

# THERMODYNAMIC PROPERTIES OF LIQUIDS, INCLUDING SOLUTIONS. VII. DEPENDENCE OF POLYMER PROPERTIES ON MOLECULAR PROPERTIES

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## ABSTRACT

The concepts underlying the writer's new theory of solutions are briefly described and related to concepts previously used by him and others. Equations are given for the concentration dependence of the enthalpy and entropy contributions to the interaction parameter  $\chi$ , for the special case of a monotonic solvent. The entropy contributions are of two kinds: (1) an orientational and vibrational randomness contribution and (2) a contribution correcting the combinatorial entropy for nonrandomness of mixing. Solutions of polyisobutylene in cyclohexane and in benzene are considered as examples. The parameters obtained for these solutions and for rubber-benzene and poly(propylene oxide)-carbon tetrachloride are compared and interpreted in terms of molecular and intermolecular properties.

## INTRODUCTION

For several years the writer has been working on a new theoretical treatment of liquids, including solutions<sup>1-8</sup>, based largely on concepts he has previously used in dealing with polymer solutions<sup>9-18</sup>. Some of these concepts have also been used by others; references will be given as each such concept is introduced.

Since the theory is still in the process of development and refinement, this paper should be considered merely a progress report. It deals specifically with solutions of polymers in solvents of low molecular weight.

The thermodynamic properties of polymer solutions have customarily been treated with the aid of the Flory-Huggins equation<sup>11,12,19</sup>, which may be written:

$$\frac{\tilde{G}_1}{RT} = \ln a_1 = \ln \phi_1 + (1 - \tilde{V}_1/\tilde{V}_2) \phi_2 + \chi \phi_2^2 \quad (1)$$

Here,

$\tilde{G}_1$  is the partial molal Gibbs free energy of the solvent

$a_1$  is the activity of the low-molecular solvent

$\phi_1$  and  $\phi_2$  are volume fractions of the components

$\tilde{V}_1, \tilde{V}_2$  is the ratio of their partial molal volumes, practically equal to the ratio of the molal volumes of the pure components

$\chi$  is an interaction parameter, approaching constancy as the concentration approaches infinite dilution.

Throughout this paper, components 1 and 2 are solvent and polymer, respectively.

Theoretically,  $\chi$  would be expected to be concentration-dependent in general, except for very dilute solutions, and there is ample experimental evidence to show that actually it is often far from constant. One of the aims of the new theory is to provide a reliable basis for estimating the concentration dependence.

Another aim of the new treatment is to provide a better understanding of the compositional and structural factors determining the magnitude of  $\chi$  and its concentration and temperature dependence. Although the writer has dealt with this problem previously in a qualitative and semiquantitative way<sup>13-18</sup>, most researchers measuring or using  $\chi$  have treated it as an empirical parameter, to be determined experimentally for each system of interest.

A third aim of the theory is to provide equations and procedures for deducing the parameters needed to describe the thermodynamic properties of polymer solutions from measurements on substances of low molecular weight and their mixtures. Moreover, since the parameters can reasonably be expected to be functions of the properties of the chemical groups in the polymer and solvent molecules and of the interactions between these groups, the theory aims to relate the polymer solution parameters to parameters characterizing the properties of the groups and their interactions.

The thermodynamic properties of interest (solubilities, vapour pressures, etc.) all depend in known ways on the Gibbs free energy,  $G$ . Because of the fundamental thermodynamic relation

$$G = H - TS \quad (2)$$

these properties thus depend on the enthalpy ( $H$ ) and the entropy ( $S$ ). Of greatest interest are the changes in  $G$ ,  $H$  and  $S$  as two or more components are mixed to form a solution.

Since

$$\Delta H = \Delta E + P\Delta V \quad (3)$$

and  $P\Delta V$  is negligible relative to  $\Delta E$ , we may write, with little error,

$$\Delta G = \Delta H - T\Delta S = \Delta E - T\Delta S \quad (4)$$

To arrive at a theory for  $\Delta G$  it is convenient to develop theoretical expressions for  $\Delta E$  and  $\Delta S$  separately and then to combine them according to this equation.

