Vapor-Liquid Equilibrium Calculations for Concentrated Polymer Solutions

The free-volume theory of polymer solutions initiated by Prigogine and developed by Flory and Patterson is reduced to practice. This theory, which represents a substantial improvement over the older theory of Flory and Huggins, facilitates calculation of solvent activities in polymer solutions from a minimum of experimental binary data. However, it is necessary to characterize each pure component with three molecular parameters which can be obtained from PVT data; such data, unfortunately, are often unavailable. Nevertheless, using reasonable approximations based on Bondi's correlations as needed, molecular parameters are given for 22 solvents and for 16 polymers. Binary parameters are given for 20 systems. Illustrative examples are presented.

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SCOPE

Polymer processing often occurs in the dissolved state, and it is therefore of practical importance in polymer-process design to know the vapor pressure of the solvent as a function of its concentration in the polymer-solvent solution. Such vapor pressures can be calculated from a theory of polymer solutions with only limited experimental data.

The well-known theory of Flory and Huggins, now 30 years old, has serious deficiencies and often gives poor results. An improved theory, first suggested by Prigogine, has been developed by several polymer chemists, notably Flory and Patterson. This paper discusses the new theory and shows how it may be used in practical design work. Toward that end, molecular parameters required for numerical results are given for a series of solvents, polymers, and binary systems.

CONCLUSIONS AND SIGNIFICANCE

The statistical-mechanical theory of Prigogine is useful for calculating solvent vapor pressures in polymer solutions containing nonpolar (or slightly polar) components. Compared to the older lattice theory, this free-volume theory gives a better estimate of the effect of solvent concentration on solvent activity. It is simple to use provided all necessary parameters are available: three molecular parameters are needed for each pure component but only one binary parameter is required. The three pure-component parameters are determined from PVT data (density as a function of temperature and pressure). These are often not at hand but reasonable estimates can sometimes be made using Bondi's correlations. In this work pure-component parameters are given for 22 common solvents and for 16 polymers. Binary parameters are presented for 20 systems. The simplified form of the Prigogine-Flory theory, as given here, is useful for calculating solvent vapor pressures as needed in polymer-process design.

Industrial polymers comprise a large fraction of the economic value of all manufactured chemicals. Polymers are often processed in solution; therefore, rational design of polymer processes often requires calculation of phase equilibria in polymer solutions.

We discuss here a theoretical treatment of polymer solution thermodynamics which can be used to calculate solvent partial pressures in binary, polymer/solvent solutions using only limited data. The partial pressure of a solvent is of practical interest in design of solvent-removal processes.

The theoretical treatment, here modified for engineering application, is based on the work of Prigogine (1953a, 1953b; 1957) and Flory (1965). For reliable application, this treatment is at present limited to the solvent concentration range of approximately 20 to 80 weight % solvent and to pressures near or below atmospheric. For practical results, the theory requires three molecular parameters for each pure component as well as one parameter characterizing binary interactions. We have determined pure-component and binary parameters for a number of systems containing common solvents and common polymers.

CONCENTRATION SCALES

We are concerned with binary solutions of polymer (subscript 2) and a relatively low-molecular-weight solvent (subscript 1). Mole fractions (x) provide an inconvenient measure of concentration for such solutions because the molecular weight of the polymer is large compared to that of the solvent. As a result, the mole

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fraction of polymer in solution is usually very small even though the weight (or volume) fraction may be close to unity.

There are four concentration scales which are convenient to use when calculating thermodynamic properties of polymer solutions: weight fraction w, volume fraction Φ, segment fraction Ψ, and site fraction θ. The basic units of measure for w, Φ, Ψ, and θ are, respectively, mass m, molar volume v, number of segments r, and number of intermolecular contact sites per segment s. (The quantity s is similar to coordination number). The concentrations Φ, Ψ, and θ are given by

$$\Phi_1 = (1 - \Phi_2) = \frac{x_1 v_1}{x_1 v_1 + x_2 v_2} \tag{1a}$$

$$\Psi_1 = (1 - \Psi_2) = \frac{x_1 r_1}{x_1 r_1 + x_2 r_2} \tag{1b*}$$

$$\theta_1 = (1 - \theta_2) = \frac{x_1 s_1}{x_1 s_1 + x_2 s_2} \tag{1c}$$

FLORY-HUGGINS POLYMER SOLUTION THEORY

The well-known Flory-Huggins theory (Flory, 1942, 1953; Huggins, 1942; Guggenheim, 1952; Prausnitz, 1969) proposed that there are two major contributions to the thermodynamic properties of binary polymer/solvent solutions: an entropy of athermal mixing and an enthalpy of mixing which is due to differences in intermolecular forces. The contributions of intermolecular forces are approximated in the Flory-Huggins theory by an empirical van Laar term. The solvent activity given by the Flory-Huggins theory is

$$a_1 = \Psi_1 \exp\left[(1 - r_1/r_2)\Psi_2 + \chi_\Psi \Psi_2^2\right] \tag{2}$$

The empirical parameter χ_Ψ is assumed to be independent of concentration. However, when that parameter is calculated from experimental activity data, it is found to vary considerably with concentration, as illustrated in Figure 1 for three binary systems. The variation of χ_Ψ with concentration is a result, in part, of the crude nature of the intermolecular force (van Laar) term in the theory.

The Flory-Huggins theory was derived on the basis that each polymer consists of a number of segments, leading to the use of segment fractions. However, the approximation often made is that $r_1/r_2 \cong v_1/v_2$; in that case segment fraction reduces to volume fraction. Thus, Equation (2) becomes

$$a_1 = \Phi_1 \exp\left[(1 - v_1/v_2)\Phi_2 + \chi_\Phi \Phi_2^2\right] \tag{3}$$

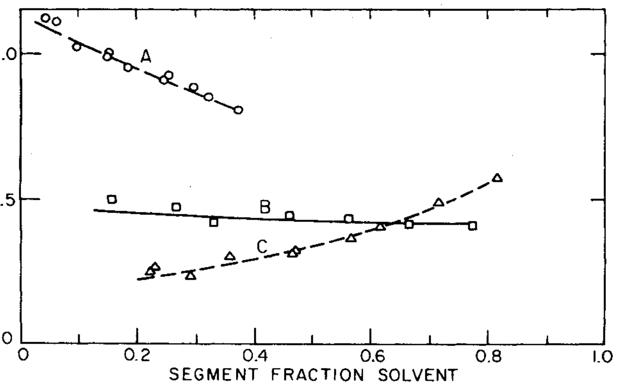

Fig. 1. Variation of interaction parameter χ with solvent concentration: A—polyisobutylene/benzene, 25°C (Eichinger and Flory, 1968); B—polyethylene/heptane, 109.9°C (van der Waals and Hermans, 1950); C—polystyrene/chloroform, 25°C (Bawn and Wajid, 1956).

