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Phase Equilibria in Polymer Solutions

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A new semiempirical equation is presented for the Gibbs energy of mixing for solutions of polymers in single and mixed solvents. The equation contains two adjustable parameters per binary mixture and can readily be extended to multicomponent systems without additional parameters. The new expression gives a very good representation of the properties of a variety of polymer solutions including those in which there are strong specific interactions such as hydrogen bonding. Parameters are determined from binary vapor pressure data.

A graphical method based on the new equation is given for predicting solubility limits in ternary systems containing one polymer and a mixed solvent. Only binary data are used. The method is demonstrated by comparisons of predicted solubility behavior with new experimental data taken on systems composed of polystyrene and the following mixed solvents: acetone-toluene, acetone-benzene, methanol-benzene, methanol-ethyl acetate, and acetone-methylcyclohexane.

The thermodynamics of polymer solutions has been discussed in many books (*10, 15, 17, 19, 25, 26, 29, 31*) and an excellent review of work prior to 1956 has been given by Tompa (*31*). Most previous work has been concerned with nonpolar solutions. In this work we present a new equation for the Gibbs energy of mixing for polymer solutions which appears to be useful for a large variety of systems including polar and hydrogen-bonded components.

The most widely known theoretical treatment of polymer solutions is that of Flory and Huggins. Flory (*11, 12*) and Huggins (*20, 21*) derived an expression for the entropy of mixing for athermal solutions containing monomeric solvent molecules and long-chain polymer solute molecules which consist of a number of contiguous segments, each equal in size to a solvent molecule. Their treatment applies only at concentrations such that the randomly coiled polymer molecules overlap one another extensively. A somewhat different treatment has been proposed for very dilute solutions (*13, 14*).

Extension of the theoretical athermal equation to nonathermal solutions was achieved semiempirically by the adoption of a van Laar term (*17, 27, 32*) for representation of the heat of mixing. The well-known expression for the molar Gibbs energy of mixing, known as the Flory-Huggins equation, is

$$\frac{\Delta g^M}{RT} = x_1 \ln \phi_1 + x_2 \ln \phi_2 + \chi \, \phi_1 \phi_2 \, (x_1 + m x_2) \qquad (1)$$

From criteria of thermodynamic stability, it can be shown that at the critical point for incipient phase separation

$$\chi = \frac{1}{2} \left(1 + \frac{1}{\sqrt{m}} \right)^2 \qquad (2)$$

Since m is usually very large, the Flory-Huggins theory predicts complete miscibility of polymer and solvent if

$$\chi \leq 1/2 \qquad (3)$$

The Flory-Huggins equation does not generally provide a quantitative description of the thermodynamic properties of polymer solutions, because contrary to the theory, numerical values of χ, as deduced from experimental data, are often a strong function of polymer concentration even for nonpolar solutions. For example, as shown in Figure 1, the value of χ for solutions of cellulose derivatives in acetone changes markedly as the volume fraction of polymer is varied; similar changes in χ have been observed for many other polymer solutions.

Burrell (*6*) and Blanks (*5*) have proposed methods for the prediction of limited miscibility in polymer solutions based upon the Flory-Huggins equation and an extended form of the regular solution theory of Hildebrand (*17*). It appears that these methods cannot be extended to systems in which specific molecular interactions occur.

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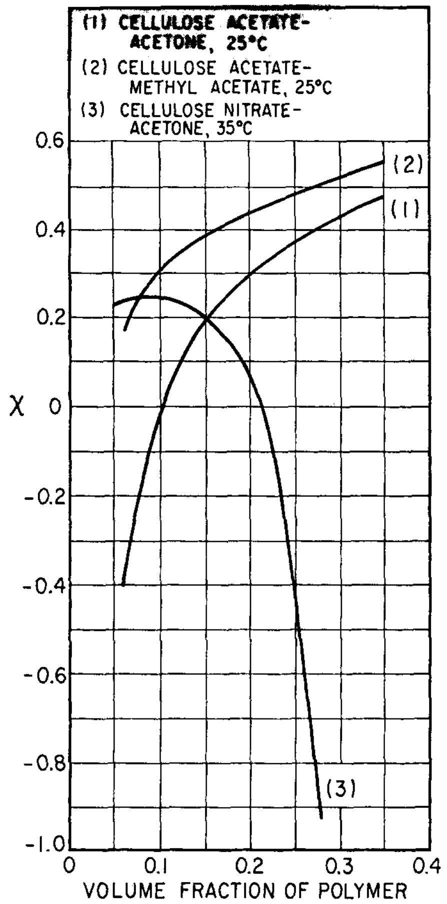


Fig. 1. Dependence of Flory-Huggins interaction parameter on concentration for solutions of cellulose derivatives.