THEORY OF THE ENTHALPY OF MIXING AND  $\chi_h^{4,5,7}$ 

A liquid is assumed to behave thermodynamically as if its molecules were each composed of one or more chemically uniform groups or segments, with these segments having 'surfaces' in mutual contact. For each type of segment ( $\alpha, \beta$ ) the average *contacting* segment surface area ( $\sigma_\alpha^0, \sigma_\beta^0$ ) is assumed to be constant at a given temperature. The relative total contact areas for the different types are assumed to be governed by equilibrium constants. This minimizes the free energy. If there are only two types of segment, hence three types of contact,

$$K = \frac{\sigma_{\alpha\beta}^2}{4\sigma_{\alpha\alpha}\sigma_{\beta\beta}} \quad (5)$$

The treatment of molecules composed of groups (segments) that are chemically different in terms of group properties and interactions is an obvious improvement over treatments in terms of the properties and interactions of whole molecules. Probably Langmuir<sup>20</sup> was the first to use the group approach, but many others have followed<sup>21-30</sup>. Deal and Derr<sup>30</sup> have given a good summary of most of the earlier work.

Langmuir<sup>20</sup>, Butler<sup>21,22</sup>, Staverman<sup>31</sup>, and others have dealt with molecular and segment surfaces and the energies associated with surface contacts, in calculating cohesive energies and related properties. This would appear to be an improvement over the Scatchard<sup>32</sup>-Hildebrand<sup>33</sup> use of energies per unit volume. Since, for steric reasons, some of the segment surfaces cannot be in contact with others, it is better to use only the (average) segment surface of each type that makes contact with other surfaces. Langmuir, Butler, and Staverman, in effect, did this. Actually, only the ratios of pairs of contacting segment surface areas are involved in properties such as the enthalpy of mixing, as will be shown, and these ratios are readily deduced from the experimental data. It is unnecessary to estimate surface areas from molecular volumes or molecular models. The writer has found that in some cases the experimental contacting surface area ratios are quite different from the estimated total surface area ratios.

The assumption that the average contacting segment surface area is constant seems to be reasonable as an approximation, except when the contact energy per unit area for one or more of the contact types is very small. For such a case, one would expect some concentration dependence of the average fraction of segment surface area that makes contact with other segment surfaces.

The commonly used, but often far from accurate, geometric mean assumption for the interaction energy for contacts between unlike molecules or segments is avoided in this theory. The relative energy values for different contact types are simply deduced (at least for simple systems) from experimental enthalpy of mixing data.

The use of equilibrium constants to relate the contact areas of the different types is logically reasonable and certainly much better than the assumption of random mixing of molecular or segment contacts, whenever the contact energies for the different types differ much. In this respect the present theory resembles the quasi-chemical treatments of Guggenheim<sup>34</sup> and Barker<sup>24</sup>.

It will be noted that the assumptions mentioned do not directly involve pressure, temperature, or volume. Unlike the theory of Prigogine<sup>35</sup> and the recent theory of Flory<sup>36</sup>, this is not an 'equation-of-state' theory. The dependence of volume and of the fundamental parameters mentioned above on temperature and pressure is now being studied. If further comparisons with experimental data show sufficiently good agreement, the new theory developed for these relationships will be reported. For the present, it need only be said that an equation-of-state treatment for solutions, that treats the volume changes on mixing (which result largely from the changes in types of intermolecular or intersegment contact) like the volume changes of the pure liquids on raising the temperature, seems to the writer very unrealistic.

