The Thermodynamics of High Polymer Solutions. IV. Phase Equilibria in the Ternary System: Polymer—Liquid 1—Liquid 2

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analogous to those obtained for fulvene by Calculation 1, are listed in Table X.

Finally, a word should perhaps be said in regard to the significance of calculated charge distributions, dipole moments, bond orders, and bond lengths which differ as markedly as do those listed in Tables VI–IX. In Table VI, for example, the numerical values given in columns 1, 2, ···4 represent successive approximations, with those in the last column presumably the most reliable. Table IX, which illustrates the application of the perturbation method, brings out two different points of interest.

Thus, the δ_r's listed in rows 1–4 of the last column are indeed self-consistent (cf. the last column of Table VI) since they are respectively equal to the q_r's listed in rows 5–8. However, the δ's given in the six preceding columns are clearly not self-consistent. In the second place, it is seen that the use of unreasonable values for the δ's, as in columns 6 and 7, leads to unreasonable charge distributions and to unreasonable moments. This fact lends some support to the otherwise arbitrary fundamental assumption (see above) that the δ's are equal to the corresponding net charges.

The Thermodynamics of High Polymer Solutions. IV. Phase Equilibria in the Ternary System: Polymer—Liquid 1—Liquid 2*

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Two approximate methods of calculating equilibrium phase diagrams in ternary systems of polymer and mixed liquids have been compared with exact phase diagrams based upon the Flory-Huggins equations. Both a "single liquid approximation" and a "complete immiscibility approximation" are worthless except for the crudest qualitative considerations. Analytical expressions for the plait points of such ternary systems (a maximum of ten) have been derived. A consideration of the solubility of polymers in mixed solvents leads to the conclusion that a polymer may be completely soluble in certain mixtures of non-solvents if its internal pressure (cohesive energy density) lies between those of the two liquids and if the two liquids are themselves completely miscible. The position of the phase boundary is nearly independent of the molecular weight of the polymer for molecular weights above 10,000. Osmotic pressures in mixed solvents are discussed, and Gee's suggestion that the osmotic pressure is zero at the critical solubility limit is confirmed.

INTRODUCTION

IN Articles I and II of this series[1,2] a first attempt was made to treat the multicomponent system involved in the fractionation of high polymers. In particular, we assumed that "solvent mixtures can be treated with a fair degree of accuracy assuming the mixture of two solvents to behave as a homogeneous liquid with respect to the polymer," this new "liquid" having average thermodynamic properties. We did not suppose this treatment, which we shall call the "single liquid approximation," to be very accurate, but used it to obtain valuable qualitative information concerning the fractionation of high polymers. The present paper attempts to consider in further detail the problem of phase equilibria in a three-component system consisting of a long-chain polymer and two ordinary liquids, with a view to determining, among other results, the limitations of such a "single liquid approximation."

THE HEAT OF MIXING OF A TERNARY SYSTEM

Van Laar,[3] Scatchard,[4] and Hildebrand[5] have shown that, in many cases, the heat absorbed in mixing two substances may be represented by the expression:

$$\Delta H_{12}{}^M = V_m A_{12}\phi_1\phi_2, \qquad (1)$$

when V_m is the volume of the mixture, ϕ_1 and ϕ_2 are the volume fractions of the respective components, and A_{12} is a constant characteristic of the system. Scatchard[6] has shown that if one makes entirely equivalent assumptions for a three-component system, one obtains

$$\Delta H_{123}{}^M = V_m(A_{12}\phi_1\phi_2 + A_{13}\phi_1\phi_3 + A_{23}\phi_2\phi_3), \qquad (2)$$

where the A's are the constants for the corresponding binary systems.

Differentiation leads to the partial molal heats

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[1] R. L. Scott and M. Magat, J. Chem. Phys. 13, 172 (1945).
[2] R. L. Scott, J. Chem. Phys. 13, 178 (1945).

[3] J. J. van Laar, "Sechs Vortrage," Zeits. f. physik. Chemie 72, 723 (1910).
[4] George Scatchard, Chem. Rev. 8, 321 (1931).
[5] J. H. Hildebrand, *Solubility of Non-electrolytes* (Reinhold Publishing Corporation, New York, 1936).
[6] G. Scatchard, Trans. Faraday Soc. 33, 160 (1937).

of mixing:

$$\Delta \bar{H}_1 = \partial \Delta H_{123}/\partial N_1 = V_1[A_{12}\phi_2{}^2 + A_{13}\phi_3{}^2$$
$$+ (A_{12} + A_{13} - A_{23})\phi_2\phi_3], \quad (3a)$$

$$\Delta \bar{H}_2 = \partial \Delta H_{123}/\partial N_2 = V_2[A_{12}\phi_1{}^2 + A_{23}\phi_3{}^2$$
$$+ (A_{12} + A_{23} - A_{13})\phi_1\phi_3], \quad (3b)$$

$$\Delta \bar{H}_3 = \partial \Delta H_{123}/\partial N_3 = V_3[A_{13}\phi_1{}^2 + A_{23}\phi_2{}^2$$
$$+ (A_{13} + A_{23} - A_{12})\phi_1\phi_2]. \quad (3c)$$

If, in addition, we assume[3-5] that the interaction energy between unlike pairs of molecules is the geometric mean of those between like pairs, then:

$$A_{ij} = (\delta_i - \delta_j)^2, \quad (4)$$

where δ_i represents the square root of the internal pressure (or "cohesive energy density"), $(\Delta E_i{}^v/V_i)^{\frac{1}{2}}$, where $\Delta E_i{}^v$ is the energy of vaporization and V_i the molal volume of component i.

We may then rewrite Eqs. (2) and (3):

$$\Delta H_{123}{}^M = V_m[(\delta_1 - \delta_2)^2\phi_1\phi_2 + (\delta_1 - \delta_3)^2\phi_1\phi_3$$
$$+ (\delta_2 - \delta_3)^2\phi_2\phi_3], \quad (5)$$

$$\Delta \bar{H}_1 = V_1[(\delta_1 - \delta_2)\phi_2 + (\delta_1 - \delta_3)\phi_3]^2, \quad (6a)$$

$$\Delta \bar{H}_2 = V_2[(\delta_2 - \delta_1)\phi_1 + (\delta_2 - \delta_3)\phi_3]^2, \quad (6b)$$

$$\Delta \bar{H}_3 = V_3[(\delta_3 - \delta_1)\phi_1 + (\delta_3 - \delta_2)\phi_2]^2. \quad (6c)$$

Each of these equations may be rearranged in a form which shows that the partial molal heat of mixing of liquid 1 with liquids 2 and 3 is equivalent to the heat of mixing of liquid 1 with a hypothetical new liquid whose δ is the volume fraction average of 2 and 3:

$$\Delta \bar{H}_1 = V_1[\delta_1 - (\phi_2\delta_2 + \phi_3\delta_3)/(\phi_2 + \phi_3)]^2(\phi_2 + \phi_3)^2, \quad (7)$$

or

$$\Delta \bar{H}_1 = V_1[\delta_1 - \delta_0]^2\phi_0{}^2, \quad (8)$$

where

$$\delta_0 = (\phi_2\delta_2 + \phi_3\delta_3)/(\phi_2 + \phi_3), \quad \phi_0 = \phi_2 + \phi_3.$$

Such a transformation may always be made and is frequently useful in dealing with one-phase systems. It should be just as valid for high polymer solutions as for those of small molecules.