The empirical parameters χ_Φ and χ_Ψ are not equal but usually differ by less than 20%. Both parameters vary with concentration, although in some systems (for example, n-heptane/polyethylene at 110°C) that variation is small.

The Flory-Huggins theory, assuming constant χ, gives only a rough representation of the activities of polymer solutions with one adjustable parameter. Since the Flory-Huggins theory is based on a rigid lattice model, it gives no equation of state. It assumes that isobaric, isothermal mixing of solvent and polymer occurs with no change of volume. An improved representation of polymer-solution properties is given by the Prigogine-Flory theory which takes volumetric factors into account.

PRIGOGINE-FLORY THEORY OF POLYMER SOULTIONS

The thermodynamic properties of pure fluids and mixtures obtained from statistical mechanics can be divided into two categories: combinatorial and noncombinatorial (Flory, 1965). The entropy of athermal mixing is a combinatorial property, while PVT properties due to intermolecular forces are noncombinatorial. The combinatorial contribution in the Flory-Huggins theory is the simplest formulation available for practical use. However, the Flory-Huggins estimate of noncombinatorial contributions is crude.

Prigogine et al. (1953a, b; 1957) developed a corresponding states theory for polymer solutions which attempts to account for noncombinatorial contributions in a more rigorous and realistic way than does the Flory-Huggins theory. The Prigogine theory, together with the Flory-Huggins combinatorial contribution (the entropy of athermal mixing), gives the most accurate representation of polymer solutions presently available for practical calculations.

The major difference between the Prigogine theory and other theories occurs in treating the degrees of freedom in the system. In the Prigogine theory, the total number of degrees of freedom of the system is divided into two categories: internal and external. Internal degrees of freedom are those which are (essentially) unaffected by the presence of neighbors, while external degrees of freedom are those which are significantly affected by the presence of neighbors. For example, translational motions of the molecules are external degrees of freedom at all densities and internal rotations tend to be external degrees of freedom at high densities. High-frequency vibrations, however, are (essentially) unaffected by the presence of neighbors and therefore they are considered internal degrees of freedom. Prigogine et al. (1953a, b; 1957) postulate than an assembly of N_2 chain molecules (containing r_2 segments each) behaves as if it were an assembly of $r_2 c_2 n_2$ spherical molecules containing one segment each; $3c_2$ is the number of external degrees of freedom per segment. We present here a simplified form of Flory's version (Flory, 1965) of the Prigogine theory.

PURE COMPONENTS

The configurational partition function for a pure fluid is

$$Q = g(N_1)(\lambda v^*)^{rcN}(\tilde{v}^{1/3} - 1)^{3rcN} \exp(-E_o/kT) \tag{4}$$

From (4) one obtains the reduced equation of state (Flory, 1965):

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[*] An equivalent, but more useful, definition of Ψ is given immediately after equation (15).

$$\frac{\tilde{p}\tilde{\nu}}{\tilde{T}} = \frac{\tilde{\nu}^{1/3}}{\tilde{\nu}^{1/3} - 1} - \frac{1}{\tilde{\nu}\tilde{T}} \tag{5}$$

At low pressure, the left side of Equation (5) is negligible, and the equation of state reduces to

$$\tilde{T} = \frac{\tilde{\nu}^{1/3} - 1}{\tilde{\nu}^{4/3}} \tag{6}$$

Pressure, temperature, and volume are reduced, respectively, by characteristic pressure p^*, characteristic temperature T^*, and characteristic specific volume v^*_{sp}. These parameters are related by

$$p^* \left(\frac{M v^*_{sp}}{r N_A} \right) = ckT^* \tag{7}$$

The parameter v^*_{sp} is the hard-core volume of one gram of fluid. The parameter T^* is a measure of the potential energy per external degree of freedom. The parameter p^* is a characteristic potential energy density.

The parameters p^*, T^*, and v^*_{sp} can be obtained from PVT data for the pure fluid, as discussed later.

BINARY MIXTURES

Flory (1965) uses a one-fluid corresponding states theory for mixtures. The configurational partition function becomes

$$Q = g(N_1, N_2)(\lambda \nu^*)^{rcN}(\tilde{\nu}^{1/3} - 1)^{3rcN} \exp(-E_o/kT) \tag{8}$$

where $\tilde{\nu}$ is the reduced volume of the mixture and where all parameters without subscript refer to the mixture. The equation of state is formally unchanged. It is assumed that Equation (8) is valid for all compositions; it ignores any effects of crystallinity. In most moderately concentrated polymer solutions this effect has small influence on thermodynamic properties (Flory, 1953).

By analogy with the pure components, we require that

$$p^* \left(\frac{M_1 v_1^*{}_{sp}}{N_A r_1} \right) = ckT \tag{9}$$

where we have asumed that

$$c = \Psi_1 c_1 + \Psi_2 c_2 \tag{10}$$

As shown by Flory (1965), we can obtain an approximate expression for E_o by accounting for all binary contacts in solution and by assuming random mixing of segments. Further, we assume that all segments in the mixture have equal surface areas of contact; this leads to

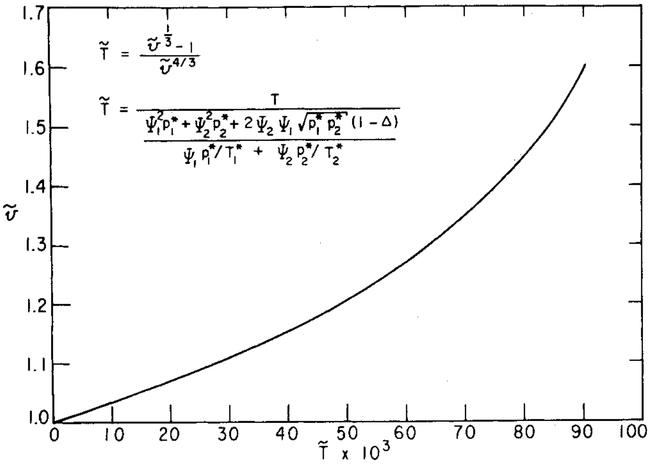

Fig. 2. Reduced volume from the Flory equation of state at zero pressure.