The inadequacy of the Flory-Huggins equation has been recognized for many years and various improved theories, especially for polar solutions, have been proposed, notably by Barker (*2*), Huggins (*18*), Rice (*34*), and Münster (*25*). These improved theories are not only very complicated but also require extensive data in order to determine numerous parameters; as a result, these theories are of very little use for practical applications. We have therefore derived and tested a new semiempirical equation containing two adjustable parameters which is a compromise between the relatively simple one-parameter equation of Flory-Huggins and the more sophisticated multiparameter theories of later authors. We are particularly concerned with polymer solutions of industrial importance, that is, with solutions of polar and hydrogen-bonded components, and with solutions of polymers in mixed solvents.

GIBBS ENERGY OF MIXING FOR A BINARY POLYMER-SOLVENT SOLUTION

An adequate description of phase equilibria in polymer solutions which is also practically useful requires an expression for the Gibbs energy of mixing that meets the following requirements:

1. It must give a reasonably accurate representation of the variation of chemical potential with polymer concentration.
2. It must contain only a small number of adjustable parameters for accurate representation. The parameters must be uniquely defined and should have at least approximate physical significance.
3. The expression should be able to predict equilibria for polymer solutions in mixed solvents with parameters obtained only from binary data. It is very desirable that there should be no necessity for additional parameters characteristic of the multicomponent system.
4. The expression for the Gibbs energy of mixing must be thermodynamically consistent. It should have general applicability for solutions of linear polymers regardless of the relative sizes of the components or the nature of molecular interactions occurring between them.

We propose here an equation which appears to fulfill all of these requirements to a very good degree of approximation. We call it the segment-interaction equation. It makes use of the local volume fraction concept of Wilson (*33*) and contains only two adjustable parameters per binary pair. For a binary solution consisting of a polymer (*2*) and solvent (*1*), the molar Gibbs energy of mixing per mole of mixture is given by

$$\frac{\Delta g^M}{RT} = x_1 \ln \xi_{11} + s_2 x_2 \ln \xi_{22} + (1 - s_2)\, x_2 \ln \phi_2 + x_1 \xi_{21}\left(\frac{g_{12} - g_{11}}{RT}\right) + s_2 x_2 \xi_{12}\left(\frac{g_{12} - g_{22}}{RT}\right) \tag{4}$$

where $(g_{12} - g_{11})$ and $(g_{12} - g_{22})$ are adjustable parameters representing molecular interaction energies.

The local volume fractions are defined as follows. The local volume fraction of solvent molecules about a central solvent molecule is

$$\xi_{11} = \frac{x_1}{x_1 + \left(\frac{V_2}{V_1}\right) \exp\left[-(g_{12} - g_{11})/RT\right] x_2} \tag{5}$$

The local volume fraction of polymer segments about a central polymer segment is

$$\xi_{22} = \frac{x_2}{\left(\frac{V_1}{V_2}\right) \exp\left[-(g_{12} - g_{22})/RT\right] x_1 + x_2} \tag{6}$$

The local volume fraction of solvent molecules about a central polymer segment is

$$\xi_{12} = \frac{\left(\frac{V_1}{V_2}\right) \exp\left[-(g_{12} - g_{22})/RT\right] x_1}{\left(\frac{V_1}{V_2}\right) \exp\left[-(g_{12} - g_{22})/RT\right] x_1 + x_2} \tag{7}$$

The local volume fraction of polymer segments about a central solvent molecule is

$$\xi_{21} = \frac{\left(\frac{V_2}{V_1}\right) \exp\left[-(g_{12} - g_{11})/RT\right] x_2}{x_1 + \left(\frac{V_2}{V_1}\right) \exp\left[-(g_{12} - g_{11})/RT\right] x_2} \tag{8}$$

The interaction energy g_{12} represents the energy between a 1-2 pair where 1 (or 2) stands for a solvent molecule or a polymer segment. We assume that these energies are independent of polymer molecular weight and we expect that they are only weak functions of temperature. Although there are three different interaction energies per binary, there are only two adjustable parameters per binary in Equation (4), namely, the two differences in interaction energies $(g_{12} - g_{11})$ and $(g_{12} - g_{22})$. The local volume fractions obey the conservation equations:

$$\xi_{12} + \xi_{22} = 1 \quad \text{and} \quad \xi_{21} + \xi_{11} = 1$$

As the differences in interaction energies become very small compared to RT, it can be shown that Equation (4)