FREE ENERGIES IN TERNARY SYSTEMS

Adding the equations of the previous section for the heat of mixing to the familiar expressions of Huggins,[7] Flory,[8] Miller,[9] and Guggenheim[10] for the entropy of high polymer solutions, we obtain the partial molal free energies of the three components in a ternary system. For a three-component system consisting of a long-chain polymer (sub-

script 3) and two liquids (subscripts 1 and 2) of equal molal volumes $(V_1 = V_2 = V_0)$, we obtain:

$$\Delta \bar{F}_1 = RT[\ln\phi_1 + (1 - (1/m))\phi_3 + \mu_{12}\phi_2{}^2$$
$$+ \mu_{13}\phi_3{}^2 + (\mu_{12} + \mu_{13} - \mu_{23})\phi_2\phi_3], \quad (9a)$$

$$\Delta \bar{F}_2 = RT[\ln\phi_2 + (1 - (1/m))\phi_3 + \mu_{12}\phi_1{}^2$$
$$+ \mu_{23}\phi_3{}^2 + (\mu_{12} + \mu_{23} - \mu_{13})\phi_1\phi_3], \quad (9b)$$

$$\Delta \bar{F}_3 = RT[\ln\phi_3 - (m-1)(\phi_1 + \phi_2) + m\mu_{13}\phi_1{}^2$$
$$+ m\mu_{23}\phi_2{}^2 + m(\mu_{13} + \mu_{23} - \mu_{12})\phi_1\phi_2], \quad (9c)$$

where m is the ratio of molal volumes of polymer and liquid (V_3/V_0), or approximately the degree of polymerization, and the μ's are constants for the corresponding binary systems such that:

$$\mu_{12} = V_0 A_{12}/RT, \quad (10a)$$

$$\mu_{13} = \mu^s + (V_0 A_{13}/RT), \quad (10b)$$

$$\mu_{23} = \mu^s + (V_0 A_{23}/RT). \quad (10c)$$

In these equations μ^s is a correction factor from the entropy. In the original Flory treatment,[8] certain second-order corrections in the statistical treatment were ignored, and μ^s, resultantly, was zero. In the more nearly accurate treatments of Huggins,[7] Miller,[9] and Guggenheim,[10] μ^s reduces to approximately $1/z$, where z is the coordination number of the quasi-lattice. Actually, we know from experiment and from recent theoretical studies[11,12] that μ^s is greater than $1/z$; for the purposes of this paper, we shall treat it as an empirical constant about 0.25 in magnitude.

If Eq. (4) holds, we may write:

$$\mu_{12} = (V_0/RT)(\delta_1 - \delta_2)^2 = (A+B)^2, \quad (11a)$$

$$\mu_{13} = \mu^s + (V_0/RT)(\delta_1 - \delta_3)^2 = \mu^s + A^2, \quad (11b)$$

$$\mu_{23} = \mu^s + (V_0/RT)(\delta_2 - \delta_3)^2 = \mu^s + B^2, \quad (11c)$$

where these equations are used to define new parameters A and B.

Using Eqs. (11abc), we may rewrite Eqs. (9abc):

$$\Delta \bar{F}_1 = RT[\ln\phi_1 + (1 - (1/m))\phi_3 + \mu^s\phi_3{}^2$$
$$+ ([A+B]\phi_2 + A\phi_3)^2], \quad (12a)$$

$$\Delta \bar{F}_2 = RT[\ln\phi_2 + (1 - (1/m))\phi_3 + \mu^s\phi_3{}^2$$
$$+ ([A+B]\phi_1 + B\phi_3)^2], \quad (12b)$$

$$\Delta \bar{F}_3 = RT[\ln\phi_3 + (m-1)(\phi_1 + \phi_2)$$
$$+ m\mu^s(\phi_1 + \phi_2)^2 + m(A\phi_1 - B\phi_2)^2]. \quad (12c)$$

We propose to calculate the equilibrium phase diagrams for ternary systems using the above equations. In any two-phase systems, the thermodynamic conditions for equilibrium require that the partial molal free energy of each component be

[7] M. L. Huggins, J. Chem. Phys. **9**, 440 (1941), Ann. N. Y. Acad. Sci. **43**, 1 (1942).

[8] P. J. Flory, J. Chem. Phys. **9**, 660 (1941); **10**, 51 (1942).

[9] A. R. Miller, Proc. Camb. Phil. Soc. **38**, 109 (1942); **39**, 154 (1943).

[10] E. A. Guggenheim, Proc. Roy. Soc. **A183**, 203 (1944).

[11] A. R. Miller, J. Chem. Phys. **16**, 841 (1948).

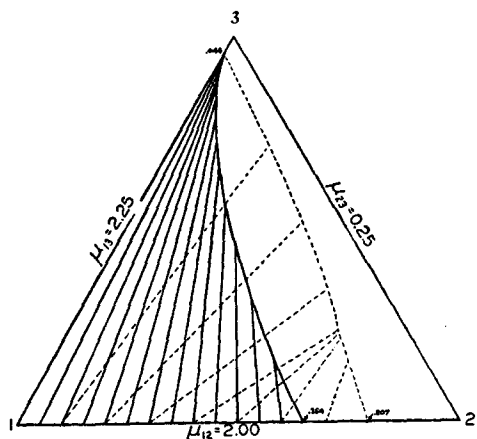[12] B. H. Zimm, Am. Chem. Soc. meeting in New York (Sept. 1947).

FIG. 1.

the same in both phases:

$$\Delta \bar{F}_1' = \Delta \bar{F}_1'', \tag{13a}$$

$$\Delta \bar{F}_2' = \Delta \bar{F}_2'', \tag{13b}$$

$$\Delta \bar{F}_3' = \Delta \bar{F}_3''. \tag{13c}$$

Upon substituting appropriate values for m, μ^s, A^2, and B^2 (or, in the more general case, m, μ_{12}, μ_{13}, and μ_{23}), one may determine the phase boundaries and the tie lines for any hypothetical system.

Before doing so, however, let us consider two approximation methods.

THE "SINGLE LIQUID" APPROXIMATION

The existence of equations of the form of (7) suggested[1,2] that one might solve the problem of a two-phase-three-component system in which one component is a high polymer by reducing it to that of a binary system: polymer plus hypothetical single liquid of average properties. Substitution of the equivalent of Eq. (8) into Eq. (12c) yields:

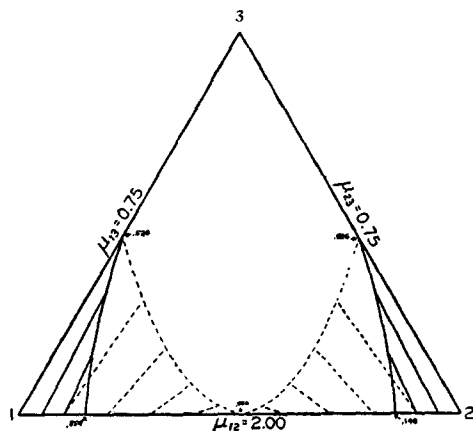$$\Delta \bar{F}_3 = RT[\ln\phi_3 - (m-1)\phi_0 + m\mu_{30}\phi_0{}^2], \tag{14}$$

FIG. 2.

where

$$\phi_0 = \phi_1 + \phi_2 = 1 - \phi_3, \tag{15}$$

$$\mu_{30} = \mu^s + [A\phi_1 - B\phi_2/\phi_1 + \phi_2]^2 = \mu_{13}(\phi_1/\phi_1 + \phi_2)$$
$$+ \mu_{23}(\phi_2/\phi_1 + \phi_2) - \mu_{12}(\phi_1\phi_2/(\phi_1 + \phi_2)^2). \tag{16}$$

A corresponding equation for the hypothetical "single liquid" would be:

$$\Delta \bar{F}_0 = RT[\ln\phi_0 + (1 - (1/m))\phi_3 + \mu_{30}\phi_3{}^2]. \tag{17}$$

For such a set of equations to be useful, we must assume that μ_{30} has the same value in both conjugate phases. With this assumption we may solve Eqs. (14) and (17) for a series of binary systems with varying values of μ_{30} (i.e., different ratios of 1 to 2, ϕ_1/ϕ_2) and obtain a complete phase diagram.

Of course, such a treatment will be rigorously accurate, if and only if the relative proportions of the two liquids are identical in the two conjugate phases; otherwise, μ_{30}' does not equal μ_{30}''. This requires that the extension of all tie lines pass through the vertex of 100 percent 3. That this condition is ever precisely satisfied (except in the trivial case that the two liquids have identical properties) is doubtful.

Figures 1 and 2 show the results of "single liquid" calculations for two simple cases, all chosen for the limit of infinite molecular weight polymer, $(m \rightarrow \infty)$.

Case I (Fig. 1), $m \rightarrow \infty$, $\mu^s = 0.25$, $A^2 = 2.0$, $B^2 = 0$ (i.e., $\mu_{13} = 2.25$, $\mu_{23} = 0.25$, $\mu_{12} = 2.00$). In this case liquid 2 has no heat of mixing with the polymer, and hence is the best possible solvent; liquids 1 and 2 are at their critical solution temperature. A real system which approximates such a situation would be polystyrene-benzene-methanol.

