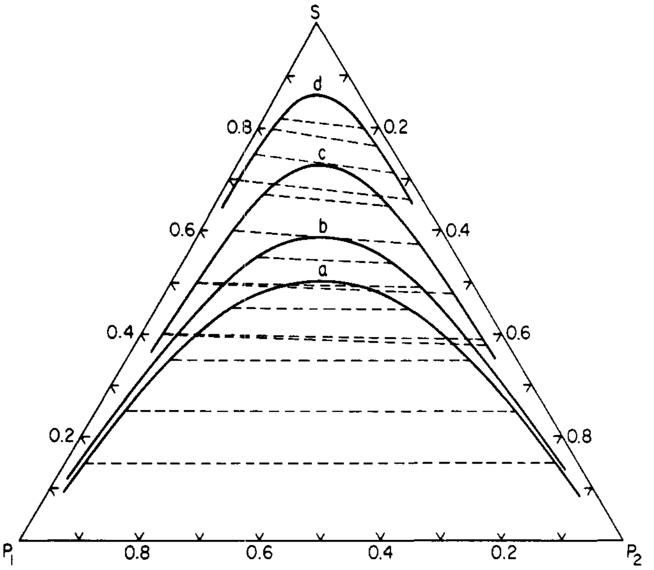

Figure 1. Binodals for a solvent-polymer 1-polymer 2 system: $m_1 = m_2 = 1000$, and $m_s = 1$. Polymer-polymer interaction $\chi_{12} = 0.004$ and the solvent-polymer interaction pairs χ_{1s} and χ_{2s} are as follows: (a) $\chi_{1s} = \chi_{2s}$; (b) 0.4, 0.44; (c) 0.4, 0.46; (d) 0.4, 0.48.

where prime indicates one phase and double prime the other.

Equation 7 is a set of three nonlinear equations with six unknowns. Among these unknowns, one can be arbitrarily chosen from phase-rule considerations. Two material-balance equations eliminate two further unknowns; thus, there are only three unknowns with three equations. In principle, eq 7 can be solved. In practice, however, it is not easy to do so.

Recently, Guffey and Wehe[13] have reported success in the calculation of multicomponent liquid-liquid equilibria using Powell's search routine.[14] In brief, what this routine does is to search the solution by minimizing the sum of squares of the residuals of the functions $f_i(\phi_i) = 0$. The algorithm used is primarily Gauss' method of iteration with Lagrange multipliers chosen by the method suggested by Levenberg.[15]

For equilibrium calculation, the functions f_i are given by

$$f_i = (\Delta\mu_i' - \Delta\mu_i'')(RT)^{-1} \tag{8}$$

Thus the objective function to be minimized is

$$\mathrm{OBJ} = \sum_i (\Delta\mu_i' - \Delta\mu_i'')^2 (RT)^{-2}$$

Strictly, OBJ should be zero at minimum, but due to round-off error, this result is never achieved. In this work convergence was considered to have been reached when

$$\mathrm{OBJ} \leqslant 10^{-10}$$

A serious complication in the numerical calculation of phase equilibrium is the existence of a trivial solution where each phase has the same composition. To avoid this the objective function must be modified by introducing a proper penalty function. Guffey and Wehe suggested the following form

$$\mathrm{OBJ} = \sum_i F_i = \sum_i \frac{(\Delta\mu_i' - \Delta\mu_i'')^2 (RT)^{-2}}{(\phi_i' - \phi_i'')^r} \tag{9}$$

The denominator is the penalty function and r is a positive, even, integral number; r must be chosen large