TABLE 1. PARAMETERS FOR A VARIETY OF POLYMER SOLUTIONS*

Polymer (2)	Solvent (1)	Polymer mol. wt.	Temp., °C.	Ref.	Range of conc.‡	Avg. % dev. of fitted a_1†	$(g_{12}$-$g_{11})$, cal./g.-mole	$(g_{12}$-$g_{22})$, cal./g.-mole
Polystyrene	Acetone	290,000	25	*1*	0.60 to 0.96 W	1.36	382.7	—19.99
	Benzene	3,332	25	*30*	0.15 to 0.39 V	0.04	—49.96	147.9
	Chloroform	290,000	25	*3*	0.28 to 0.89 W	0.26	—145.6	319.6
	Cyclohexane	25,900	34	*22*	0.25 to 0.80 V	0.32	382.2	—16.54
	Cyclohexane	440,000	34	*22*	0.25 to 0.80 V	0.23	386.6	—20.01
	n-Propyl acetate	290,000	25	*3*	0.56 to 0.91 W	0.57	175.2	38.03
	Toluene	3,332	40	*30*	0.15 to 0.39 V	0.06	—38.89	117.9
	Toluene	290,0000	25	*4*	0.26 to 0.89 W	1.06	—53.03	158.4
Polypropylene glycol	Methanol	1,955	25	*9*	0.13 to 0.53 W	0.03	284.5	—21.07
	Methanol	3,350	25	*9*	0.12 to 0.46 W	0.05	286.9	—14.53
Polyethylene oxide	Chloroform	6,000	25	*1*	0.21 to 0.51 V	0.71	284.1	—351.5
Polyethylene glycol	Water	3,000	55	*23*	0.50 to 0.97 W	2.73	839.9	—342.5
	Water	5,000	60	*23*	0.74 to 0.95 W	1.69	837.7	—328.5
Cellulose acetate	Acetone	104,000	25	*24*	0.10 to 0.50 W	0.23	840.0	—250.1
	Dioxane	104,000	25	*24*	0.10 to 0.50 W	0.20	479.1	—194.7
	Methyl acetate	104,000	25	*24*	0.10 to 0.50 W	0.12	470.0	—130.4
	Pyridine	104,000	25	*24*	0.10 to 0.50 W	0.10	9.57	29.85
Cellulose nitrate	Acetone	94,000	35	*24*	0.10 to 0.50 W	1.25	123.5	—1408
	Methyl acetate	94,000	35	*24*	0.10 to 0.50 W	1.75	92.91	—1528
Rubber	Acetone		0	*7*	0.84 to 0.96 V	2.10	506.9	48.88
	Ethyl acetate		25	*7*	0.62 to 0.98 V	1.20	346.6	7.03
	Methyl ethyl ketone		25	*7*	0.61 to 0.92 V	0.70	412.6	—3.40
Polypropylene	Diethyl ketone		25	*8*	0.43 to 0.68 V	0.34	571.7	—14.94
	Diisobutyl ketone		25	*8*	0.65 to 0.84 V	0.56	334.6	—4.91

* A complete tabulation of parameters for all polymer solutions considered in this work is presented in reference *16*.
† a_1 denotes solvent activity.
‡ Range of concentration refers to polymer concentration in weight (W) or volume (V) fraction.

reduces to the well-known Flory-Huggins equation; that is, in the limit

$$\text{as} \quad \frac{(g_{12}-g_{11})}{RT} \to 0$$

$$\text{and} \quad \frac{(g_{12}-g_{22})}{RT} \to 0$$

$$\left(\frac{\Delta g^M}{RT}\right) = x_1 \ln \phi_1 + x_2 \ln \phi_2 + \left(\frac{2g_{12}-g_{11}-g_{22}}{RT}\right) x_1\phi_2 \tag{9}$$

Equation (9) is identical to the Flory-Huggins equation with

$$\chi \equiv \left(\frac{2g_{12}-g_{11}-g_{22}}{RT}\right) \tag{10}$$

DATA REDUCTION

In order to determine a unique pair of parameters $(g_{12}-g_{11})$ and $(g_{12}-g_{22})$ for a binary polymer solution, experimental information must be obtained on the variation of solvent activity with composition over a broad composition range. The vapor pressure of the solvent in solution is related to its chemical potential μ_1 (or activity a_1) by

$$\frac{1}{RT}\left(\frac{\partial n_T \Delta g^M}{\partial n_1}\right)_{T,P,n_2} = \frac{\Delta\mu_1}{RT} = \ln \frac{P_1}{P_1^o} + \frac{B_1(P_1-P_1^o)}{RT} + \frac{V_1(P_1^o-P_1)}{RT} \tag{11}$$

$$a_1 = \exp(\Delta\mu_1/RT) \tag{12}$$

When Equation (4) is substituted into Equation (11) we obtain

$$\begin{aligned}\frac{\Delta\mu_1}{RT} &= s_1 \ln\left(\frac{x_1}{x_1+Ax_2}\right) + s_1 A\left(\frac{x_2}{x_1+Ax_2}\right) \\ &\quad - s_2 B\left(\frac{x_2}{Bx_1+x_2}\right) + (1-s_1)\ln\left(\frac{x_1V_1}{x_1V_1+x_2V_2}\right) \\ &\quad + (1-s_1)\left(\frac{x_2V_2}{x_1V_1+x_2V_2}\right) \\ &\qquad + (s_2-1)\left(\frac{x_2V_1}{x_1V_1+x_2V_2}\right) \\ &\quad + \frac{s_1AG_1x_2}{(x_1+Ax_2)} - \frac{s_1x_1AG_1x_2}{(x_1+Ax_2)^2} \\ &\qquad + \frac{s_2BG_2x_2}{(Bx_1+x_2)} - \frac{s_2B^2G_2x_1x_2}{(Bx_1+x_2)^2}\end{aligned} \tag{13}$$

where

$$A \equiv \frac{V_2}{V_1}\exp(-[g_{12}-g_{11}]/RT)$$

$$B \equiv \frac{V_1}{V_2}\exp(-[g_{12}-g_{22}]/RT)$$

$$G_1 \equiv (g_{12}-g_{11})/\text{RT} \qquad G_2 \equiv (g_{12}-g_{22})/\text{RT}$$

Equation (13) is not a simple algebraic expression but, at constant temperature, it contains only two parameters. In all of our calculations with Equation (13) we used a digital electronic computer. Solvent activities were calculated as a function of solution composition with vapor pressure data for a variety of binary polymer mixtures.