Case II (Fig. 2), $m \rightarrow \infty$, $\mu^s = 0.25$, $A^2 = 0.50$, $B^2 = 0.50$ (i.e., $\mu_{13} = 0.75$, $\mu_{23} = 0.75$, $\mu_{12} = 2.00$). In this case the two liquids are entirely equivalent in their solvent power for the polymer, and are again at their critical solution temperature. The "single liquid" approximation yields the interesting result that the polymer, while only partially miscible with either pure liquid, is miscible in all proportions with certain mixtures.

THE "COMPLETE IMMISCIBILITY" APPROXIMATION

A second kind of approximation is obtained if we assume arbitrarily that two of the three components are completely immiscible. If, for example, 1 and 3 are completely immiscible, the system will consist of a phase consisting of 1 and 2 only in equilibrium with a phase consisting of 2 and 3 only. Were this true, we would obtain the phase diagram (which consists of tie lines extending from the 1,2 edge of the triangle to the 2,3 edge) by equating the partial molal free energies of 2 in the two

phases:

$$RT[\ln\phi_2' + \mu_{12}(\phi_1')^2] = RT[\ln\phi_2''$$
$$+ (1 - (1/m))(\phi_3'') + \mu_{23}(\phi_3'')^2], \quad (18)$$

or

$$\ln\phi_2' + \mu_{12}(1 - \phi_2')^2 = \ln\phi_2''$$
$$+ (1 - (1/m))(1 - \phi_2'') + \mu_{23}(1 - \phi_2'')^2. \quad (19)$$

Given a value of ϕ_2'', we may calculate ϕ_2' and hence determine the phase diagram. Common sense will dictate the choice of which pair to choose as completely immiscible.

Figure 3 shows the "complete immiscibility" approximation for Case I of the previous section, assuming the polymer (3) and the non-solvent (1) are completely immiscible. For Case II, the miscibility region is obviously so large as to render this approximation absurd.

Consideration of the assumptions involved will show that where the right pairs are chosen in each of the two approximate methods, they represent extreme cases, and the correct phase diagram will be intermediate. For example, the next section will show that the true phase diagram for Case I lies between those of Fig. 1 and Fig. 3.

THE CORRECT PHASE DIAGRAMS

The exact calculation of the phase diagrams of a three-component system is extremely difficult without the aid of the preceding approximations. Since no analytical expression for the phase boundary and the tie lines exists, they must be determined by a laborious trial and error process. The amount of calculation is measurably reduced if the molecular weight is increased without limit ($m \to \infty$), for in this case, one conjugate phase necessarily contains no polymer ($\phi_3' = 0$), and the tie lines end on the 1,2 edge of the triangle. Six such systems have been calculated ($m \to \infty$, $\mu^s = 0.25$).

Case I. $A^2 = 2.0$, $B^2 = 0$ ($\mu_{12} = 2.0$, $\mu_{13} = 2.25$, $\mu_{23} = 0.25$). (See Fig. 4.) As previously noted, this corresponds to a system in which a polymer of extremely high molecular weight is mixed with the best possible solvent with which there is no heat of mixing; the third component is a strong precipitant just miscible with the solvent. The plait point is at 79.3 percent solvent, 20.7 percent precipitant, not at 64.6 percent -35.4 percent, as predicted by the "single liquid" approximation, or at 100 percent solvent, as required by the "complete immiscibility" treatment. The failure of the latter was expected; the reason for the inadequacy of the former is also clear; the tie lines show that the proportions of solvent and non-solvent in the two conjugate phases are widely different.

Case IA. $A^2 = 1.0$, $B^2 = 0$ ($\mu_{12} = 1.0$, $\mu_{13} = 1.25$, $\mu_{23} = 0.25$). (See Fig. 5.) This represents a system of polymer-solvent-precipitant in which the pre-
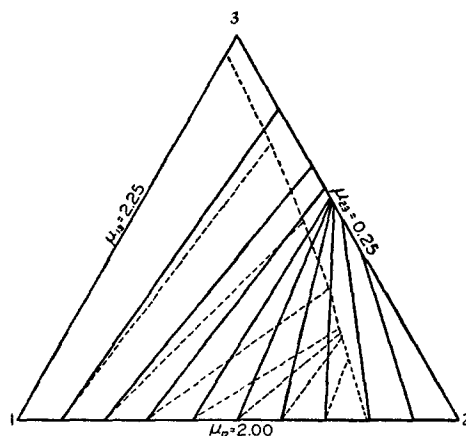

FIG. 3.

cipitant is not so effective, having a heat of mixing with the solvent only half that in Case I. The real system polystyrene-benzene-isopropanol should correspond roughly to that shown in Fig. 5.

Case 1B. $A^2 = 2.2$, $B^2 = 0$ ($\mu_{12} = 2.2$, $\mu_{13} = 2.45$, $\mu_{23} = 0.25$). (See Fig. 6.) On the other hand, the solvent and non-solvent may be partially immiscible. In such a case, a three-phase region results, as shown in Fig. 6. A real system which might approach this behavior is polyisobutylene-cyclohexane-methanol.

Case II. $A^2 = 0.5$, $B^2 = 0.5$ ($\mu_{12} = 2.0$, $\mu_{13} = 0.75$, $\mu_{23} = 0.75$). Figure 7 represents the hypothetical case of a polymer midway in internal pressure between two liquids at their critical solution temperature. The polymer is, in fact, completely miscible in all proportions with a 50–50 mixture of the two liquids, but the two-phase region is not nearly so large as that predicted by the single liquid approximation. Hence, as in Case I, the true phase diagram lies intermediate between the extremes of the two approximational methods.

Case IIA. $A^2 = 0.4$, $B^2 = 0.4$ ($\mu_{12} = 1.6$, $\mu_{13} = 0.65$, $\mu_{23} = 0.65$). Figure 8 represents a situation similar

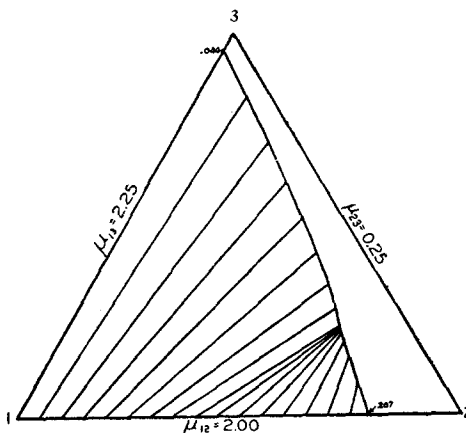FIG. 4.

to II, but with a sizeable range of complete miscibility, due to the smaller heat effects.

Case IIB. $A^2 = 0.55$, $B^2 = 0.55$ ($\mu_{12} = 2.2$, $\mu_{13} = 0.80$, $\mu_{23} = 0.80$). Figure 9 illustrates the analogous phase diagram for the case in which the two liquids are only partially miscible (as in Case IB). Here again a three-phase region exists.

DETERMINATION OF PLAIT POINTS

Exact determination of these diagrams for more than a few cases, even for the limit of infinite molecular weight, would be almost prohibitively difficult. Fortunately, one may obtain useful information by solving analytically for the plait point, which corresponds to the critical point in a binary system.

According to Gibbs,[13] one may obtain the coordinates of the plait point (or "critical phase" in his terminology) by solving two simultaneous equations, both expressed as secular determinants:

$$\begin{vmatrix} \dfrac{\partial^2 F}{\partial n_1{}^2} & \dfrac{\partial^2 F}{\partial n_1 \partial n_2} \\[2mm] \dfrac{\partial^2 F}{\partial n_1 \partial n_2} & \dfrac{\partial^2 F}{\partial n_2{}^2} \end{vmatrix} = U = 0, \qquad (20)$$

$$\begin{vmatrix} \dfrac{\partial U}{\partial n_1} & \dfrac{\partial U}{\partial n_2} \\[2mm] \dfrac{\partial_2 F}{\partial n_1 \partial n_2} & \dfrac{\partial^2 F}{\partial n_2{}^2} \end{vmatrix} = V = 0, \qquad (21)$$

where F in the above equation represents the total free energy of the system, and the n's numbers of molecules of the various components.