$$\frac{-E_0}{r_1 N_1 + r_2 N_2} = \frac{p^*}{\tilde{\nu}} \left(\frac{M_1 v_1^*{}_{sp}}{r_1 N_A} \right) \tag{11}$$

where

$$p^* = \Psi_1^2 p_1^* + \Psi_2^2 p_2^* + 2\Psi_1 \Psi_2 p_{12}^* \tag{12}$$

and

$$p_{12}^* = (p_1^* p_2^*)^{1/2}(1 - \Delta)$$

The binary parameter Δ indicates deviation from the geometric-mean assumption for the binary interaction energy density p_{12}^*. Substituting Equations (12) and (10) into (9) gives

$$T^* = \frac{p^*}{\Psi_1 p_1^*/T_1^* + \Psi_2 p_2^*/T_2^*} \tag{13}$$

The reduced volume of the mixture $\tilde{\nu}$ must be obtained from Equation (5); it can be obtained graphically from Figure 2, a plot of $\tilde{T}$ versus $\tilde{\nu}$. A good first approximation for $\tilde{\nu}$ is given by

$$\tilde{\nu} = \Psi_1 \tilde{\nu}_1 + \Psi_2 \tilde{\nu}_2 \tag{14}$$

From Equation (8), at low or moderate pressures, the solvent activity is given by

$$a_1 = \Psi_1 \exp \left\{ (1 - r_1/r_2)\Psi_2 + \frac{p_1^* M_1 v_1^*{}_{sp}}{RT_1^*} \left[3 \ln\left(\frac{\tilde{\nu}_1^{1/3} - 1}{\tilde{\nu}^{1/3} - 1} \right) + 1/\tilde{T}_1(1/\tilde{\nu}_1 - 1/\tilde{\nu}) \right] + \frac{\Psi_2^2 M_1 v_1^*{}_{sp}}{RT\tilde{\nu}} (p_1^* + p_2^* - 2p_{12}^*) \right\} \tag{15}$$

where

$$\Psi_1 = w_1 v_1^*{}_{sp}/(w_1 v_1^*{}_{sp} + w_2 v_2^*{}_{sp}) = 1 - \Psi_2$$

$$\tilde{\nu}_1 = v_{1sp}/v_1^*{}_{sp}; \quad \tilde{\nu}_2 = v_{2sp}/v_2^*{}_{sp} \quad \text{(at solution temperature)}$$

We have chosen the standard state for a_1 to be that of pure, saturated solvent at solution temperature T. Since the parameter v^*_{sp} is a measure of molecular size, the segment ratio r_1/r_2 is given by

$$\frac{r_1}{r_2} = \frac{M_1 v_1^*{}_{sp}}{M_2 v_2^*{}_{sp}} \tag{16}$$

as suggested by Flory (1965). Thus, one must arbitrarily fix either r_1 or r_2 to determine the other. We have set r_1 equal to unity.

The parameter Δ is obtained from experimental activity coefficients, as described later.

It is useful to define Γ_1, a segment-fraction activity coefficient of the solvent, equal to a_1/Φ_1. As indicated by Equation (15), there are three contributions to $\ln \Gamma_1$: (1) an athermal, combinatorial contribution, $\ln \Gamma_1^{\text{ath}}$; (2) a free-volume contribution, $\ln \Gamma_1^{\text{f.v.}}$; and (3) an intermolecular force contribution, $\ln \Gamma_1^{\text{i.f.}}$. From Equation (15) we have

$$\ln \Gamma_1 = \ln \Gamma_1^{\text{ath.}} + \ln \Gamma_1^{\text{f.v.}} + \ln \Gamma_1^{\text{i.f.}} \tag{17}$$

$$\ln \Gamma_1^{\text{ath.}} = (1 - r_1/r_2)\Psi_2 \tag{18}$$

$$\ln \Gamma_1^{\text{f.v.}} = \frac{p_1^* M_1 v_1^*{}_{sp}}{RT_1^*} \left[3 \ln\left(\frac{\tilde{\nu}_1^{1/3} - 1}{\tilde{\nu}^{1/3} - 1} \right) + 1/\tilde{T}_1(1/\tilde{\nu}_1 + 1/\tilde{\nu}) \right] \tag{19}$$

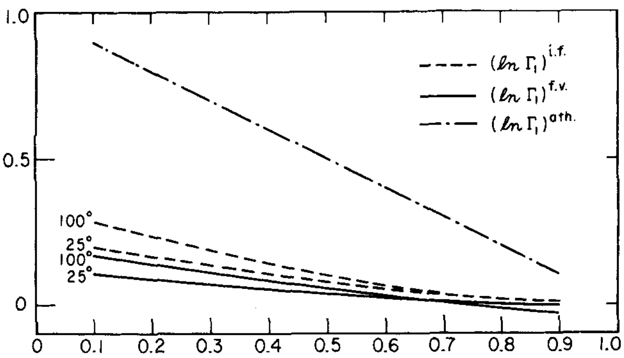

Fig. 3. Contributions to activity coefficient of benzene in cis-1,4-polyisoprene/benzene solutions ($\Delta = 0.010$ at 25°C; $\Delta = 0.002$ at 100°C).

$$\ln \Gamma_1^{\text{i.f.}} = \frac{\Psi_2^2 M_1 v_1{}^*_{sp}}{RT\tilde{v}} (p_1^* + p_2^* - 2p_{12}^*) \qquad (20)$$

To illustrate typical magnitudes of these three contributions, Figure 3 shows contributions to $\ln \Gamma_1$ for the system *cis*-1,4-polyisoprene/benzene at 25°C and 100°C. The athermal contribution is dominant, but the intermolecular force contribution is larger than the free volume contribution. The free volume and intermolecular force contributions increase with rising temperature for this system.

Figure 3 demonstrates why the Flory-Huggins theory of polymer solutions, despite its deficiencies, represents data well for many systems. The Flory-Huggins theory consists of an athermal term $\ln \Gamma_1^{\text{ath.}}$ plus an empirical term $\chi_\Psi \Psi_2^2$. The term $\chi_\Psi \Psi_2^2$ represents the effect of intermolecular forces, according to the Flory-Huggins theory. However, when $\chi_\Psi \Psi_2^2$ is determined by fitting the Flory-Huggins theory to experimental data, the term in fact represents the sum of $\ln \Gamma_1^{\text{f.v.}}$ and $\ln \Gamma_1^{\text{i.f.}}$. For systems in which $\ln \Gamma_1^{\text{ath.}}$ is much larger than $(\ln \Gamma_1^{\text{f.v.}} + \ln \Gamma_1^{\text{i.f.}})$, the Flory-Huggins theory accurately predicts $\ln \Gamma_1$. The system polyisoprene/benzene at 25°C is such a case. However, when $\ln \Gamma_1^{\text{f.v.}}$ and $\ln \Gamma_1^{\text{i.f.}}$ are of comparable importance to $\ln \Gamma_1^{\text{ath.}}$, the Flory-Huggins theory usually gives poor prediction of $\ln \Gamma_1$ because $\chi_\Psi \Psi_2^2$ provides too crude an estimate of contributions from differences in free volumes and intermolecular forces.

The Prigogine-Flory theory offers a quantitative attempt to calculate thermodynamic properties of polymer solutions taking into account differences in the extent of expansion (free volume) of the components. The Prigogine-Flory treatment leads to a corresponding states principle for polymer solutions from which, in principle, all excess thermodynamic properties can be obtained.

The Prigogine-Flory theory is, however, limited in application to dense fluid phases consisting of nonpolar or only slightly polar substances. If the Prigogine-Flory theory is used to model thermodynamic data for relatively expanded liquids (for example, saturated liquid *n*-pentane at 200°C), then the characteristic molecular parameters for pure substances obtained from such modeling lose much of their physical meaning even though experimental data can still be represented with good accuracy.