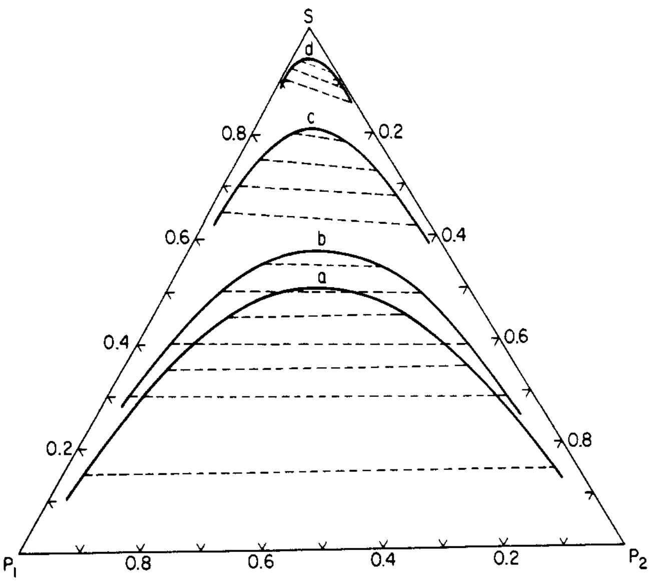

Figure 2. Binodals for a solvent-polymer 1-polymer 2 system: $m_1 = m_2 = 1000$, and $m_s = 1$. $\chi_{12} = 0.004$, and χ_{1s} and χ_{2s} are: (a) $\chi_{1s} = \chi_{2s}$; (b) 0.1, 0.15; (c) 0.2, 0.3; (d) 0.3, 0.45.

enough so that the denominator increases faster than the numerator as ϕ_i' approaches ϕ_i'' near the trivial solution, but r should not be so high to cause F_i to become too large. Usually 4 or 2 is the most satisfactory value.

The penalty function is applied only to those component whose compositions in both phases vary during the search process. In this work ϕ_s' in one phase was always fixed; therefore, no penalty function was used for F_s. Instead, a fixed number was substituted such that the magnitude of F_s was comparable to F_1 and F_2. This fixed number was calculated from

$$\left(\frac{|\phi_{10}' - \phi_{10}''| + |\phi_{20}' - \phi_{20}''|}{2}\right)^r$$

Subscript zero denotes the initial guess for equilibrium compositions.

When the values of ϕ_i are close to zero, the search routine often gives a negative value of ϕ_i. When this happens, the chemical potential is arbitrarily set to zero and each F_i is then multiplied by an additional penalty function, $\exp(-100\,\phi_i)$, to make ϕ_i positive.

The routine requires an initial guess of equilibrium compositions. Contrary to Guffey and Wehe, we found that a guess reasonably close to the true equilibrium compositions is essential to guarantee a successful search. This is necessary because the response surface of the chemical potential is flat; only very near the equilibrium point does it show a narrow, steep well. Unfortunately, the penalty function sometimes creates a local minimum or maximum.

Because of the least-squares nature of the objective function and because of numerical differentiation using a fixed step size, proper scaling is necessary to give the same magnitude for all F_i. Since the chemical potential of a polymer in the solution is usually greater than that of the solvent by a factor m, the chemical potential per unit segment was used throughout the calculation. Scaling of ϕ_i is equally important.

Results

Figure 1 shows binodal curves for a ternary solution containing two polymers with equal molar volume ratio, $m_1 = m_2 = 1000$; the interaction parameter between polymers $\chi_{12} = 0.004$. Curve a represents the symmetrical