An entirely equivalent set of equations may be obtained in a perhaps more physically obvious

manner as follows: If we consider first not the limiting case of the plait point, but two separate conjugate phases, we find that in addition to Eqs. (13abc), another condition (not independent of these) is satisfied. This is that if one plots the total free energy along the extended tie line connecting the two conjugate phases, the two conjugate phases may be identified as the points where a straight line is tangent simultaneously.

If we now approach the limit of the plait point, we find that the two points of tangency approach each other and finally become identical. Such a situation is mathematically equivalent to the coalescence of two points of inflection, a situation which requires that the second and third derivatives vanish. In the phase diagram there is at the plait point a line tangent to the phase boundary which we may regard as the extension of a limiting tie line. If we define a variable q as the coordinate of a point along this line, we may write:

$$d^2 F/dq^2 = 0, \qquad (21a)$$

$$d^3 F/dq^3 = 0. \qquad (21b)$$

We may replace the total free energy, without loss of generality, by that per mole:

$$F = x_1 \Delta \bar{F}_1 + x_2 \Delta \bar{F}_2 + x_3 \Delta \bar{F}_3, \qquad (22)$$

where the x's represent mole fractions, and we may write the familiar Gibbs-Duhem-Margules relation as:

$$x_1 d\Delta \bar{F}_1 + x_2 d\Delta \bar{F}_2 + x_3 d\Delta \bar{F}_3 = 0. \qquad (23)$$

Using these relations, one may show that the conditions for the plait point are:

$$d\Delta \bar{F}_1/dq = 0, \qquad (24a)$$

$$d\Delta \bar{F}_2/dq = 0, \qquad (24b)$$

$$d\Delta \bar{F}_3/dq = 0, \qquad (24c)$$

$$(dx_1/dq) \cdot (d^2 \Delta \bar{F}_1/dq^2) + (dx_2/dq)(d^2 \Delta \bar{F}_2/dq^2)$$
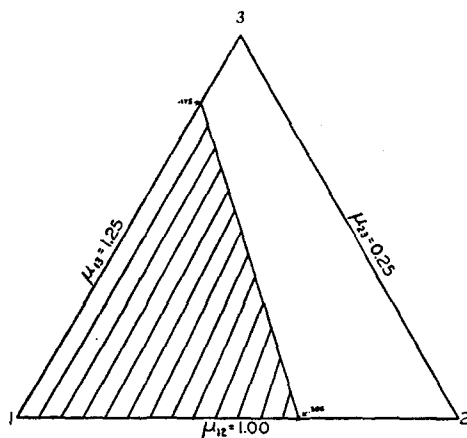$$+ (dx_3/dq)(d^2 \Delta \bar{F}_2/dq^2) = 0. \qquad (25)$$
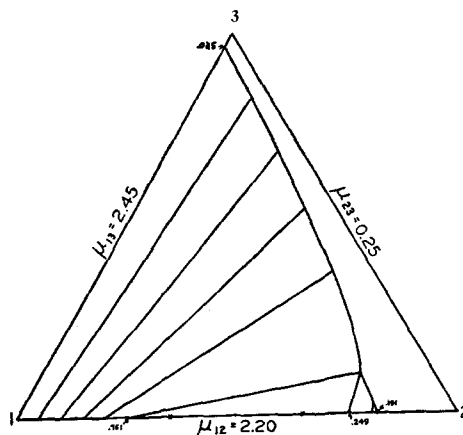
FIG. 5.

FIG. 6.

[13] J. Willard Gibbs, *Thermodynamics*, Vol. I of *Collected Works* (Longmans, Green, & Company, New York, 1931).

This gives us three independent equations[14] which permit us to solve for the coordinates of the plait point, and the slope of the tangent line.

By either method shown above, one is led upon substitution of Eqs. (9abc) to the following complicated expressions:

$$\phi_1+\phi_2+m\phi_3-2[\mu_{12}\phi_1\phi_2+m\mu_{13}\phi_1\phi_3 \\ +m\mu_{23}\phi_2\phi_3]+Qm\phi_1\phi_2\phi_3=0, \quad (26)$$

$$m\phi_3{}^2[(1-2\mu_{13}\phi_1)(1-\phi_1[\mu_{13}+\mu_{12}-\mu_{23}]) \\ +(1-2\mu_{23}\phi_2)(1-\phi_2[\mu_{23}+\mu_{12}-\mu_{13}])] \\ -(1-2\mu_{12}\phi_1\phi_2)^2+\phi_3[\mu_{12}(\phi_1{}^2+4\phi_1\phi_2+\phi_2{}^2) \\ +\mu_{13}(\phi_1{}^2-\phi_2{}^2)+\mu_{23}(\phi_2{}^2-\phi_1{}^2) \\ -2(\phi_1+\phi_2)-1]=0, \quad (27)$$

where

$$Q=2\mu_{12}\mu_{13}+2\mu_{12}\mu_{23}+2\mu_{13}\mu_{23}-\mu_{12}{}^2-\mu_{13}{}^2-\mu_{23}{}^2. \quad (28)$$

If Eq. (4) holds true, Eqs. (11abc) for the μ's are valid, and on substitution of Eqs. (11abc) into Eq. (28), we obtain:

$$Q=4\mu^s(A+B)^2=4\mu^s\mu_{12}. \quad (29)$$

Since μ^s is positive, Q is necessarily positive unless Eq. (4) fails. Were μ^s zero (as in the original oversimplified Flory equation[7]), Q would vanish and Eqs. (26) and (27) would simplify. Negative values of Q are possible only if Eq. (4) is invalid. Since Eq. (4) is fairly satisfactory in the absence of dipoles, we shall expect to find negative values of Q only when one or more of the components, either polymer or liquid or both, are decidedly polar substances.

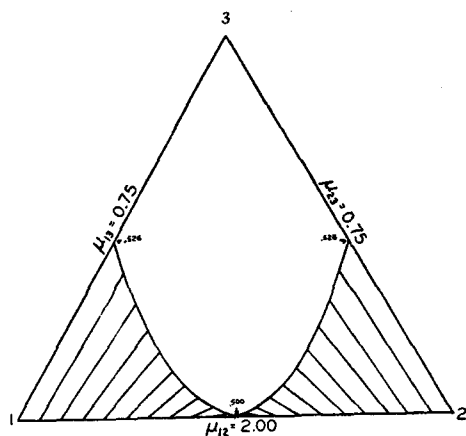The set of simultaneous equations (26) and (27) have a maximum of twelve possible solutions, of which two are spurious.[15]

FIG. 7.

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[14] Equations (24abc) are essentially the limiting case of Eqs. (13abc), but they do not represent at the limit, three independent equations, inasmuch as the third can be obtained from the other two by means of Eq. (23). Hence the need of Eq. (25).

[15] Two roots correspond to the points in the binary system 1,2 where the partial molal free energies are minima or maxima, and must be discarded. This does not exclude a real plait point if the binary system is at its critical solution temperature.
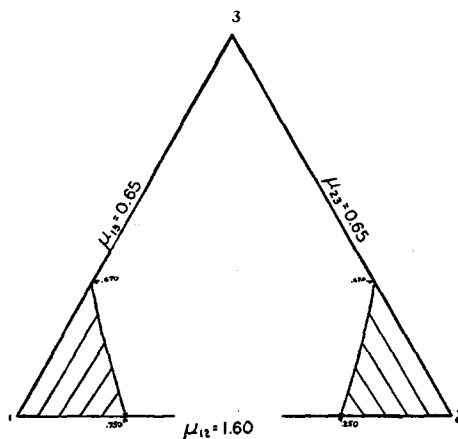

FIG. 8.

If $Q=0$, then there are only six possible solutions to the pair of simultaneous equations. This is not to say that in any real system there are ten (or six) different real roots. Some may be imaginary, and some degenerate. Others may be outside the triangular diagram and be without physical meaning.

For the moment, let us confine ourselves to the solutions of Eqs. (26) and (27) in the limit of extremely high molecular weight polymer $(m\to\infty)$. Two of the solutions are degenerate at the limit of infinite molecular weight, leaving a maximum of eight different solutions (or five for the case $Q=0$), which are given in Appendix I. Of these eight, for any given set of μ's, only a few, never more than three, are of physical significance. The most important correspond to the two solutions of the equations:

$$1-2\mu_{13}\phi_1-2\mu_{23}\phi_2+Q\phi_1\phi_2=0, \quad (30)$$

$$\phi_3=0. \quad (31)$$

The plait points indicated by crosses in Figs. 5–10 are solutions of these equations.