Flory (1965) shows that a simple relationship between the characteristic parameters exists:

$$p^* v^*_{sp} M = c R T^*$$

where M is molecular weight and $3c$ is now the number of external degrees of freedom per molecule. The lower limit for c is unity since an isolated, spherical molecule has 3 translational degrees of freedom ($3c = 3$) corresponding to three directions in which it can translate. Therefore, if the computed value of c ($= p^* v^*_{sp} M/RT^*$) is less than unity, the physical significance of the parameters is obscured and the physical basis of the theory is no longer justified. Values of c less than unity may be obtained from experimental data if the Prigogine-Flory theory is applied to fluids which are either not dense or highly polar or both. Highly polar compounds may interact with one another, decreasing the number of external degrees of freedom per molecule ($3c$) more than anticipated by the theory, while application of the theory over a large range of densities violates the assumed constancy of c.

VAPOR-LIQUID EQUILIBRIUM IN POLYMER SOLUTIONS

At equilibrium in a binary solution, the fugacity of the solvent vapor equals the fugacity of the solvent in solution:

$$f_1^{\text{vapor}} = f_1^{\text{liquid}} \qquad (21)$$

Since the polymer is nonvolatile, the vapor phase is pure solvent. We are interested only in low or moderate pressures; therefore, we use the virial equation of state to represent the behavior of the solvent vapor. The vapor-phase fugacity is given by (Prausnitz, 1969)

$$f_1^{\text{vapor}} = p_1 \exp\left(\frac{B_1 p_1}{RT}\right) \qquad (22)$$

TABLE 1. CHARACTERISTIC PARAMETERS FOR SOLVENTS[*]

Solvent (data source)	v^*_{sp}, ml/g	p^*, bar × 10^{-3}	T^*, °K × 10^{-3}	Temp. range, °C
Acetone (a, b)	1.02[†]	2.92	5.07	0-200
Acrylonitrile (a, b)	1.00[†]	4.48	5.06	0-200
Benzene (a, c)	0.890	5.77	4.78	0-200
Carbon tetrachloride (c)	0.487	5.66	4.70	−20-70
Chlorobenzene (d)	0.734	5.91	5.55	25-150
Chloroform (a, b)	0.546[†]	3.21	5.28	0-200
Cyclohexane (e, f, h)	1.02	5.13	5.06	0-200
1,2-dichloroethane (a, b)	0.656[†]	4.99	5.44	−15-200
Diethyl ether (a, b)	1.06	2.51	4.31	0-120
Dimethyl formamide (b, m)	0.917	4.31	6.24	0-190
p-dioxane (a, b)	0.806[†]	3.37	5.73	0-200
Ethyl acetate (a, b)	0.897	4.89	4.82	0-200
Ethyl benzene (a, j)	0.926	5.37	5.21	15-90
Ethylene glycol (i)	0.776	8.25	6.36	25-200
n-heptane (a, c)	1.14	3.85	4.84	0-200
Methyl ethyl ketone (a, k)	0.958	5.73	4.59	10-60
Nitrobenzene (d)	0.696	7.11	6.11	25-150
n-pentane (a, b)	1.22	2.66	4.33	0-200
Styrene (a, b)	0.923	5.64	5.92	0-200
2,2,4-trimethylpentane (a, b)	1.13	4.56	4.84	0-180
Vinyl acetate (b, l)	0.863[†]	3.87	5.12	0-200
p-xylene (b)	0.971	5.05	5.93	0-200

Data Sources: (a) Timmermans, 1950; 1965; (b) Bondi, 1968; (c) Rowlinson, 1969; (d) Gibson and Loeffler, 1939; (e) Wood and Gray, 1952; (f) Abe and Flory, 1965; (g) Höcker et al., 1971a; (h) Höcker et al., 1971b; (i) Gibson and Loeffler, 1941; (j) Höcker and Flory, 1971; (k) Flory and Höcker, 1971; (l) Perry's Chemical Engineer's Handbook, 1950; (m) Du Pont Product Information Bulletin.

[†] Correlation of Bondi adjusted to fit one experimental datum.

[*] Some values of c (per molecule) computed from characteristic parameters in Table 1 are slightly less than unity for reasons discussed in the text.

The fugacity in the liquid is given by

$$f_1^{\text{liquid}} = \Omega_1 w_1 p_1^{\text{sat}} \exp\left(\frac{B_1 p_1^{\text{sat}}}{RT}\right) \tag{23}$$

or

$$f_1^{\text{liquid}} = \Gamma_1 \Psi_1 p_1^{\text{sat}} \exp\left(\frac{B_1 p_1^{\text{sat}}}{RT}\right) \tag{24}$$

where Ω_1 is an activity coefficient based on weight fraction, and Γ_1 is based on segment fraction. In Equations (23) and (24), the standard-state fugacity is that of the pure saturated liquid at system temperature T. The activity coefficient Ω_1 is more suitable as a fundamental quantity found directly from experimental data, while Γ_1 is more easily related to theory. The numerical difference between Ω_1 and Γ_1 at a given solvent concentration is usually less than 20%.

PURE-COMPONENT PARAMETERS

Following Flory (1965), the pure-component characteristic parameters p^*, v^*_{sp}, and T^* can be obtained from PVT data for each pure substance. We omit subscripts in this section, since here we refer only to pure components. We assume that these parameters are independent of temperature and density over the experimental range of temperature and density used in their determination.

HARD-CORE VOLUME

Differentiating (5), the pure-component equation of state, with respect to temperature at constant pressure and taking the limit as pressure goes to zero, we obtain

$$\alpha \equiv 1/v \left(\frac{\partial v}{\partial T}\right)_p = \frac{3\tilde{\nu}^{1/3} - 3}{4T - 3\nu^{1/3} T} \tag{25}$$

The parameter v^*_{sp} was obtained from Equation (25) by minimizing the sum of the squares of the percent deviations between calculated and experimental values of α over a range of temperature. Note that α used *in* (25) is the zero-pressure limit of α, which is equivalent to α obtained at atmospheric pressure.