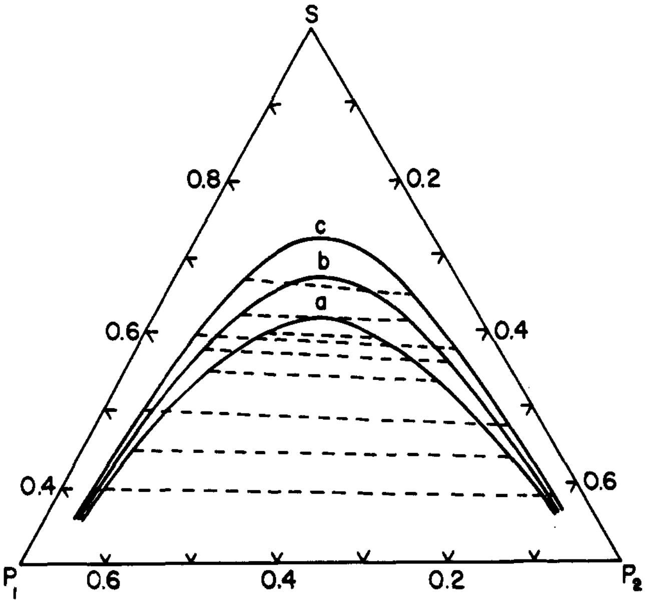

Figure 3. Binodals for a solvent-polymer 1-polymer 2 system: $m_1 = m_2 = 1000$, and $m_s = 1$. $\chi_{12} = 0.004$ and χ_{1s} and χ_{2s} are: (a) 0.1, 0.16; (b) 0.3, 0.36; (c) 0.4, 0.46.

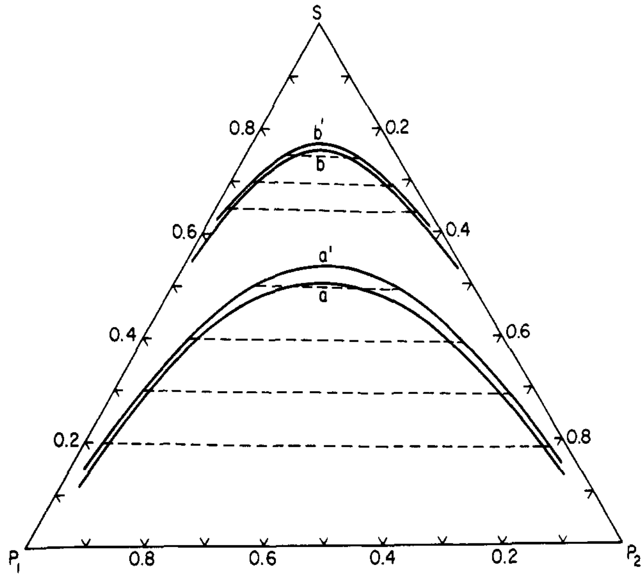

Figure 4. Binodals for a solvent-polymer 1-polymer 2 system: $m_1 = m_2 = 1000$, and $m_s = 1$. For a and a', $\chi_{12} = 0.004$, and (a) $\chi_{1s} = \chi_{2s}$; (a') $\chi_{1s} = 0.3$, $\chi_{2s} = 0.33$. For b and b', $\chi_{12} = 0.008$, and (b) $\chi_{1s} = \chi_{2s}$; (b') $\chi_{1s} = 0.3$, $\chi_{2s} = 0.33$.

case where $\chi_{1s} = \chi_{2s}$ for different values of χ_{1s} and χ_{2s}. As expected, the binodals are independent of the values of χ_{1s}. When χ_{1s} differs from χ_{2s} as shown by curves b, c, and d, the limiting miscibility decreases or ϕ_s increases from 0.51 to 0.86 as the difference in χ increases from 0 to 0.08.

Figures 2 and 3 show the solvent effect (increasing χ_{1s}) with fixed χ_{1s}/χ_{2s} ratio and fixed $\chi_{1s} - \chi_{2s}$, respectively. The effect is most severe for the larger values of χ_{1s} or, in other words, for poorer solvents as opposed to good ones. If the ratio χ_{1s}/χ_{2s} is greater than 2, the polymer mixture is hardly compatible except for very small values of χ_{1s}.

By varying the values of χ_{12} from 0.004 to 0.008 but keeping χ_{1s} and χ_{2s} the same, the two sets of binodals given in Figure 4 show that the influence of solvent on miscibility is not significantly changed. Increasing χ_{12} simply shifts the curve upward.