SOLUBILITY IN MIXED SOLVENTS

When a sufficiently small amount of a non-solvent is added to a solution, no phase separation results. However, as one increases the amount of non-solvent, a point is reached at which two phases appear, one rich in polymer, and we speak of "precipitation." For high molecular weights, this point, which may be called a "precipitation threshold" or a "critical solubility limit," is very sharp and represents the boundary between a region of complete miscibility of polymer and solvent mixture and a region where the solubility of the polymer is extremely small. It is easily seen that these limits are identical with the plait points calculated in the previous section. We may therefore use Eqs. (30) and (31) to define these limits.

There are, in general, either two real or two imaginary solutions to Eqs. (30) and (31). When
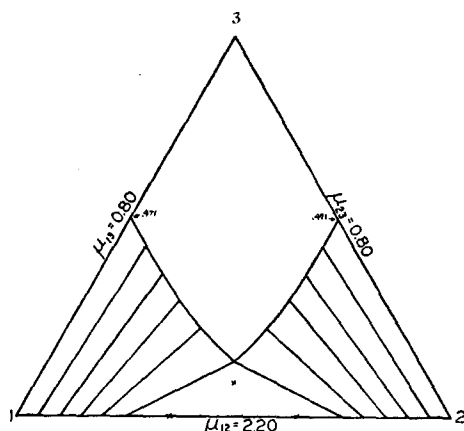
FIG. 9.

the roots are real, either or both may lie outside the diagram. Only real roots for which ϕ_1 and ϕ_2 lie between zero and one are of physical significance. The phase diagram will include two, one, or no critical solubility limits, depending on the number of such real roots.

Three different cases have to be distinguished, depending on the solvent properties of the two liquids.

(a) Both liquids solvents: Reference to the familiar problem of two components[8,16] shows that for both liquids to be solvents (i.e., miscible in all proportions with the polymer) the mathematical conditions are: $\mu_{13} < \frac{1}{2}$; $\mu_{23} < \frac{1}{2}$. For positive values of Q, there are no solutions between zero and one; which means the polymer is completely miscible with all possible solvent mixtures. If, however, $\mu_{12} > 2$ (which corresponds to a negative Q), the two liquids are themselves immiscible, and there will be an intermediate two-phase region.[17]

(b) One solvent; one non-solvent: In this familiar solvent-precipitant system, $\mu_{13} < \frac{1}{2}$, $\mu_{23} > \frac{1}{2}$ or, conversely, $\mu_{13} > \frac{1}{2}$, $\mu_{23} < \frac{1}{2}$. Normally, there is one, and only one, root between zero and one, corresponding to the one physically necessary in a transition between a solvent and non-solvent. See, for example, Figs. 4 and 5. As before, if $\mu_{12} > 2$, a region in which the two liquids are immiscible complicates the diagram, in one of several ways. For positive values of Q there is a three-phase region, as in Fig. 6. For negative values of Q, there may be two two-phase regions isolated from each other.

(c) Two non-solvents: For this system $\mu_{13} > \frac{1}{2}$, $\mu_{23} > \frac{1}{2}$. Under these conditions there are either zero or two solutions between zero and one. For negative Q's there are no such roots. For positive Q's there

[16] M. L. Huggins, J. Am. Chem. Soc. 64, 1712 (1942).
[17] In this case, the two solubility limits are not plait points; the plait point of the two-phase region is in the interior of the diagram corresponding to a different solution than those represented by Eqs. (30) and (31).

are two roots provided that:

$$\mu_{13} + \mu_{23} - 1 < \mu_{12} < 2 \qquad (32)$$

When $\mu_{12} > 2$, the situation is again complicated by the immiscibility of the two liquids. The significant conclusion is essentially that already obtained from Figs. 7 and 8—namely, that under certain circumstances (namely, those defined by Eq. (32)) mixtures of two non-solvents may be good solvents (i.e., show complete miscibility with the polymer).[18] While the conclusions from the first two cases are physically obvious, this was not.

Very similar conclusions were reached in an earlier treatment by Gee[19] based upon an equation similar to, but different from, our Eqs. (30) and (31). The relation between the two treatments will be discussed in Appendix II.

Of great significance is the fact that Gee showed experimentally in six cases that rubbers could be dispersed in appropriate mixtures of non-solvents, in agreement with the theoretical conclusions.

POLYMERS OF FINITE MOLECULAR WEIGHT

The previous sections have dealt exclusively with polymers of extremely high molecular weight or, strictly speaking, the limiting case of infinite molecular weight. Let us now examine the effect of finite molecular weight upon the conclusions already arrived at. Calculation of detailed phase diagrams for any but infinite molecular weights would be almost impossibly difficult. One may expect, however, that for reasonably high molecular weights the phase diagrams will be very similar to the limiting ones. We may appraise the magnitude of the difference by determining several points on the phase diagram: the two conjugate phases (if any) in the binary systems, polymer-liquid 1, and polymer-liquid 2, and the plait points of the system. The extent to which these differ from the corresponding points for $m \to \infty$ will illuminate the problem.

We cannot explicitly solve Eqs. (26) and (27) for finite molecular weights, but we may expand around the solution for $m = \infty$ and obtain solutions as series expansion in inverse powers of m. If we expand about the roots of Eqs. (30) and (31), we obtain a power series of $m^{-\frac{1}{2}}$. For the particular case (corresponding to Fig. 5), $\mu_{12} = 2.0$, $\mu_{13} = 2.25$, $\mu_{23} = 0.25$ ($Q = 2.0$), we obtain four such solutions, three of which are outside the phase diagram. The one solution of physical significance is:

$$\phi_1 = 0.2071 + (0.290/m^{\frac{1}{2}}) + \cdots, \qquad (33a)$$

$$\phi_2 = 0.7929 - (0.730/m^{\frac{1}{2}}) + \cdots, \qquad (33b)$$

$$\phi_3 = (0.440/m^{\frac{1}{2}}) + \cdots. \qquad (33c)$$

[18] This effect is not entirely precluded for $\mu_{12} > 2$. Even here a small region of complete solubility may exist. The mathematical conditions for this are far more complicated.
[19] G. Gee, Trans. Faraday Soc. 40, 468 (1944).

Using these equations for the plait point, the phase boundaries for various molecular weights have been estimated, and are shown in Fig. 10. As one can easily see, above molecular weights of 10,000 ($m=100$), the diagrams are almost indistinguishable from the limiting case. This is in agreement with the well-known features of fractional precipitation in which, after the precipitation threshold is reached, a few more drops of precipitant suffice to bring down successive fractions.

For Case IA a similar situation holds. Solving the equations, one finds for the plait point:

$$\phi_1 = 0.3660 + (0.534/m^{\frac{1}{3}}) + \cdots, \quad (34a)$$

$$\phi_2 = 0.6340 - (1.173/m^{\frac{1}{3}}) + \cdots, \quad (34b)$$

$$\phi_3 = (0.639/m^{\frac{1}{3}}) + \cdots. \quad (34c)$$

These are very similar to Eqs. (33abc), except that the change with molecular weight is greater, in agreement with the lowered sensitivity of milder precipitants.

The existence of expansions such as Eqs. (33) and (34) does not guarantee the existence of a plait point for all values of m; below certain values of m, the series may no longer converge—in which case the plait point does not exist. Equation (33) is a case in point; for very low values of m (below about 10), it does not converge.

THREE-PHASE REGIONS

We may regard a three-phase region as resulting from the overlapping of three two-phase regions, one corresponding to each side of the triangle. With each two-phase region is associated a plait point, so we may consider the existence of three real non-degenerate solutions to the plait point equation as a necessary (but not always sufficient) condition for a three-phase region. For $m = \infty$, a consideration of the eight possible solutions (Appendix I) shows that for there to be three real solutions, μ_{12} must exceed 2.0, corresponding to the physically obvious requirement that the two liquids 1 and 2 be only partially miscible. For finite molecular weights, however, a small three-phase region may persist for values of μ_{12} slightly less than 2.0. Since these regions are small and vanish rapidly[20] with decreasing μ_{12}, they may largely be ignored.