TABLE 2. CHARACTERISTIC PARAMETERS FOR POLYMERS

Polymer (data source)	v^*_{sp}, ml/g	p^*, bar × 10^{-3}	T^*, °K × 10^{-3}	Temp. range, °C
Polyacrylic acid (a)	0.694	9.07	7.27	0-200
Polyacrylonitrile (a,b)	0.816†	7.27	28.6	0-200
Poly-*n*-butylmethacrylate (a, d)	0.832	6.50	8.01	0-200
Polychloroprene (a, d)	0.702†	7.60	7.60	0-200
Polydimethylsiloxane (a, c)	0.861	3.35	5.10	0-130
Polyethylacrylate (a, c)	0.728	5.70	6.58	20-150
Polyethylene, high density (e)	1.04	4.40	7.37	115-160
Polyethylene, low density (a, f)	0.999	6.50	6.80	90-125
Polyethylene oxide (g)	0.753	6.72	6.45	45-70
Polyisobutylene (h)	0.954	4.41	7.87	0-150
cis-1,4-polyisoprene (a, i)	0.932††	5.22	7.46	25-150
Polymethylmethacrylate (a, c)	0.762	11.4	11.4	25-150
Polypropylene, atactic (a, c)	1.00	5.59	6.94	0-200
Polystyrene, atactic (j)	0.817	5.34	7.97	0-200
Polyvinyl acetate (a, c)	0.729	6.96	7.40	20-180
Polyvinyl chloride (a, d)	0.624†	8.76	7.96	0-200

Data Sources: (a) Bondi, 1968; (b) Walker, 1952; (c) McGowan, 1969; (d) Lewis, 1968; (e) Orwoll and Flory, 1967; (f) Polymer Handbook; (g) Booth and Devoy, 1971; (h) Eichinger and Flory, 1968a; (i) Wood and Martin, 1964; and (j) Höcker et al., 1971a.

† Correlation of Bondi adjusted to reproduce amorphous density below melting temperature.

†† Correlation of Bondi adjusted to reproduce one experimental density datum.

CHARACTERISTIC TEMPERATURE, T*

Equation (6) can be rearranged to give

$$T = T^* \left(\frac{\tilde{\nu}^{1/3} - 1}{\tilde{\nu}^{4/3}}\right) \tag{26}$$

Using previously found values of v^*_{sp}, the parameter T^* was obtained over a range of temperature from Equation (26) by minimizing the sum of the squares of the % deviations between calculated and experimental temperatures.

CHARACTERISTIC PRESSURE, p*

Differentiating (5) with respect to temperature, holding volume constant, and taking the limit as pressure goes to zero, yields

$$\gamma \equiv \left(\frac{\partial p}{\partial T}\right)_v = p^*/(\tilde{\nu}^2 T) \tag{27}$$

Using previously found values of v^*_{sp}, the parameter p^* was obtained by minimizing the sum of the squares of the percent deviations between calculated and experimental values of γ.

Pure-component parameters p^*, v^*_{sp}, and T^* and data sources are shown in Table 1 for solvents and in Table 2 for polymers. In many cases experimental PVT data are not available; in these cases, the corresponding-states correlations of Bondi (1968) were used to estimate PVT properties.

Polymer solutions are often of interest at temperatures well below the melting temperature (or glass transition temperature) of the pure polymer. However, polymers in solution behave as if they were amorphous, even at temperatures below the polymer melting temperature, as long as the solvent concentration is greater than approximately 20 weight %. Therefore, it is useful to obtain the parameters p^*, T^*, and v^*_{sp} for polymers over a temperature range which is, in part, below the polymer's liquid region. To do so, we require experimental or estimated values of α, γ, and v_{sp} for amorphous polymer over the desired temperature range.

In order to obtain PVT properties for polymers as they would behave below their melting temperatures if they were amorphous, Bondi's corresponding states correlation for polymer density (1968) was adjusted (by adjusting Bondi's parameter c) to fit either a measured density datum above the melting temperature, or, preferably, the estimated density of the amorphous polymer below the melting temperature (Lewis, 1968). The parameter c, thus obtained, was then used in Bondi's correlations for density, α, and γ. The values of p^*, T^*, and v^*_{sp} given in Table 2 refer to amorphous polymers over the indicated temperature range.

We have used experimental or estimated values of v_{sp}, α, and γ in obtaining the parameters shown in Tables

TABLE 3. INTERACTION PARAMETERS FOR BINARY POLYMER/SOLVENT SOLUTIONS

Polymer	Solvent	Temp., °C	$w_1 \times 10^2$	$\Delta \times 10^2$
Polyethylene (low-density)	heptane (a)	109.9	15.6-74.7	−2.82
Polyisoprene (cis-1,4-)	benzene (b)	25	10-95	0.986
		100	5.45-41.1	0.182
	acetone (c)	10	1.3-6.4	6.72
		25	3.9-15.7	5.39
	methyl ethyl ketone (c)	25	2.9-35.6	3.74
		45	9.5-38.5	3.61
	ethyl acetate (c)	25	5.0-37.0	3.20
		50	3.45-18.2	3.36
Polystyrene (atactic)	chloroform (d)	25	22.3-86.9	−3.34
		50	20.3-86.6	−2.77
	acetone (d)	25	18.4-46.1	−0.538
		50	15.5-25.3	0.526
	methyl ethyl ketone (e)	10	60.6-88.0	1.08
		50	60.6-88.0	1.36
	ethyl benzene (f)	10	63.2-89.9	0.945
		35	75.0-89.6	0.893
		60	75.0-89.6	−1.84
	cyclohexane (g)	24	7.67-48.5	2.61
		34	7.20-49.2	2.58
		44	6.80-48.2	2.50
	benzene (h)	20	24.1-59.2	0.445
	carbon tetrachloride (h)	20	26.7-67.3	−0.0532
	dioxane (h)	20	22.6-38.6	−0.640
Polydimethylsiloxane	benzene (i)	25	2.95-49.8	0.281
Polyvinyl acetate	benzene (j)	30	2.6-55.1	0.671
	vinyl acetate (j)	30	7.4-56.6	−3.71
Polyethylene oxide	benzene (k)	45.8	32.1-73.9	0.000
		70	2.9-73.8	−0.013
Polyisobutylene	benzene (l)	10	22.5-45.4	1.11
		25	4.37-37.3	1.72
		39.6	23.4-47.6	1.27
	pentane (l, m)	25	2.86-58.4	−1.00
		35	18.8-52.3	−1.06
		45	51.1-87.7	−1.32
		55	18.2-52.8	−0.853
	cyclohexane (l)	25	12.8-56.9	0.520

Data Sources (a) van der Waals and Hermans, 1950; (b) Gee and Treloar, 1942; (c) Booth et al., 1964; (d) Bawn and Wajid, 1956; (e) Flory and Höcker, 1971; (f) Höcker and Flory, 1971; (g) Krigbaum and Geymer, 1959; (h) Baughan, 1948; (i) Newing, 1950; (j) Nakajima et al., 1959; (k) Booth and Devoy, 1971; (l) Eichinger and Flory, 1968b; and (m) Baker et al., 1962.

1 and 2. (Alternatively, the pairs β and γ or α and β could have been substituted for the pair α and γ since $\alpha = \beta\gamma$). These parameters are tentative and require modification as new PVT data become available.

BINARY INTERACTION PARAMETERS

The optimum value of the binary parameter Δ was obtained for 20 binary systems by minimizing the sum of the squares of the percent deviations between experimental values of Ω_1 and those calculated from Equation (15) for several solvent concentrations at a given temperature. Table 3 gives the values of Δ obtained along with the concentration ranges and data sources.

The parameter Δ is nearly, but not completely, independent of concentration because of deficiencies in the theory. The parameter Δ varies slightly with concentration in part because the term E_0 in Equation (8) assumes random mixing of segments. However, in strongly nonideal solutions this assumption is poor because of energetic preferences in segmental orientations. The values of Δ in Table 3 should only be used in the specified concentration ranges.