Binary parameters were then obtained by a least squares iteration (*16*). Table 1 shows parameters thus obtained with standard deviations in fitted solvent activity. A more complete tabulation of parameters is presented in reference *16*.

The systems appearing in Table 1 represent virtually all of those for which reliable vapor pressure data are available over a solution composition range sufficiently broad to permit determination of unique parameters. Equation (4) appears to give an excellent representation of the properties of a variety of polymer solutions. Lack of suitable data for parameter determination has restricted application of Equation (4) to solutions of only a few types of polymers: polystyrene, polyglycols, polyethers, rubber, polypropylene, and cellulose derivatives. There is good reason to believe, however, that Equation (4) should apply equally well to solutions of any linear polymer consisting of identical, repeating structural units. Unfortunately, available osmotic pressure data for solutions of several other types of polymers (for example, polymethacrylate and polyvinyl acetate) do not cover a range of composition sufficiently broad for unique parameter determination.

Table 1 indicates that an excellent representation of data is obtained even for those systems in which strong specific interactions (such as hydrogen bonding) exist between like and unlike components. To illustrate the ability of Equation (13) to represent the experimental data, Figure 2 compares calculations based on Equation (13) with those obtained by the Flory-Huggins equation for the polyethylene oxide-chloroform system. Maximum and minimum experimental values of χ were used in the construction of the limiting pairs of Flory-Huggins curves. The experimental data are also shown and it is evident that Equation (13) with two parameters gives a much better representation than Equation (1) with only one parameter.

The parameters in Table 1 follow qualitative trends to be expected from the nature of the intermolecular forces involved. For example, a positive value of $(g_{12} - g_{11})$ in the methanol-polypropylene glycol system indicates that the energy of a methanol-methanol interaction is stronger than the interaction between methanol and an ether segment; both g_{12} and g_{11} are negative by convention but $|g_{11}|>|g_{12}|$. A tendency for parameters to vary with molecular weight of the polymer has not been observed. Parameters are not available over a sufficiently wide temperature range for most of the systems to allow definite conclusions to be made concerning temperature dependence of the interaction energy differences.

Equation (4) has also been applied to the reduction of vapor pressure data for binary solutions of monomeric components (*16*). It was shown that with Equation (4) the representation of binary data for solutions in which strong, specific interactions occur, is approximately equivalent to that obtained by use of a five-parameter Margules equation.

PHASE EQUILIBRIUM IN POLYMER-MIXED SOLVENT SYSTEMS

One of the advantages of Equation (4) is that it can be generalized to a multicomponent solution without further assumptions. For a solution containing N components the Gibbs energy of mixing is

$$\frac{\Delta g_M}{RT} = \sum_{i=1}^{N} \{[s_i x_i \ln \xi_{ji} + (1-s_i)\, x_i \ln \phi_i] + \sum_{\substack{j=1\\(j\neq i)}}^{N-1} [s_i x_i \xi_{ii}\,(g_{ij} - g_{ii})/RT]\} \quad (14)$$

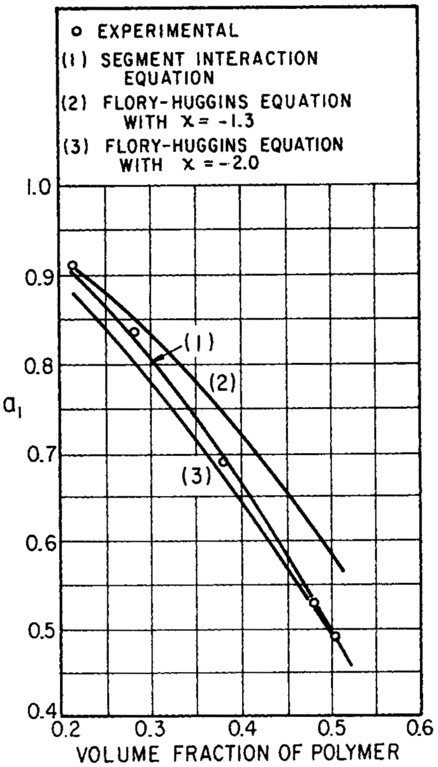


Fig. 2. Solvent activity in polyethylene oxide-chloroform solutions at 25°C.