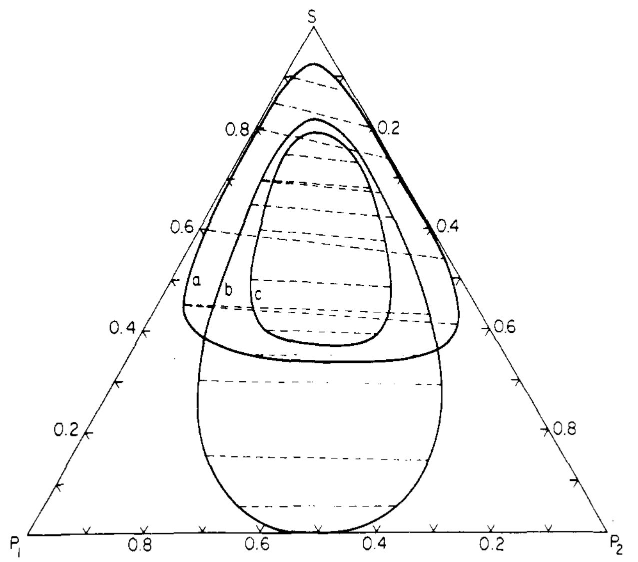

Figure 5. Binodals for $\chi_{12} \leq$ critical value: $m_1 = m_2 = 1000$, and $m_s = 1$. Values of interaction parameters χ_{12}, χ_{1s}, and χ_{2s} are: (a) −0.002, 0.3, 0.45; (b) 0.002, 0.4, 0.48; and (c) 0.0015, 0.4, 0.48.

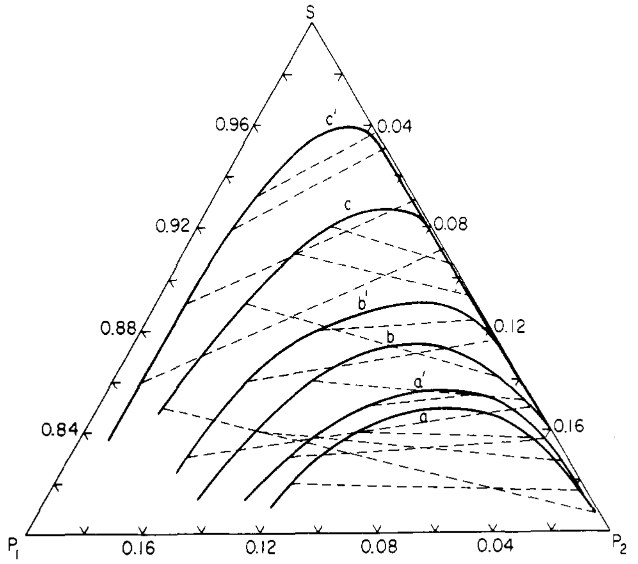

Figure 6. Binodals for a solvent-polymer 1-polymer 2 system: $m_1 = 4000$, $m_2 = 250$, and $m_s = 1$. $\chi_{12} = 0.02$, and χ_{1s} and χ_{2s} are: (a) 0.1, 0.15; (a') 0.15, 0.1; (b) 0.2, 0.3; (b') 0.3, 0.2; (c) 0.3, 0.45; (c') 0.45, 0.3.

Low miscibility is not the only consequence which results from the solvent effect: the tie lines for the system with unequal solvent-polymer interactions are no longer horizontal. The distribution of solvent in the two equilibrium phases is in favor of that phase which is richer in the polymer that has the favorable solvent-polymer interaction. It is also noticeable that the difference in χ_{is} causes the binodal to shift slightly toward the side corresponding to the higher χ_{is}.

Binodals were also calculated for cases where χ_{12} is below the critical, including negative χ_{12}. A few examples are given in Figure 5. As found by Patterson[11] from his calculation of spinodals, the binodal becomes a closed loop at critical χ_{12} as the lower critical point touches the line of zero solvent. Further decrease of χ_{12} causes the lower critical point to move away from the base line. Figure 5 also shows the solvent effect on the miscibility gap.