The existence of three real mathematical solutions to the plait point equation does not necessitate their existence as physically real plait points. Some, or all, may be inside the three-phase region. The

three plait points required by a three-phase region are shown by crosses for Cases IB and IIB in Figs. 6 and 9.

OSMOTIC PRESSURES IN MIXED SOLVENTS

The success of the theories of Huggins and Flory et al.[1-10] in explaining the osmotic pressures of high polymer solutions suggests that the treatment of three-component systems developed in the preceding pages be applied to the interpretation of osmotic pressures in mixed solvents.

Thermodynamic equilibrium is reached only when the partial molal free energy of each of the diffusible components is the same on both sides of the membrane. Mathematically, these conditions are expressed in Eqs. (35a) and (35b), where the zero superscript indicates the polymer-free phase:

$$\ln\phi_1{}^0 + \mu_{12}(\phi_2{}^0)^2 = \ln\phi_1 + [1 - (1/m)]\phi_3 + \mu_{12}\phi_2{}^2 \\ + \mu_{13}\phi_3{}^2 + (\mu_{12} + \mu_{13} - \mu_{23})\phi_2\phi_3 + (\pi V_0/RT), \quad (35a)$$

$$\ln\phi_2{}^0 + \mu_{12}(\phi_1{}^0)^2 = \ln\phi_2 + [1 - (1/m)]\phi_3 + \mu_{12}\phi_1{}^2 \\ + \mu_{23}\phi_3{}^2 + (\mu_{12} + \mu_{23} - \mu_{13})\phi_1\phi_3 + (\pi V_0/RT). \quad (35b)$$

No exact analytical expression for π can be obtained from equations of such a form, but we may obtain a solution in the form of a series expansion in powers of ϕ_3, the volume fraction of the non-diffusible polymer. Equation (36) gives the first two terms of such an expression (the derivation will be found in Appendix II).

$$\frac{\pi V_0}{RT} = \frac{\phi_3}{m} \\ + \frac{1 - 2\mu_{13}\phi_1{}^0 - 2\mu_{23}\phi_2{}^0 + Q\phi_1{}^0\phi_2{}^0}{2(1 - 2\mu_{12}\phi_1{}^0\phi_2{}^0)}\phi_3{}^2 + \cdots. \quad (36)$$

At equilibrium the solvent ratios are not usually the same in both places. The relation between the two may be obtained again, as a series expansion in powers of ϕ_3:

$$\frac{\phi_1}{\phi_2} = \frac{\phi_1{}^0}{\phi_2{}^0}\left\{1 - \phi_3\frac{[\mu_{13} - \mu_{23} + \mu_{12}(\phi_1{}^0 - \phi_2{}^0)]}{(1 - 2\mu_{12}\phi_1{}^0\phi_2{}^0)} + \cdots\right\}. \quad (37)$$

We can see from this equation that true equilibrium requires the exchange of what may be rather considerable quantities of the two liquids. As Gee[21] has noted in a similar treatment to this one, it is hardly possible that the solvent distribution throughout the two cells of the osmometer reaches equilibrium in the short time required for a single osmotic pressure measurement. He suggests that equilibrium is set up between two thin layers in contact with the membrane. In such a situation, there would be a concentration gradient across the

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[20] For example, consider the case $\mu_{12} = 2$, $\mu_{13} = 2$, $\mu_{23} = 0$ ($Q=0$). For all values of m between 17.7 and ∞, there is a small three-phase region. If we let $\mu_{12} = \mu_{13}$ and decrease μ_{12}, these limits converge until the three-phase region vanishes absolutely at $\mu_{12} = \mu_{13} = 1.984$ and $m = 15.5$. Below this value of μ no three-phase region can exist for any value of m.

[21] G. Gee, Trans. Faraday Soc. 40, 463 (1944).

cells of the osmometer which would be gradually reduced by slow exchange through the membrane. After this initial quasi-equilibrium is reached, the osmotic pressure will change only slightly. (Mathematical analysis indicates that the further change in π depends only on higher powers of ϕ_3 than the second.) An alternative, and perhaps less probable, hypothesis involves the assumption that the initial quasi-equilibrium is reached by gross flow of the solvent mixture through the membrane until the total free energy per "mole" of the mixed liquids is equal on both sides, followed by subsequent disproportionation through the membrane. In such a hypothesis, the initial quasi-equilibrium is obtained without alternation of the solvent ratio $(\phi_1^0/\phi_2^0 = \phi_1/\phi_2)$, and we have a "single liquid" approximation. With these assumptions we obtain an osmotic pressure π^*, which we designate by an asterisk to distinguish it from the true equilibrium osmotic pressure:

$$(\pi^* V_0/RT) = \ln(1-\phi_3) + [1-(1/m)]\phi_3 + (\mu_{13}\phi_1^0 + \mu_{23}\phi_2^0 - \mu_{12}\phi_1^0\phi_2^0)\phi_3^2. \quad (38)$$

Expanding in powers of ϕ_3 for comparison with Eq. (36), we find:[22]

$$\frac{\pi^* V_0}{RT} = \frac{\phi_3}{m} + \frac{1-2\mu_{13}\phi_1^0 - 2\mu_{23}\phi_2^0 + 2\mu_{12}\phi_1^0\phi_2^0}{2}\phi_3^2 + \cdots. \quad (39)$$

We see that the first terms are identical and equivalent to van't Hoff's Law. The coefficients of the second term, while different, are, in both cases, essentially independent of molecular weight. Thus use of the familiar π/c vs. c extrapolation to determine the molecular weight is justified, whether π^* or the true osmotic pressure π is the measured quantity. For convenience we shall denote the coefficients of the second term in (36) and (39), a_2 and a_2^*, respectively, using the same convention as for π and π^*. Hence,

$$a_2 = \frac{1-2\mu_{13}\phi_1^0 - 2\mu_{23}\phi_2^0 + Q\phi_1^0\phi_2^0}{2(1-2\mu_{12}\phi_1^0\phi_2^0)}, \quad (40)$$

$$a_2^* = \frac{1-2\mu_{13}\phi_1^0 - 2\mu_{23}\phi_2^0 + 2\mu_{12}\phi_1^0\phi_2^0}{2}. \quad (41)$$

Figure 11 shows the variation of a_2 and a_2^* with the composition of the mixed solvent for the conditions of Case I ($\mu_{12} = 2.0$, $\mu_{23} = 0.25$, $\mu_{13} = 2.25$). The differences are marked, and presumably appropriate experimental measurements could determine

[22] If we apply the condition $V_1 = V_2$ to Eq. (18) of Gee's paper,[21] we obtain Eq. (39) rather than Eq. (36), although he did not consciously introduce the single liquid approximation. This anomaly is explained in Appendix II.

which represents the initial equilibrium. Measurement of the change in osmotic pressure over longer periods of times than those involved in the usual measurement would also be illuminating.

It should be noted that the numerator of a_2 is identical with (30), which defined the critical solubility limits for polymers of very high molecular weight. We may therefore conclude that at the critical solubility limit the osmotic pressure is zero (or, more accurately, that the second term, $a_2\phi_3^2$, is zero).

ACKNOWLEDGMENTS

APPENDIX I

The Ten Solutions of the Plait Point Equation

We have noted that there are ten possible solutions to the set of simultaneous equations (26) and (27). For $m = \infty$, these may be separated into various classes, as follows:

(1–4) For $m = \infty$ there are two solutions corresponding to the two roots of Eqs. (30) and (31), previously given:

$$1 - 2\mu_{13}\phi_1 - 2\mu_{23}\phi_2 + Q\phi_1\phi_2 = 0, \quad (30)$$

$$\phi_3 = 0. \quad (31)$$

Each of these roots is doubly degenerate, and for finite molecular weights there are four roots. If one expands in powers of $m^{-\frac{1}{2}}$, there are two pairs; within each pair, even powers of $m^{-\frac{1}{2}}$ are identical; odd powers have the same coefficients but opposite signs. One member of each pair corresponds to a negative ϕ_3 (i.e., is outside the diagram) and may be disregarded.

The above roots are imaginary unless the following conditions are satisfied:

$$(Q - 2\mu_{12})(Q - 4\mu_{13} - 4\mu_{23} + 2\mu_{12}) > 0.$$

The conditions under which these solutions are of physical significance have been discussed in detail previously.