To illustrate application of Equation (15) coupled with Tables 1, 2, and 3, Figures 4 and 5 show calculated and experimental partial pressures for polystyrene/chloroform and polyisobutylene/benzene solutions, each at two temperatures. For systems in Table 3 average absolute errors in the calculated solvent partial pressures are typically between 3 and 4%.

The solvent partial pressure is sensitive to the value of Δ even though the magnitude of Δ is usually small compared to unity. Unfortunately, there are not enough reliable data available in the published literature to correlate values of Δ using group-contribution or other methods. At present, no general statements can be made with certainty concerning the value of Δ or its temperature derivative. Figures 6 and 7 illustrate the effect of variation of Δ for two typical systems.

SOLUTIONS CONTAINING POLYDISPERSE POLYMERS

Equation (15) was derived for a binary solution containing a monodisperse polymer. However, most industrial polymers are mixtures containing molecules of different molecular weights. Flory (1944, 1953) and Koningsveld and Staverman (1968) have discussed the effect of polydispersity on vapor-liquid and liquid-liquid equilibria. Their conclusions may be summarized as follows: vapor-liquid equilibria are insensitive to polymer molecular weight distribution as long as the polymer molecular weight is large and the molecular weight distribution is

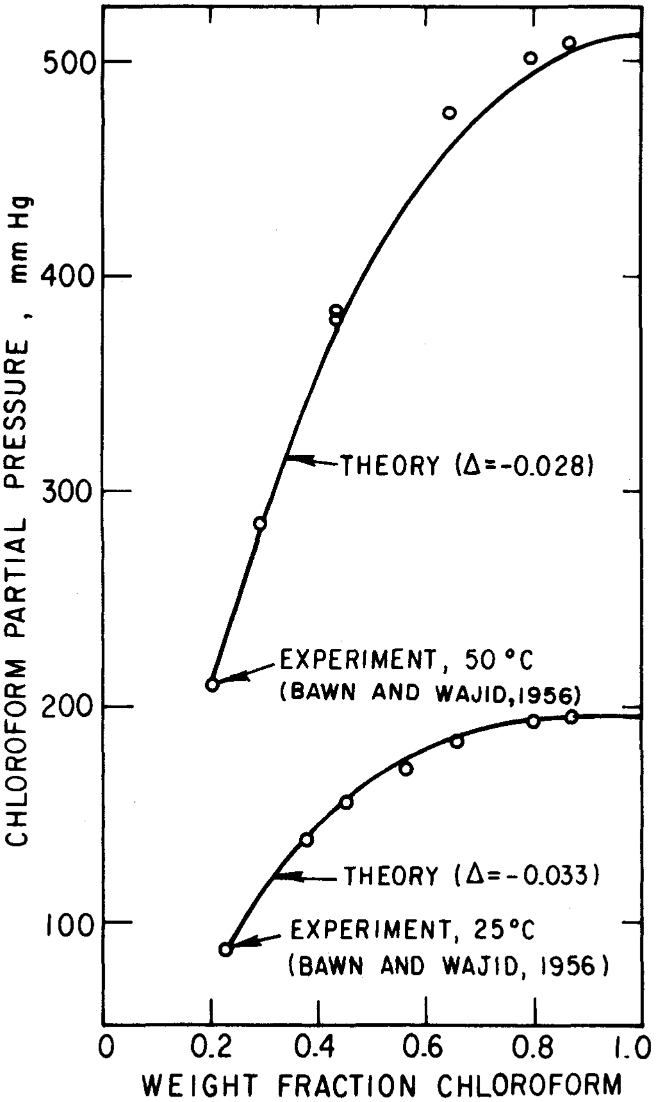

Fig. 4. Partial pressure of chloroform in solutions of polystyrene.

not broad. Liquid-liquid phase equilibria, however, are more sensitive to polymer molecular weight distribution, especially if the molecular weight distribution is broad or if the solution is near its critical state. Critical phenomena in polymer solutions are greatly affected by molecular weight distribution, as shown by Koningsveld and Staverman (1968) and by Siow et al. (1972).

LIMITED MISCIBILITY

The Prigogine-Flory theory can be used to provide guidance on the presence or absence of limited miscibility in binary, polymer/solvent solutions. To illustrate, Figure 8 shows a plot of benzene activity in *cis*-1,4-polyisoprene at 25°C versus weight fraction benzene for three values of Δ. Benzene activity was calculated using Equation (15). The lower curve ($\Delta = 0.00986$) represents the best fit of experimental data. The data show that the system is completely miscible because the solvent activity never exceeds unity. The middle curve ($\Delta = 0.02$) also shows no phase separation but is close to incipient instability; it shows that a small increase in activity causes a large increase in benzene concentration for weight fractions greater 0.58. The upper curve ($\Delta = 0.04$) shows phase separation since a_1 becomes greater than unity for all benzene weight fraction greater than 0.22.

CONCLUSION

We have presented a simplified version of the Prigogine-Flory theory of polymer solutions, suitable for engineering calculations for moderately concentrated, binary polymer/solvent solutions at low or moderate pressures. We have prepared tables of pure-component and binary parameters required in the theory for 22 solvents, 16 polymers, and 37 binary mixtures. Using the parameters, partial pressures of solvents in binary polymer/solvent solutions can be calculated within 3 to 4% in most cases.

The theory is limited to nonpolar systems or to moderately polar systems with no significant hydrogen bonding. It is applicable to solutions where the crystallinity of the pure polymer at solution temperature is small and where solvent concentrations range from approximately 20 to 80 weight %.

For many systems the modified Prigogine-Flory theory represents solvent vapor pressure data much more accurately than the Flory-Huggins theory. The simplified version of the Prigogine-Flory theory should prove useful for practical engineering calculations.