From the assumptions stated at the start of this section, one can readily deduce equations for the excess energy (or enthalpy) of a solution in terms of segment and intersegment parameters and an equilibrium constant or constants.  $\chi_h$ , the enthalpy part of the interaction parameter, is related to the excess enthalpy per mole ( $\bar{H}^E$ ) by the equation:

$$\chi_h = \frac{1}{RT\phi_2^2} \left( \frac{\partial \bar{H}^E}{\partial N_1} \right)_{N_2} \quad (6)$$

where  $N_1$  and  $N_2$  are numbers of solvent and solute molecules, respectively. Applying this relationship, one obtains, for a ditonic solution, containing only two kinds of segments:

$$\chi_h = \frac{\epsilon_\Delta z_\beta}{RT\phi_2^2} \left( \frac{1 - z_\alpha g_K}{1 + z_\alpha z_\beta K' g_K / 2} \right) \quad (7)$$

where

$$K' = 4 \left( \frac{1}{K} - 1 \right) \quad (8)$$

$z_\alpha$  and  $z_\beta$  are contacting surface fractions, related to volume fractions by the equations

$$z_\beta = 1 - z_\alpha = \frac{(r_\sigma/r_v) \phi_2}{1 + (r_\sigma/r_v - 1) \phi_2} \quad (9)$$

and

$$g_K = \frac{-2}{z_\alpha z_\beta K'} \left[ 1 - (1 + K' z_\alpha z_\beta)^{\frac{1}{2}} \right] \quad (10)$$

In these equations  $\epsilon_\Delta$  measures the change in energy when contacts between like segment surfaces are exchanged for contacts between unlike segment surfaces;  $r_\sigma$  is the ratio of the contacting surface area of a segment of the  $\beta$  type to that of a segment of the  $\alpha$  type;  $r_v$  is the ratio of the segment volumes of the two types; and  $K$  is the equilibrium constant, determining the relative areas of contact of the three types (see equation 5).

The three parameters ( $\epsilon_\Delta$ ,  $r_\sigma$ ,  $K$ ) can be determined from good heat of mixing data for a polymer-solvent system or from data on other solutions (not necessarily *polymer* solutions) containing the same segment types.

THEORY OF THE ENTROPY OF MIXING<sup>6</sup> AND  $\chi_s^{4-7}$ 

The molal entropy change on perfectly random mixing of two types of equal sized molecules is

$$\Delta \tilde{S}_M^* = -R(x_1 \ln x_1 + x_2 \ln x_2) \quad (11)$$

a result which, if the heat of mixing is zero, leads to Raoult's law. If the molecules are of unequal size,

$$\Delta \tilde{S}_M = -R(x_1 \ln \phi_1 + x_2 \ln \phi_2) \quad (12)$$

For perfectly random mixing, the excess entropy of mixing resulting from the size difference is

$$\tilde{S}_{rm}^E = \Delta \tilde{S}_M - \Delta \tilde{S}_M^* = -R [x_1 \ln (\phi_1/x_1) + x_2 \ln (\phi_2/x_2)] \quad (13)$$

If the equilibrium constant  $K$  is not 1, the mixing is not perfectly random. The probability that a segment of one type contacts another segment of the same type is not equal to the probability that it contacts a segment of the other type, even when the numbers of the two types are equal. The writer has deduced an equation for the departure of the combinatorial entropy from what it would be for perfectly random mixing and from this he has obtained the combinatorial entropy correction to  $\chi_s$ :

$$\chi_{s,cc} = \frac{-\sigma_a^2}{4\phi_2^2} \left[ \ln \left( \frac{1 - z_\beta g_K}{z_\alpha} \right) + \left( \frac{z_\beta - 2z_\beta^2}{1 + K' z_\alpha z_\beta g_K / 2} - z_\alpha z_\beta g_K \right) \ln \left( 1 + \frac{1 - g_K}{z_\alpha z_\beta g_K^2} \right) \right] \quad (14)$$

The parameters involved are  $r_s$  and  $K$ , which can be obtained from the heat of mixing or the excess volume of mixing, and  $\sigma_a^0$ , which is a measure of the average segment surface area that acts independently in contacting other segment surfaces. It does not now appear possible to deduce the magnitude of the last parameter theoretically, but perhaps after it has been determined empirically for a sufficient number of solutions it will become possible to estimate it for others.