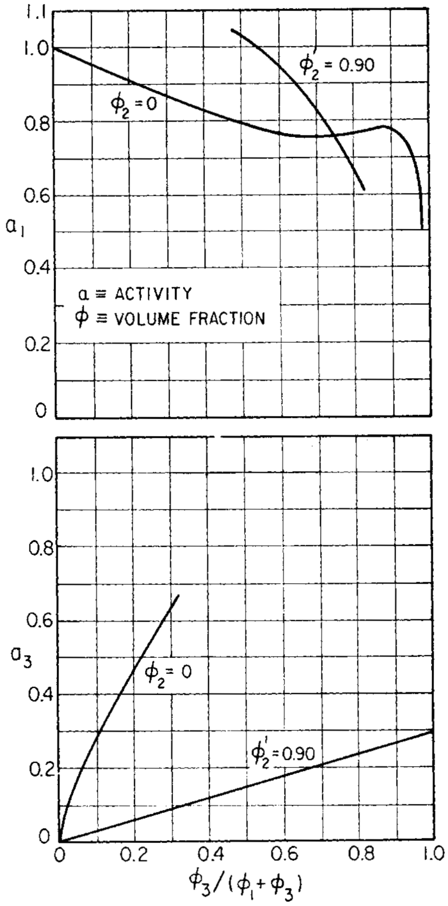
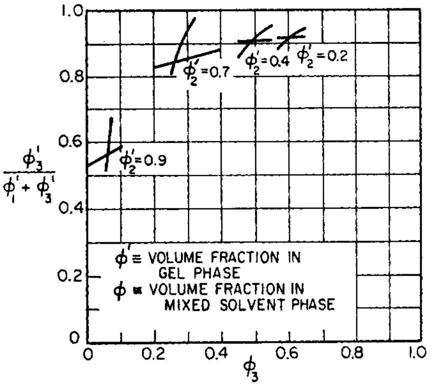


Fig. 3. Concentration dependence of calculated monomer activities. Methanol (1)-polystyrene (2)-benzene (3) system.

$$\xi_{ii} = \frac{x_i V_i}{\sum_{k=1}^{N} x_k V_k \exp\left[-(g_{ik} - g_{ii})/RT\right]} \tag{15}$$

$$\xi_{ji} = \frac{x_j V_j \exp\left[-(g_{ij} - g_{ii})/RT\right]}{\sum_{k=1}^{N} x_k V_k \exp\left[-(g_{ik} - g_{ii})/RT\right]} \tag{16}$$

Equation (14) may be used to predict equilibrium phase compositions in ternary systems with limited miscibility. No additional approximations are made in the application of the equation. In principle, the treatment applies with complete generality to ternary systems composed of one or more polymeric species regardless of molecular weight. However, the analytical form of the relations between liquid compositions in the two phases is sufficiently cumbersome to render impractical the application to such a completely general case. The relations may be considerably simplified by limiting the treatment to solutions containing one polymeric component and two (or more) solvents and by imposing the restriction that in a two-phase system essentially all of the polymeric species be contained in one of the two phases. This limitation is not serious for engineering purposes because it corresponds to the technically interesting case of determining the solubility of a polymer in a mixed solvent.



PREDICTED EQUILIBRIUM PHASE COMPOSITIONS

GEL PHASE			SOLVENT PHASE	
ϕ_1'	ϕ_2'	ϕ_3'	ϕ_1	ϕ_3
0.072	0.200	0.728	0.40	0.60
0.054	0.400	0.546	0.51	0.49
0.048	0.700	0.252	0.74	0.26
0.044	0.900	0.056	0.94	0.06

Fig. 4. Prediction of equilibrium phase composition. Methanol (1)-polystyrene (2)-benzene (3) system.

GRAPHICAL CALCULATION OF PHASE DIAGRAMS

A rapid graphical method has been developed for the construction of a ternary phase diagram for a polymer-mixed solvent system. The method is briefly described below and illustrated in Figures 3 and 4 for the methanol (1)-polystyrene (molecular weight, 300,000) (2)-benzene (3) system at 25°C. The steps are as follows:

Let

$a_1 \equiv$ activity of component 1 in the solvent phase
$a_1' \equiv$ activity of 1 in the phase containing polymer
$\phi_1 \equiv$ volume fraction of 1 in the solvent phase
$\phi_1' \equiv$ volume fraction of 1 in the phase containing polymer

1. For the solvent phase, a_1 is calculated and plotted as a function of ϕ_3.
2. For the solvent phase, a_3 is calculated and plotted as a function of ϕ_3.
3. For a specified value of ϕ_2', a_1', and a_3' are calculated and plotted as functions of the composition parameter $\phi_3'/(\phi_1' + \phi_3')$.
4. From the above plot, values of $\phi_3'/(\phi_1' + \phi_3')$ and ϕ_3 corresponding to equal values of a_1' and a_1 are determined and plotted in the form of $\phi_3'/(\phi_1' + \phi_3')$ as a function of ϕ_3.
5. Step 4 is repeated for equal values of a_3' and a_3.
6. The point of intersection of the curves plotted in steps 4 and 5 corresponds to the condition $a_1 = a_1'$ and $a_3 = a_3'$. Gel and solvent phase compositions correspond to the values of $\phi_3'/(\phi_1' + \phi_3')$ and ϕ_3 defining the point of intersection. Failure of the curves to intersect indicates complete solubility. Two points of intersection are observed for the case in which a mixture of two swelling solvents acts as a solvent for the polymer.