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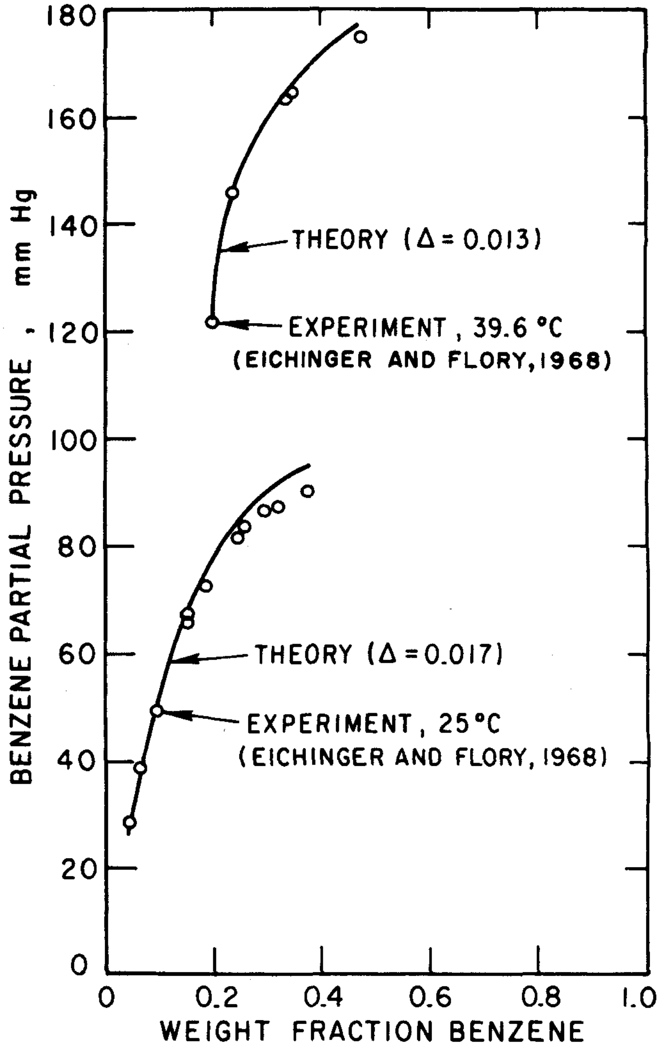

Fig. 5. Partial pressure of benzene in solutions of polyisobutylene.

NOTATION

a_i = activity of i with pure saturated i at solution temperature as a reference state
B_1 = second virial coefficient of pure solvent at solution temperature
$3c_i$ = number of external degrees of freedom per segment of i
E_0 = potential energy of the system with all segments in their rest positions
f_i = fugacity of component i
$g(N_1, N_2)$ = Flory (1942) combinatorial factor
k = Boltzmann's constant
ln = natural logarithm
M_i = molecular weight of substance i
m_i = mass of i in solution
m = total mass of solution
N_i = number of molecules of i
p = total, hydrostatic pressure
$\tilde{p}$ = p/p^* = reduced pressure of the solution
p_i = partial pressure of i in solution
p_i^{sat} = saturation pressure of i at solution temperature
p_i^* = characteristic pressure of i
p_{12}^* = $(p_1^* p_2^*)^{1/2}\,(1 - \Delta)$ = characteristic binary interaction pressure
Q = configurational canonical partition function
r_i = number of segments per molecule of i

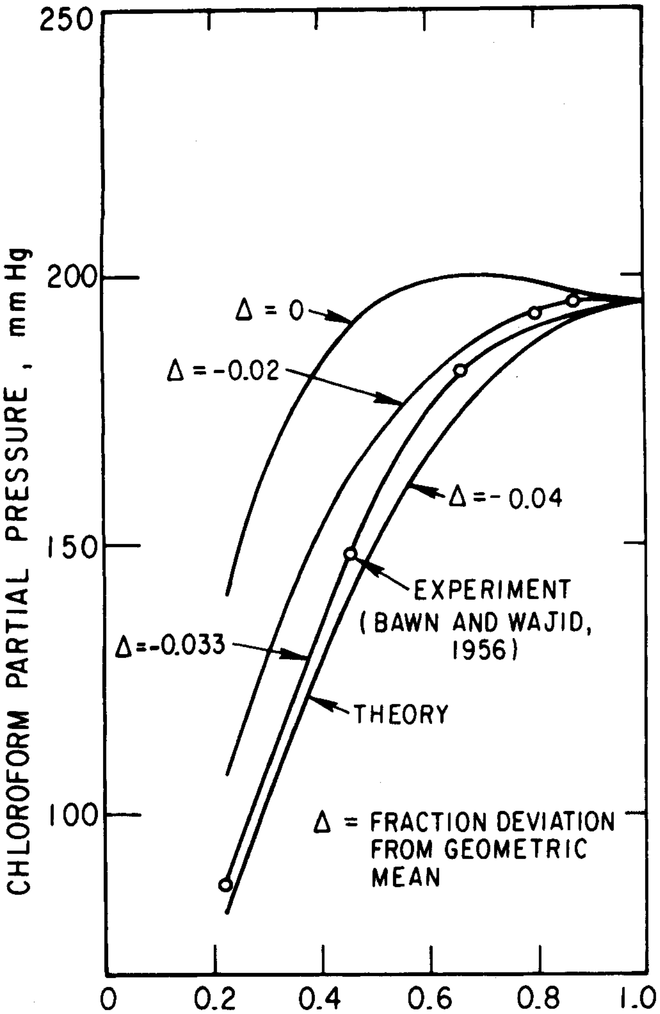

Fig. 6. Effect of deviation fom geometric mean on partial pressure of chloroform in polystyrene/chloroform solutions at 25°C.

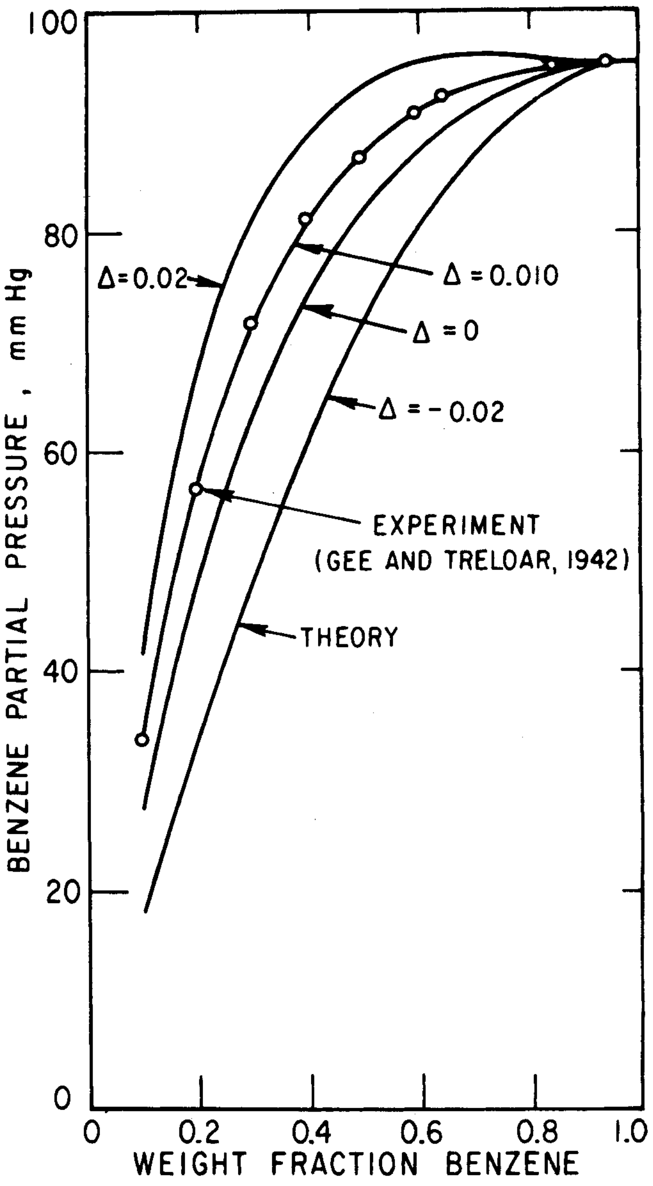

Fig. 7. Effect of deviation from geometric mean on partial pressure of benzene in cis-1,4-polyisoprene/benzene solutioss at 25°C.