Part of the entropy of a liquid is related to the vibrations and oscillations of the molecules and of their parts. Also, for nonrigid molecules (such as most polymers), there is an entropy contribution related to the randomness of orientation of the rigid segments relative to their neighbours. These contributions to the total entropy must change as the environments of the molecules and segments change, hence as the concentration of a solution changes. Making the simplest approximation—that there is a straight-line relation between the randomness and the average fraction of the contacting surface area of a segment that makes contact with a surface of the same kind—equations have been derived for the excess 'orientational randomness' entropy,  $\tilde{S}_{or}^E$ , and the corresponding contribution to the interaction parameter,  $\chi_{s,or}$ . It seems reasonable to assume that these equations apply, not only to the segment orientational randomness entropy, but also to other vibrational and orientational entropy contributions that depend on close-neighbour environment.

The equation for  $\chi_{s,or}$  is

$$\chi_{s,or} = \frac{-k'_s z_\beta}{r_\sigma \phi_2^2 (1 + k'_s z_\alpha g_K)} \left[ \frac{z_\beta - z_\alpha}{(1 + K' z_\alpha z_\beta)^{\frac{1}{2}}} + z_\alpha g_K \right] \quad (15)$$

In addition to the  $K'$  (or  $K$ ) and  $r_\sigma$  parameters, there is a new one,  $k'_s$ , related to the total randomness change when the neighbours contacting an average segment change from all solvent to all polymer. This parameter can at present only be determined empirically. Later, however, it may become possible to estimate it from the molecular compositions and structures. Alternatively, it may become possible to deduce  $k'_s$  from measurements on solutions containing appropriately related low-molecular chain compounds.

If there are no other contributions to the excess entropy,

$$\tilde{S}^E = \tilde{S}_{rm}^E + \tilde{S}_{cc}^E + \tilde{S}_{or}^E \quad (16)$$

$$\chi_s = \chi_{s,cc} + \chi_{s,or} \quad (17)$$

$$\chi = \chi_h + \chi_s \quad (18)$$

## APPLICATIONS TO SPECIFIC SYSTEMS

It is desirable to test both (1) the degree of agreement between the theoretical equations and experimentally derived values of  $\chi$  and its components, and (2) the applicability to polymer solutions of parameters deduced from solutions containing only molecules of low molecular weight. The second kind of test cannot yet be made, since the necessary parameters from low-molecular systems have not yet been evaluated. There are suitable data for a few polymer solutions, however, to permit appropriate tests of the first class to be made. Results for the rubber-benzene<sup>4,5</sup> and poly(ethylene oxide)-carbon tetrachloride<sup>4-6</sup> systems have already been reported. Two more systems will now be discussed. As before, each will be treated as a ditonic system, each solvent molecule being considered a segment of one kind ( $\alpha$ ) and each polymer mer (base unit) being considered a segment of another kind ( $\beta$ ).

### Polyisobutylene-cyclohexane

Data have been published for the heat of mixing at low polymer concentrations and for activities over the whole range of concentrations. From these data,  $\chi_h$  and  $\chi$  can be calculated.

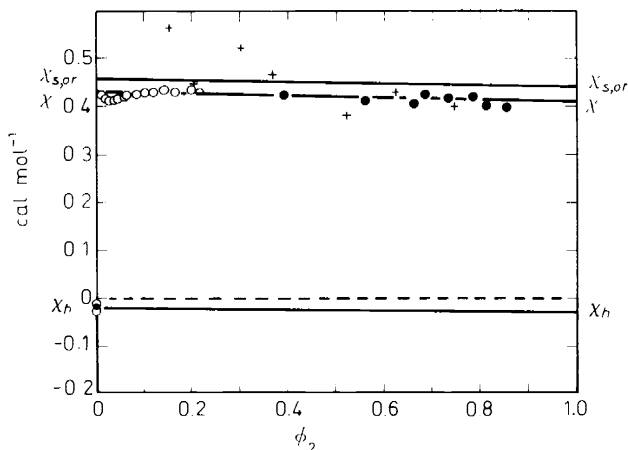
The heat of mixing is negative and very small. Two measurements by Watters, Daoust and Rinfret<sup>37</sup> lead to values of  $\chi_h^0$  of  $-0.017$  and  $-0.028$ . Measurements by Delmas, Patterson and Somcynsky<sup>38</sup> lead to  $\chi_h^0 = -0.024$ . All are for  $25^\circ\text{C}$ .