Calculations have been made for five ternary systems; these are compared with experimental results below. Each system consists of polystyrene and two solvents, one or both of which may be a swelling medium for the polymer. The parameters used for each system are presented in Table 2.

COMPARISON OF EXPERIMENTAL AND PREDICTED PHASE DIAGRAMS

Methanol (1)-Polystyrene (2)-Benzene (3) System

The ternary phase diagram for this system was determined at 27°C. for a polystyrene fraction having a molecular weight of 500,000 by Schulz and Jirgenson (28). Their data are presented in Figure 5 with gel compositions and tie lines predicted by Equation (14). Gel, as used in this context, refers to the swollen polymer phase at the equilibrium degree of swelling.

Estimation of parameters for two of the binary pairs was necessary. Binary parameters for methanol-polystyrene are not available. The methanol-polystyrene segment

Table 2. Parameters Used in Prediction for Systems Represented in Figures 5 to 9

System	Parameters, cal./g.-mole					
	g_{12}-g_{11}	g_{12}-g_{22}	g_{13}-g_{11}	g_{13}-g_{33}	g_{23}-g_{22}	g_{23}-g_{33}
Methanol(1)-polystyrene(2)-benzene(3) (Figure 5)	891.6	−66.73	891.6	−66.73	147.9	−49.98
Acetone(1)-polystyrene(2)-toluene(3) (Figure 6)	383.7	0	251.6	−34.70	158.4	−53.05
Acetone(1)-polystyrene(2)-benzene(3) (Figure 7)	383.7	0	300.2	−134.0	147.9	−49.98
Methanol(1)-polystyrene(2)-ethyl acetate(3) (Figure 8)	906.8	−67.86	518.7	120.0	38.67	178.0
Acetone(1)-polystyrene(2)-methylcyclohexane(3) (Figure 9)	383.7	0	555.1	95.16	−4.026	382.2

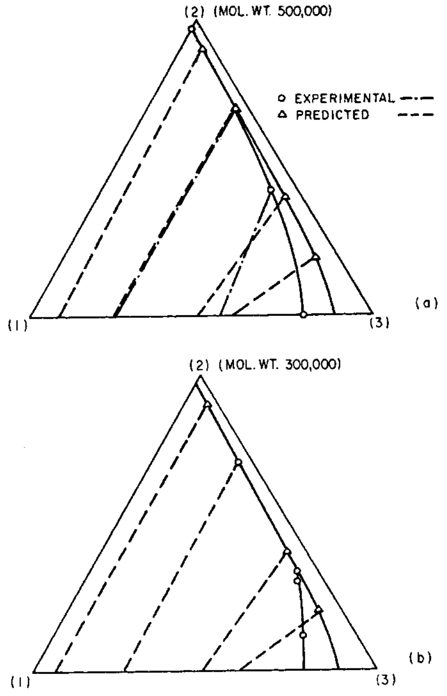


Fig. 5. Comparison of experimental and predicted ternary phase diagrams for the methanol (1)-polystyrene (2)-benzene (3) system.

interaction is expected to be energetically similar to a methanol-benzene interaction. Therefore parameters for this monomeric binary were used to represent the methanol-polystyrene binary. The methanol-benzene parameters were obtained from vapor-pressure data at 35°C. and were assumed, of necessity, to be invariant with temperature over the 25° to 35°C. range. The benzene-polystyrene parameters are those obtained directly from binary polymer solution data at 25°C., and are given in Table 2. Considering the approximations used in the estimation of parameters the agreement between theory and experiment is surprisingly good.

Part *B* of Figure 5 presents the predicted ternary phase diagram for polystyrene with a molecular weight of 300,000. The parameters used were the same as those for the polymer of higher molecular weight. Experimentally determined precipitation points (*16*) are included for comparison. As expected, the experimental precipitation points differ very slightly from those for the polystyrene of the higher molecular weight. A similar divergence between predicted and observed phase boundaries is observed in the dilute-polymer region.

Acetone (1)-Polystyrene (2)-Toluene (3)

Predicted and observed phase boundaries are presented in Figure 6 for polystyrene with a molecular weight of 300,000. As in the previous case, estimation of parameters at 25°C. was necessary for two of the binaries. The parameters used for the acetone-polystyrene binary differ slightly from those determined from the binary solution vapor pressure data $(g_{12} - g_{11}) = 382.7$ cal. and $(g_{12} - g_{22}) = -19.99$ cal. The latter set of parameters does not predict immiscibility. The experimentally measured gel composition for this binary corresponding to maximum polymer swelling is 45 vol. % polystyrene (*16*). An increase in $(g_{12} - g_{22})$ from -19.99 to 0 cal. was sufficient to produce a predicted gel composition of approximately 48 vol. %. The final parameters used in all subsequent work for the acetone-polystyrene binary at 25°C. were $(g_{12} - g_{11}) = 382.7$ cal. and $(g_{12} - g_{22}) = 0$ cal.