For $Q = 0$ there are only two roots instead of four (or one at the limit $m = \infty$).

(5,6) Two more limiting solutions to the plait point equations are given by:

$$1 - 2\mu_{12}\phi_1\phi_2 = 0, \quad (43)$$

$$\phi_3 = 0. \quad (44)$$

We may obtain a solution for finite molecular weights by expanding in powers of m^{-1}. In so doing, we must avoid the spurious solutions (referred to in note 15) in which the solutions of Eqs. (43) and (44) are valid for all molecular weights, and all but the leading terms in the ex-

pansion vanish. In the true solutions the m^{-1} terms of ϕ_3 vanish, leaving the first non-zero term that in m^{-2}. Equal and opposite terms in m^{-1} exist, however, for ϕ_1 and ϕ_2.

Values of μ_{12} between 0 and $+2$ give only imaginary solutions to Eqs. (43) and (44). Negative values of μ_{12} give plait points outside the triangular diagram which are without physical meaning. Only for $\mu_{12} > 2$ are the plait points given by (43) and (44) of physical significance, and even then they are always inside a triangular three-phase region which they help to define.

(7–10) Four more solutions, for which, in general, ϕ_3 is not zero even in the limit $m = \infty$, correspond to the four possible sets of solutions to the equations:

$$1 - 2\mu_{13}\phi_1 - 2\mu_{23}\phi_2 + Q\phi_1\phi_2 = 0, \qquad (45)$$

$$(1 - 2\mu_{13}\phi_1)(1 - \phi_1[\mu_{13} + \mu_{12} - \mu_{23}])$$
$$+ (1 - 2\mu_{23}\phi_2)(1 - \phi_2[\mu_{23} + \mu_{12} - \mu_{13}]) = 0. \quad (46)$$

One of the four may be expressed explicitly:

$$\phi_1 = \frac{1}{\mu_{13} + \mu_{12} - \mu_{23}}, \qquad (47a)$$

$$\phi_2 = \frac{1}{\mu_{23} + \mu_{12} - \mu_{13}}, \qquad (47b)$$

$$\phi_3 = 1 - \frac{2\mu_{12}}{(\mu_{13} + \mu_{12} - \mu_{23})(\mu_{23} + \mu_{12} - \mu_{13})}. \quad (47c)$$

The other three solutions do not simplify except in special cases.

In the particular instance that $Q = 0$, we may set $\mu_{12} = (A + B)^2$, $\mu_{13} = A^2$, $\mu_{23} = B^2$. There are six solutions, including one pair which is degenerate at $m = \infty$. We tabulate these solutions here for $m = \infty$:

	ϕ_1	ϕ_2	ϕ_3
1,2	$\dfrac{1 - 2B^2}{2(A^2 - B^2)}$	$\dfrac{1 - 2A^2}{2(B^2 - A^2)}$	0
5	$\dfrac{1 + \left(1 - \dfrac{2}{(A+B)^2}\right)^{\frac{1}{2}}}{2}$	$\dfrac{1 - \left(1 - \dfrac{2}{(A+B)^2}\right)^{\frac{1}{2}}}{2}$	0
6	$\dfrac{1 - \left(1 - \dfrac{2}{(A+B)^2}\right)^{\frac{1}{2}}}{2}$	$\dfrac{1 + \left(1 - \dfrac{2}{(A+B)^2}\right)^{\frac{1}{2}}}{2}$	0
7	$\dfrac{1}{2A(A+B)}$	$\dfrac{1}{2B(A+B)}$	$1 - \dfrac{1}{2AB}$
8	$\dfrac{B}{2A^2(A+B)}$	$\dfrac{A}{2B^2(A+B)}$	$1 - \dfrac{A^2 - AB + B^2}{2A^2B^2}$.

APPENDIX II

Expansion of the Osmotic Pressure Equation

Given the thermodynamic equations for the partial molal free energies (Eq. (35ab)), we wish to obtain $\pi V_0/RT$ as a power series in ϕ_3:

$$\ln\phi_1^0 + \mu_{12}(\phi_2^0)^2$$

$$= \ln\phi_1 + \left(1 - \frac{1}{m}\right)\phi_3 + \mu_{12}\phi_2^2 + \mu_{13}\phi_3^2$$

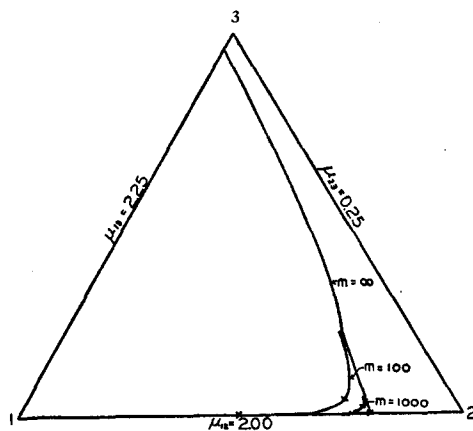$$+ (\mu_{12} + \mu_{13} - \mu_{23})\phi_2\phi_3 + \frac{\pi V_0}{RT}, \quad (35a)$$

FIG. 10.

$\ln\phi_2{}^0 + \mu_{12}(\phi_1{}^0)$

$$= \ln\phi_2 + \left(1 - \frac{1}{m}\right)\phi_3 + \mu_{12}\phi_1{}^2 + \mu_{23}\phi_3{}^2$$

$$+ (\mu_{12} + \mu_{23} - \mu_{13})\phi_1\phi_3 + \frac{\pi V_0}{RT}. \quad (35b)$$

We introduce a variable ϵ to relate the solvent ratios in the two cells, such that

$$\frac{\phi_1}{\phi_1 + \phi_2} = \frac{\phi_1}{1 - \phi_3} = \phi_1{}^0 + \epsilon, \quad (48a)$$

$$\frac{\phi_2}{\phi_1 + \phi_2} = \frac{\phi_2}{1 - \phi_3} = \phi_2{}^0 - \epsilon. \quad (48b)$$

We substitute in Eqs. (35ab) for ϕ_1 and ϕ_2, obtaining equations in terms of the variables π, $\phi_1{}^0$, $\phi_2{}^0$, ϕ_3, and ϵ.

$$\frac{\pi V_0}{RT} + \left(1 - \frac{1}{m}\right)\phi_3 + \ln(1 - \phi_3) + \ln\left(1 + \frac{\epsilon}{\phi_1{}^0}\right)$$

$$+ \mu_{12}[(\phi_2{}^0 - \epsilon)^2(1 - \phi_3)^2 - (\phi_2{}^0)^2] + \mu_{13}\phi_3{}^2$$

$$+ (\mu_{12} + \mu_{13} - \mu_{23})(\phi_2{}^0 - \epsilon)(1 - \phi_3)\phi_3 = 0. \quad (49a)$$

$$\frac{\pi V_0}{RT} + \left(1 - \frac{1}{m}\right)\phi_3 + \ln(1 - \phi_3) + \ln\left(1 - \frac{\epsilon}{\phi_2{}^0}\right)$$

$$+ \mu_{12}[(\phi_1{}^0 + \epsilon)^2(1 - \phi_3)^2 - (\phi_1{}^0)^2] + \mu_{23}\phi_3{}^2$$

$$+ (\mu_{12} + \mu_{23} - \mu_{13})(\phi_1{}^0 + \epsilon)(1 - \phi_3)\phi_3 = 0. \quad (49b)$$