R = gas constant
T = absolute temperature
$\tilde{T}$ = T/T^* = reduced temperature of solution [See equation (4)]
T^* = characteristic temperature of the solution [See equation (4)]
T_i^* = characteristic temperature of i
v = molar volume
v^*_{sp} = characteristic volume per gram of solution
v^*_{isp} = characteristic volume per gram of pure i
w_i = weight fraction of i in solution
x_i = mole fraction of i in solution

Greek Letters

α = $1/v\ (\partial v/\partial T)_p$ = coefficient of thermal expansion
β = $-1/v\ (\partial v/\partial p)_T$ = isothermal compressibility
γ = $(\partial p/\partial T)_v$ = thermal pressure coefficient
Γ_i = a_i/Ψ_i = segment fraction activity coefficient of i
Δ = $1 - p_{12}^*/(p_1^* p_2)^{1/2}$ = deviation of binary intermolecular interaction parameter, p_{12}^*, from geometric mean of p_1^* and p_2^*
λ = geometrical packing constant

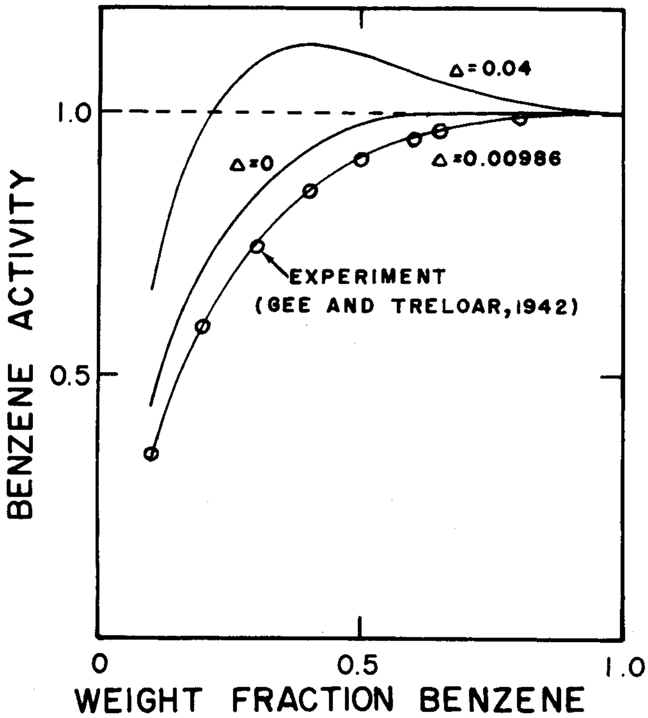

Fig. 8. Benzene activity in cis-1,4-polyisoprene at 25°C showing miscibility and immiscibility with change in Δ.

$\tilde{v}$ = v_{sp}/v^*_{sp} = reduced volume per segment of solution
$\tilde{v}_i$ = $v_{isp}/v_i{}^*_{sp}$ = reduced volume of pure *i* per segment of pure *i*
Φ_i = $x_i v_i/\Sigma_i x_i v_i$ = volume fraction of *i* in solution
χ = Flory-Huggins binary interaction parameter
Ψ_i = $m_i v_i{}^*_{sp}/\Sigma_i m_i v_i{}^*_{sp}$ = segment fraction of *i* in solution
Ω_i = a_i/w_i = weight-fraction activity coefficient of *i*

Subscripts

1 = solvent
2 = polymer
sp = quantity per gram

Superscripts

~ = reduced quantity
ath. = athermal, combinatorial contribution
f.v. = free volume contribution
i.f. = intermolecular force contribution
sat = saturated

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Optimization of Parallel Reactions in a Tubular Reactor by Feed Distribution

The system of isothermal, isobaric, perfect gas reactions with stoichiometric kinetics

$$A_1 + A_2 \underset{k_2}{\overset{k_1}{\rightleftharpoons}} A_3 + A_4;\ 2A_1 \xrightarrow{k_3} A_5$$

taking place in a tubular reactor is considered where A_3 is desired and A_5 undesired. A class of optimum selectivity problems is formulated, and distributed bypass of A_1 is investigated. It is shown that there are cases where the performance of the best plug flow reactor can be improved substantially (sometimes by more than 100%) by the bypass of A_1, but there are also cases where bypass is fruitless.

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SCOPE

It is well known that there are cases in which delaying the addition of a reactant to reactor (either in space or time) is accompanied by an improvement in performance. In fact, there are simple tests which can be used to determine whether a given reactor can be improved by infinitesimal bypass: Jackson and Senior (1968), Horn and Tsai (1967). It is not possible to say a priori however whether for a given physical system and objective function there will be significant benefit. The literature on feed distribution may be classified into three categories:

1. Variable volume reactors (for example Siebenthal-Aris (1964), and Graves (1968), who studied a semibatch stirred tank reactor in which the liquid level changes as the reaction proceeds).
2. Fixed volume reactors, for which it is assumed in the model that the volumetric flow rate of the main stream is unchanged by addition of the side stream (for example, the side stream consists of concentrated material which rapidly dissolves in the main stream with negligible volume change: for example, Jackson and Senior (1968); van de Vusse and Voetter (1961)).
3. Fixed volume reactors where it is assumed that the reacting mixture behaves as a perfect gas mixture: (for example, Dyson and Horn (1967), Dyson and Graves (1968)).

Reactors of the second class have probably received the most attention in the literature, and intuitive arguments have been developed to explain qualitatively effects which have been derived accurately by rigorous analysis. These intuitive arguments are of course applicable to all the above classes of reactors but do not lead to good numerical estimates of the magnitude of the benefit resulting from feed distribution any more than do the simple tests referred to above.

The published work on reactors of the third class has been limited to single reactions. In the present manuscript we describe the results of some calculations on the system:

$$\begin{gathered} A_1 + A_2 \underset{k_2}{\overset{k_1}{\rightleftharpoons}} A_3 + A_4 \\ 2A_1 \xrightarrow{k_3} A_5 \end{gathered} \tag{1}$$

carried out in a tubular reactor with main feed A_1 and subsidiary feed A_2 (see Figure 1). Isothermal, isobaric operation with a perfect gas mixture and stoichiometric kinetics was assumed. The substance A_3 is consided to be the desired product and A_5 an undesirable waste product. This system of reactions is interesting because there is competition for the A_1 molecules between other A_1 molecules and A_2 molecules so that it seems natural to bypass the feed of A_1 in order to suppress the undesired reaction. Also, the first reaction is reversible so that by increasing the reactor

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