Unequal Molar Volume of Polymers. The effect on compatibility of unequal molar volumes of two polymers

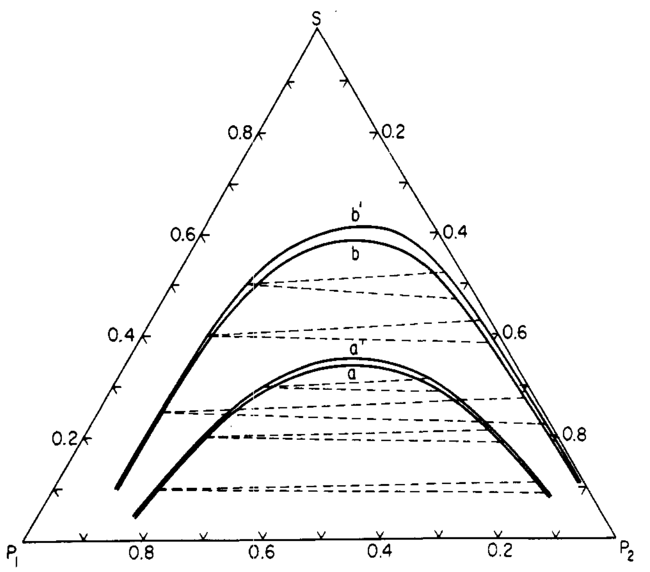

Figure 7. Binodals for a solvent-polymer 1-polymer 2 system: For set a: $m_1 = 1000$, $m_2 = 500$, and $m_s = 1$. $\chi_{12} = 0.004$ and χ_{1s} and χ_{2s} are (a) 0.1, 0.15; and (a′) 0.15, 0.1. For set b: $m_1 = 1000$, $m_2 = 250$, and $m_s = 1$. $\chi_{12} = 0.008$, and χ_{1s} and χ_{2s} are (b) 0.2, 0.3; and (b′) 0.3, 0.2.

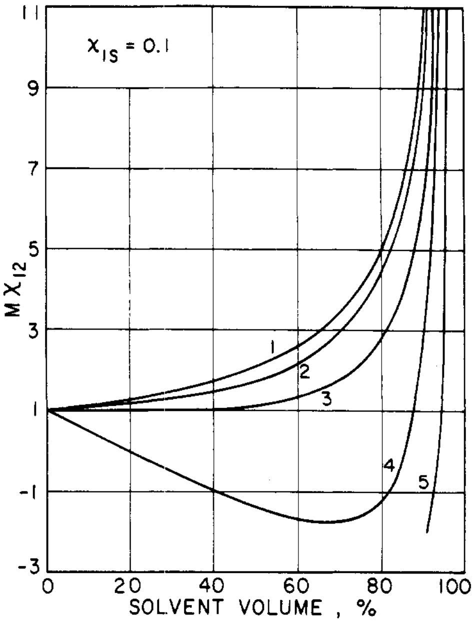

Figure 8. Calculated limiting miscibility for $\chi_{1s} = 0.1$. $\chi_{2s} - \chi_{1s}$ are given as (1) 0.0; (2) 0.05; (3) 0.1; (4) 0.15; (5) 0.2.

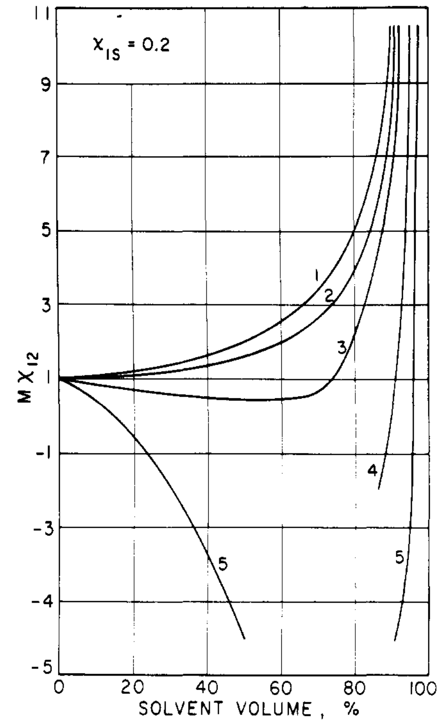

Figure 9. Calculated limiting miscibility for $\chi_{1s} = 0.2$. $\chi_{2s} - \chi_{1s}$ are given as (1) 0.0; (2) 0.05; (3) 0.1; (4) 0.15; (5) 0.2.