We wish to eliminate ϵ and obtain π as a function of $\phi_1{}^0$, $\phi_2{}^0$, and ϕ_3. Anticipating that ϵ is proportional to ϕ_3 (and higher powers), as will later be shown, we expand Eqs. (49ab) in powers of ϕ_3 and
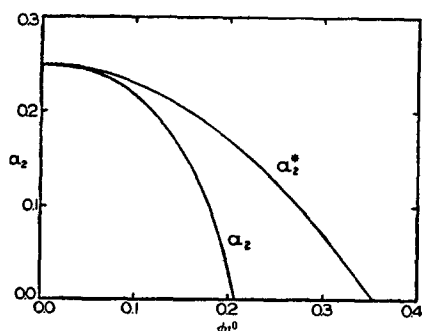
ϵ, dropping powers higher than $\phi_3{}^2$, $\phi_3\epsilon$, or ϵ^2:

$$\frac{\pi V_0}{RT} + \phi_3\left[(\mu_{12} + \mu_{13} - \mu_{23})\phi_2{}^0 - 2\mu_{12}(\phi_2{}^0)^2 - \frac{1}{m}\right]$$

$$+ \epsilon\left[\frac{1}{\phi_1{}^0} - 2\mu_{12}\phi_2{}^0\right] + \phi_3{}^2[\mu_{13}\phi_1{}^0 + \mu_{23}\phi_2{}^0$$

$$- \mu_{12}\phi_1{}^0\phi_2{}^0 - \tfrac{1}{2}] + \phi_3\epsilon[4\mu_{12}\phi_2{}^0 - (\mu_{12} + \mu_{13} - \mu_{23})]$$

$$+ \epsilon^2\left[-\frac{1}{2(\phi_1{}^0)^2} + \mu_{12}\right] + \cdots = 0. \quad (50a)$$

$$\frac{\pi V_0}{RT} + \phi_3\left[(\mu_{12} + \mu_{23} - \mu_{13})\phi_1{}^0 - 2\mu_{12}(\phi_1{}^0)^2 - \frac{1}{m}\right]$$

$$- \epsilon\left[\frac{1}{\phi_2{}^0} - 2\mu_{12}\phi_1{}^0\right] + \phi_3{}^2[\mu_{13}\phi_1{}^0 + \mu_{23}\phi_2{}^0$$

$$- \mu_{12}\phi_1{}^0\phi_2{}^0 - \tfrac{1}{2}] - \phi_3\epsilon[4\mu_{12}\phi_1{}^0 - (\mu_{12} + \mu_{23} - \mu_{13})]$$

$$+ \epsilon^2\left[-\frac{1}{2(\phi_2{}^0)^2} + \mu_{12}\right] + \cdots = 0. \quad (50b)$$

If we multiply Eq. (50a) by $\phi_1{}^0$, Eq. (50b) by $\phi_2{}^0$, and add, we eliminate the term in ϵ:

$$\frac{\pi V_0}{RT} - \frac{\phi_3}{m} + \phi_3{}^2[\mu_{13}\phi_1{}^0 + \mu_{23}\phi_2{}^0 - \mu_{12}\phi_1{}^0\phi_2{}^0 - \tfrac{1}{2}]$$

$$- \phi_3\epsilon[\mu_{13} - \mu_{23} + \mu_{12}(\phi_1{}^0 - \phi_2{}^0)]$$

$$+ \epsilon^2\left[\mu_{12} - \frac{1}{2\phi_1{}^0\phi_2{}^0}\right] + \cdots = 0. \quad (51)$$

Alternatively, we substract Eq. (50b) from Eq. (50a), eliminating π:

$$\phi_3[\mu_{13} - \mu_{23} + \mu_{12}(\phi_1{}^0 - \phi_2{}^0)]$$

$$+ \epsilon\left[\frac{1}{\phi_1{}^0\phi_2{}^0} - 2\mu_{12}\right] + \phi_3\epsilon[2\mu_{12}]$$

$$+ \epsilon^2\left[\frac{\phi_1{}^0 - \phi_2{}^0}{2(\phi_1{}^0)^2(\phi_2{}^0)^2}\right] + \cdots = 0, \quad (52)$$

or

$$\epsilon = -\phi_3 \frac{[\mu_{13} - \mu_{23} + \mu_{12}(\phi_1{}^0 - \phi_2{}^0)]\phi_1{}^0\phi_2{}^0}{1 - 2\mu_{12}\phi_1{}^0\phi_2{}^0} + \cdots. \quad (53)$$

Since ϵ occurs only in square terms in Eq. (51), we need only use the first term of the expansion in Eq. (53). Substituting for ϵ in Eq. (51), we obtain the desired equation:

$$\frac{V_0}{RT} = \frac{\phi_3}{m}$$

$$+ \frac{1 - 2\mu_{13}\phi_1{}^0 - 2\mu_{23}\phi_2{}^0 + Q\phi_1{}^0\phi_2{}^0}{2(1 - 2\mu_{12}\phi_1{}^0\phi_2{}^0)}\phi_3{}^2 + \cdots. \quad (36)$$

We may obtain ϕ_1, ϕ_2 and the ratio ϕ_1/ϕ_2 as functions of ϕ_1^0, ϕ_2^0, and ϕ_3:

$$\phi_1 = (\phi_1^0 + \epsilon)(1 - \phi_3) = \phi_1^0$$

$$- \phi_3 \left[\phi_1^0 + \frac{\mu_{13} - \mu_{23} + \mu_{12}(\phi_1^0 - \phi_2^0)}{1 - 2\mu_{12}\phi_1^0\phi_2^0} \right] + \cdots. \quad (54a)$$

$$\phi_2 = (\phi_2^0 - \epsilon)(1 - \phi_3) = \phi_2^0$$

$$- \phi_3 \left[\phi_2^0 + \frac{\mu_{23} - \mu_{13} + \mu_{12}(\phi_2^0 - \phi_1^0)}{1 - 2\mu_{12}\phi_1^0\phi_2^0} \right] + \cdots. \quad (54b)$$

$$\frac{\phi_1}{\phi_2} = \frac{\phi_1^0 + \epsilon}{\phi_2^0 - \epsilon} = \frac{\phi_1^0}{\phi_2^0}$$

$$\times \left(1 - \phi_3 \frac{[\mu_{13} - \mu_{23} + \mu_{12}(\phi_1^0 - \phi_2^0)]}{(1 - 2\mu_{12}\phi_1^0\phi_2^0)} + \cdots \right). \quad (37)$$

We have noted that Gee,[21] although starting with equations entirely equivalent to our Eq. (35ab) did not obtain an equation equivalent to our Eq. (39), but rather a single liquid approximation equivalent to our Eq. (36).

This discrepancy is apparently due to the introduction of a variable r (analogous to our ϵ), and in the subsequent expansion retaining no powers of r higher than the first. This is tantamount to dropping the $\phi_3\epsilon$ and ϵ^2 terms from Eq. (51). But since $\epsilon \sim \phi_3$, there is no justification for dropping these terms unless the ϕ_3^2 term is dropped also. If one solves Gee's Eq. (14), retaining terms in r^2, one obtains an equation entirely equivalent to our Eq. (36), if $V_1 = V_2$ (i.e., setting Gee's variable $l = 1$).

Gee's treatment of solubility [19] depends upon his assumption that the ϕ_3^2 term in π vanishes at the critical solubility limit (an assumption which we have proved to be correct). Since he inadvertently calculated a_2^*, rather than a_2, his results, while in qualitative agreement with ours, are not exactly equivalent, to the extent that $a_2^* \neq a_2$.

The Thermodynamics of High Polymer Solutions. V. Phase Equilibria in the Ternary System: Polymer 1—Polymer 2—Solvent*

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A thermodynamic analysis of phase equilibria similar to that developed in Part IV when applied to the ternary system of two polymers and a solvent leads to an explanation of the usual incompatibility of different high polymers in solution. Unless their heat of mixing is virtually zero or negative, two high polymers are always immiscible in the absence of a solvent; the primary role of the solvent is non-specific, merely one of diluting the polymer mixture and decreasing the heat of interaction of the polymers. The recent experiments of Dobry and Boyer-Kawenoki show reasonable agreement with these theoretical conclusions. Osmotic pressures of mixed polymers are discussed; such measurements would permit determination of μ_{12}, the interaction constant of the two polymers.

INTRODUCTION

THE incompatibility of certain high polymers in solution is a phenomenon long familiar to polymer chemists, especially in the fields of paints and varnishes. Recently, Dobry and Boyer-Kawenoki[1] have examined phase separation for a large number of three-component systems, and find incompatibility of two polymers in the same solvent to be the normal situation. The application of thermodynamic analysis to the ternary systems involving one polymer and two liquids[2] suggests the extension of such a treatment to the corresponding system of two polymers and one solvent.

THE TWO POLYMER SYSTEM

First let us consider a mixture of two chain polymers in the absence of a solvent. (We ignore the mechanical problems involved and assume that equilibrium is reached somehow.) Flory,[3] Scott and Magat,[4] and Guggenheim[5] have derived expressions for the free energy of mixtures of polymers of different molecular weight. The equations of Flory and of Scott and Magat, although based

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