Parameters for the acetone-toluene binary were those obtained from data at 45°C. They were assumed to be invariant with temperature. Parameters for the toluene-polystyrene binary were those determined from data at 25°C.

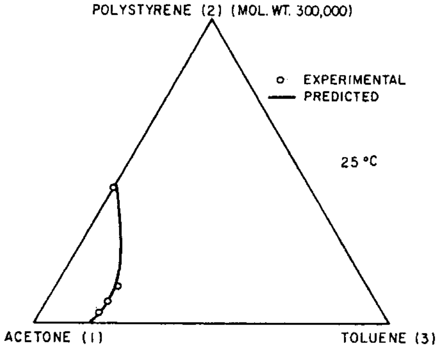
Figure 6 indicates that the predicted and observed gel points lie on a smooth curve and that the segment interaction equation satisfactorily predicts ternary solubility phenomena for this system with no additional ternary parameters.

Acetone (1)-Polystyrene (2)-Benzene (3)

Predicted and observed phase boundaries are presented in Figure 7. The molecular weight of the polystyrene is again 300,000. Parameters for the acetone-polystyrene binary are the same as those used previously. Parameters for the acetone-benzene binary were obtained from binary data at 45°C. and were assumed to be invariant with temperature. The benzene-polystyrene parameters were determined from binary data at 25°C. As in the previous case, the predicted and observed gel points lie along a smooth curve.

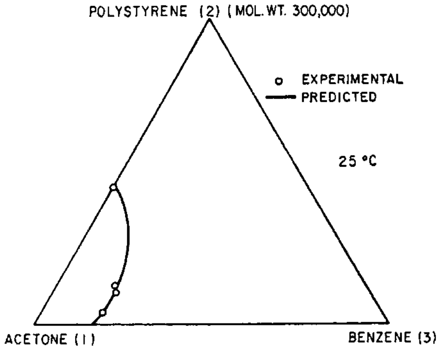
Methanol (1)-Polystyrene (2)-Ethyl Acetate (3)

Predicted and observed phase boundaries are presented in Figure 8. For this system, estimation of parameters at 25°C. for all three binaries was necessary. The methanol-polystyrene parameters are the same as those earlier. The



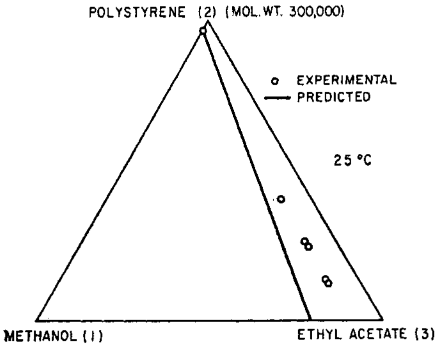
NOTE: PREDICTIONS ARE BASED ON LIMITED DATA FOR BINARY SYSTEMS.

Fig. 6. Experimental and predicted phase boundaries for the acetone-polystyrene-toluene systems.



NOTE: PREDICTIONS ARE BASED ON LIMITED DATA FOR BINARY SYSTEMS.

Fig. 7. Experimental and predicted phase boundaries for the acetone-polystyrene-benzene system.



NOTE: PREDICTIONS ARE BASED ON LIMITED DATA FOR BINARY SYSTEMS.

Fig. 8. Experimental and predicted phase boundaries for the methanol-polystyrene-ethyl acetate systems.

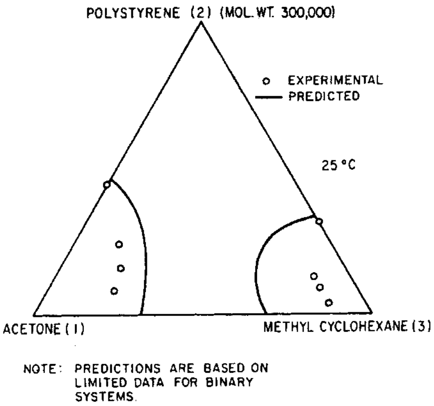


Fig. 9. Experimental and predicted phase boundaries for the acetone-polystyrene-methylcyclohexane system.

methanol-ethyl acetate parameters were obtained from data at 50°C. and were assumed to be independent of temperature. Parameters used for the ethyl acetate-polystyrene binary are those determined from data on the *n*-propyl acetate–polystyrene binary.

Figure 8 indicates that the deviation between the experimental and predicted curves increases as the dilute-polymer solution region is approached. Considering the gross assumptions made in estimating the binary parameters, (particularly that concerning the temperature independence of the methanol-ethyl acetate parameters in the range 25° to 50°C.), the degree of agreement between theory and experiment is satisfactory.