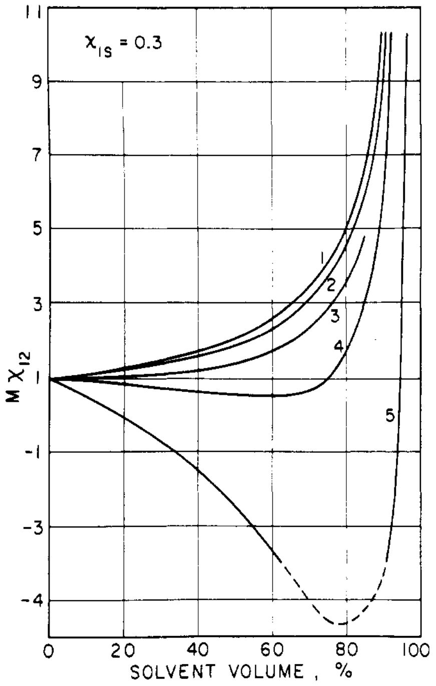

Figure 10. Calculated limiting miscibility for $\chi_{1s} = 0.3$. $\chi_{2s} - \chi_{1s}$ are given as (1) 0.0; (2) 0.03; (3) 0.06; (4) 0.09; (5) 0.15.

was found to be similar to that given in Scott's treatment, regardless of whether the solvent-polymer interactions are identical or not. Decreasing the molecular weight of one of the polymers, the binodal shifts toward the lower molecular weight polymer and eventually the curve becomes similar to that of a polymer-solvent-nonsolvent system. The presence of a small polymer promotes the solubility of the high molecular weight polymer in the solvent.

However, when the solvent-polymer interaction parameters are interchanged between two polymers of different sizes, the incompatibility increases as the higher χ_{is} is assigned to the higher molecular weight polymer, as shown in Figure 6. This coupling effect increases as χ_{is} increases. There is no appreciable coupling effect when the ratio of m_1/m_2 is below 2 as it can be seen from Figure 7.

Limiting Miscibility: Threshold Point. Limiting miscibilities of two-polymer mixtures in one solvent were determined for different interaction parameters. The results are plotted in Figures 8-12 as solvent volume per cent *vs.* $M\chi_{12}$ with χ_{1s} and $(\chi_{1s} - \chi_{2s})$ as parameters. M is the reciprocal of the critical χ_{12}; it is defined by

$$\frac{1}{M} = \frac{1}{2}\left(\frac{1}{\sqrt{m_1}} + \frac{1}{\sqrt{m_2}}\right)^2 \qquad (10)$$

The justification for using $M\chi_{12}$ rather than χ_{12} is that eq 2-5 for the chemical potentials contain the terms $m_1\chi_{12}$ and $m_2\chi_{12}$. To combine these two terms into a single parameter, some intermediate value of m_1 and m_2 must be

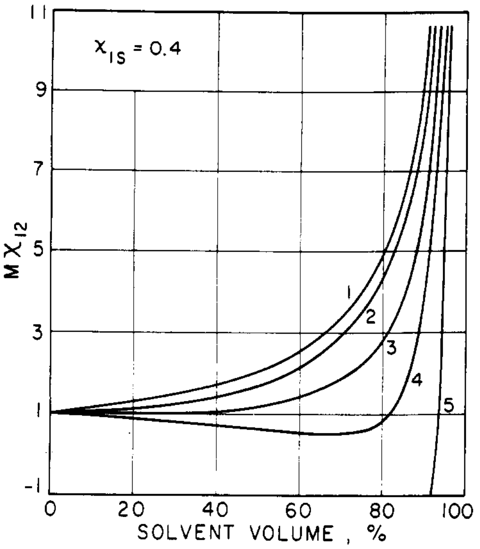

Figure 11. Calculated limiting miscibility for $\chi_{1s} = 0.4$. $\chi_{2s} - \chi_{1s}$ are given as (1) 0.0; (2) 0.04; (3) 0.06; (4) 0.08; (5) 0.1.

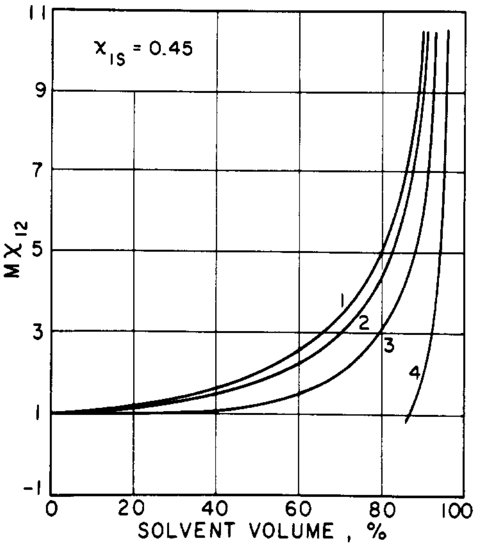

Figure 12. Calculated limiting miscibility for $\chi_{1s} = 0.45$. $\chi_{2s} - \chi_{1s}$ are given as (1) 0.0; (2) −0.03; (3) 0.05; (4) 0.07.

employed. Equation 10 appears to be useful for this purpose because it satisfies all the asymptotic conditions.

Curves where $(\chi_{1s} - \chi_{2s}) = 0$ are the same for all χ_{1s} because the symmetrical system is independent of χ_{1s}. All the curves approximately converge to the critical point, *i.e.*, $M\chi_{12} = 1.0$ at zero solvent per cent. The curve may be roughly divided into two regions; for $M\chi_{12} < 4$, the miscibility is very sensitive to the value of $M\chi_{12}$ whereas for $M\chi_{12} > 4$ miscibility remains almost constant.

Discussion

We have presented a method of computation for phase equilibria in systems containing two polymers and one solvent based on Flory-Huggins theory. Previously, such calculations were considered to be extremely difficult. The numerical method presented here usually requires less than 100 calculations of chemical potentials for one point which means less than 1 sec of computing time on a CDC 6400 computer.

The binodals calculated show the effects of polymer-polymer and solvent-polymer interactions as well as that of molecular weight on polymer incompatibility. It supports many experimental observations where Scott's simple approximation fails. For example, Kern[10] found that benzene is a better solvent than ethyl acetate for polystyrene-poly(methyl methacrylate) mixtures. Using data compiled by Sheehan and Bisio,[16] the interaction parameters are $\chi_{1s} = 0.437$ and $\chi_{2s} = 0.446$ for benzene-polymers, and 0.475 and 0.486 for ethyl acetate-polymers. It follows, at least qualitatively, that both ternary systems are slightly asymmetric and, in view of the lower χ values, that benzene is a better solvent than ethyl acetate.

In the case where the solvent-polymer interactions are $\chi_{1s} = 0.27$ and $\chi_{2s} = 0.45$, even at zero χ_{12} the polymers are incompatible in dilute solution. On the other hand, for a small value of χ_{12} with a solvent equally good for each polymer, the polymers are miscible in any proportion. This may be the case for the system cellulose acetate-nitrocellulose-acetic acid.

Figures 8-12 are useful for the selection of a solvent for a particular polymer mixture and also for estimation of the threshold point which for the asymmetrical case is usually different from the critical point. Since there exists a coupling effect of molecular weight and interaction parameter as shown in Figure 6, Figures 8-12 can only be used for polymer mixtures with moderate molecular weight difference. If m_1/m_2 is large, it is advisable to determine the threshold point by direct calculation of phase equilibrium.

For $M\chi_{12}$ smaller than unity, the binodal curve shows a closed loop. It is not difficult to see qualitatively why this is so. With χ_{12} of two chemically similar polymers less than the critical χ_{12}, the two polymers are completely miscible without solvent. Since the polymers are of comparable size, the excess entropy of mixing is small. As solvent is added to the mixture, the excess entropy contribution to the Gibbs energy of mixing becomes important and phase separation occurs. This phenomenon is not uncommon for systems of small molecules; for example, the acetic acid-aniline-cyclohexane system shows a closed loop binodal at 50°.

One polymer system which has been reported to show a closed loop is the diphenyl ether-polyethylene-atactic polypropylene system.[17] It is to be expected that for such concentrated polymer solutions a very long period of time is required to reach equilibrium.

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