Acetone (1)-Polystyrene (2)-Methylcyclohexane (3)

This system is one of the interesting types, wherein the polymer is completely soluble in mixtures of certain proportions of the two liquids which individually act as swelling media (nonsolvents) for the polymer. Estimation of parameters at 25°C. for all three binaries was necessary. Acetone-polystyrene parameters are the same as those used previously. Parameters for acetone-methylcyclohexane were determined from binary data at 45°C. and were assumed to be invariant with temperature. Parameters for methylcyclohexane-polystyrene were determined by recourse to those determined from data on the cyclohexane-polystyrene binary at 34°C. The experimentally observed equilibrium gel composition for the methylcyclohexane-polystyrene binary was determined to be 32 to 33 vol. % polymer (*16*). A change of 16 cal. (from —20.01 to —4.00 cal.) in $(g_{12} - g_{22})$ yielded a predicted equilibrium gel composition of 34 vol. %. The final choice of parameters was made on this basis.

Figure 9 shows that qualitative agreement between theory and experiment is obtained. The divergence seems particularly pronounced in the methylcyclohexane-rich region. As in the previous case, the qualitative agreement is satisfying in view of the assumptions made in parameter estimation.

CONCLUSIONS

The segment-interaction equation appears to give a very good representation of the thermodynamic properties of polymer solutions. It is particularly gratifying that this semiempirical equation, with only two adjustable parameters, is applicable to a variety of polymer solutions including those which exhibit specific interactions such as hydrogen bonding.

The segment-interaction equation is readily generalized to multicomponent systems and appears to be useful for the prediction of solubility limits in polymer-mixed solvent systems. Agreement between prediction and experiment for five ternary systems is surprisingly good, considering the approximations that were made in estimating the binary parameters. The examples illustrate that in order to obtain a semiquantitative prediction of solubility phenomena for systems in which a set of binary polymer-solvent energy interaction parameters are missing, an estimate of the desired parameters may be obtained from data on a monomeric binary whose components exhibit energetic effects similar to those in the solvent-polymer binary.

The degree of generality and applicability of the segment-interaction equation can be assessed only in the future when reliable experimental data on a larger variety of polymer solutions become available.

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NOTATION

A,B = parameters defined for use in Equation (19)
a = activity
B_1 = second virial coefficient, Equation (11)
G_1,G_2 = parameters defined for use in Equation (19)
g_{ij},g_{ii} = parameters representing energies of *i-j* or *i-i* molecular interactions, cal./g.-mole
Δg^M = molar Gibbs energy of mixing
m = molar volume ratio of polymer to solvent, Equation (1) $\equiv V_2/V_1$
N = number of components
n = number of moles
P = pressure
P_1 = observed vapor pressure of solvent in equilibrium with the solution
P_1^o = vapor pressure of pure solvent
R = universal gas constants, 1.987 cal./(g.-mole)(°K.)
s = number of segments per polysegmented molecule
T = absolute temperature, °K.
V_1,V_2 = molar volumes of solvent and polymer, respectively
x = mole fraction

Greek Letters

χ = Flory-Huggins interaction parameter, Equation (1)
ξ = local volume fraction as defined by Equations (5) to (8), (15), and (16)
ξ_{ii},ξ_{ij} = local volume fraction of species *i* about a central segment of type *i* and *j*, respectively
ϕ = volume fraction
μ = chemical potential

Superscripts

o = pure component
$'$ = phase containing polymer

Subscripts

1,3 = liquids of normal molecular weight
2 = polymer
i,j = components *i*, *j*
T = total

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Reduction of Single Particles and Packed Beds of Hematite with Carbon Monoxide

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Sintered spheres of reagent grade hematite and particles of vermilion ore were reduced by carbon monoxide-carbon dioxide mixtures over the temperature range 820° to 920°C. If all the weight loss were assumed to occur at a single hematite-iron interface, then the early stages of reduction could be correlated by a series combination of the individual resistances due to boundary-layer transport, transport through the reduced iron shell, and interfacial chemical reaction. Sintering and cracking affected the reduction at later stages. Particle reducibility, measured as rate of weight loss, was independent of particle porosity.

Packed beds of similar sized vermilion ore particles were reduced with carbon monoxide-carbon dioxide mixtures at temperatures between 820° and 920°C. Barner's and Spitzer's methods of estimating fixed-bed reduction rates and exit gas compositions were modified to include the multiple-step, single-particle kinetic models. The resulting predictions of fractional reduction agreed closely with the present data; however, theoretical and experimental exit gas compositions differed considerably.

Due to the great industrial importance of pig iron production, there is intense economic interest both in optimizing current iron ore reduction processes, for example, blast furnaces, and in developing more economical reduction and smelting techniques. Often, reduction of iron ore lumps with hot reducing gases containing carbon monoxide, carbon dioxide, hydrogen, and water is involved.

The present work had three goals. First, single-particle reduction data were taken in order to elucidate the roles played by industrially controllable variables such as reduction temperature, reducing gas composition, and intraparticle porosity. Second, isothermal reduction runs were made with fixed beds of vermilion ore particles. A better understanding of fixed-bed reduction was desired as a step toward evaluating the considerable economic potential to be gained by optimizing the temperature, flow rate, and composition of the reducing gas and the size, porosity, and

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