Figure 1 shows points for these results and for  $\chi$  values calculated from vapour sorption data at  $25^\circ$  by Eichinger and Flory<sup>39</sup>, vapour pressure data at  $25^\circ$  by Bawn and Patel<sup>40</sup>, and osmotic pressure data at  $30^\circ$  by Flory and Daoust<sup>41</sup>.

Der Minassian and Magat<sup>42</sup> have also made vapour pressure measure-

ments, at 15° and 50°, from which they have deduced average values of  $\chi$  of 0.48 and 0.42, respectively. Their individual data points, presented graphically only, show a gradual trend, with  $\chi$  decreasing, at 15°, from about 0.51 at  $\phi_2 = 0.3$  to about 0.45 at  $\phi_2 = 0.8$ .

The  $\chi$  data by Flory and coworkers<sup>39, 41</sup>, plotted in *Figure 1*, seem the most reliable. For comparison with their vapour sorption data at 25°, perhaps the osmotic pressure values (at 30°) should all be increased by about 0.01, but for the present this will be neglected.



*Figure 1.* The interaction parameter  $\chi$  and its components for polyisobutylene-cyclohexane solutions. The curves are theoretical, for  $r_\sigma = 0.505$ ,  $K' = 0$ ,  $\epsilon_A = -18.4$  cal mol<sup>-1</sup>,  $k'_s = -0.222$ .

Data points for  $\chi_h$ :

- Delmas, Patterson, Somcynsky<sup>38</sup> (25°)
- Watters, Daoust, Rinfret<sup>37</sup> (25°)

Data points for  $\chi$ :

- Flory and Daoust<sup>41</sup> (30°)
- Eichinger and Flory<sup>39</sup> (25°)
- + Bawn and Patel<sup>40</sup> (25°)

The very low heats of mixing indicate random mixing of the contacts, hence  $K = 1$ ,  $K' = 0$  and  $\chi_{s,cc} = 0$ .

There are three parameters to be determined from these data:  $\epsilon_A$ ,  $k'_s$  and  $r_\sigma$ . They can be computed, using the equations given, from three data points. Assuming  $\chi_h = -0.025$  at  $\phi_2 = 0$ ,  $\chi = 0.429$  at  $\phi_2 = 0$ , and  $\chi = 0.414$  at  $\phi_2 = 0.70$ , one obtains  $\epsilon_A = -18.4$ ,  $k'_s = -0.222$ , and  $r_\sigma = 0.505$ . The curves in *Figure 1* (practically straight lines) for  $\chi_h$ ,  $\chi_s = \chi_{s,or}$  and their sum,  $\chi$ , were drawn to conform to these parameters.

The results for this system illustrate the important contribution made to  $\chi$  (and hence to the Gibbs free energy of mixing) by the entropy of orientational and vibrational randomness, which has often been neglected in solution theories.

A rough check on the  $r_\sigma$  parameter can be obtained from measurements, by Eichinger and Flory<sup>39</sup>, of the excess volumes of mixing at 25°, for three concentrations. The writer has shown<sup>43</sup> that, if the distribution of the three types of intersegment contact is determined by the equilibrium constant  $K$ , the excess volume should depend on concentration according to an equation

like that deduced for the excess enthalpy, except for replacement of the parameter  $\varepsilon_{\Delta}$  by  $v_{\Delta}$ . This equation may be put in the form

$$\tilde{V}^E = v_{\Delta} x_1 z_{\beta} g_K \quad (19)$$

which, if  $K' = 0$ , reduces to

$$\tilde{V}^E = v_{\Delta} \left( \frac{r_{\sigma} x_1 x_2}{x_1 + r_{\sigma} x_2} \right) \quad (20)$$

The  $v_{\Delta}$  values calculated from Eichinger and Flory's three data points, using this relation with  $r_{\sigma} = 0.505$ , are  $-0.92$ ,  $-0.86$  and  $-0.89 \text{ cm}^3 \text{ mol}^{-1}$ .

Figure 2 shows that the curve for the average parameter,  $-0.89$ , fits the reported data fairly well.

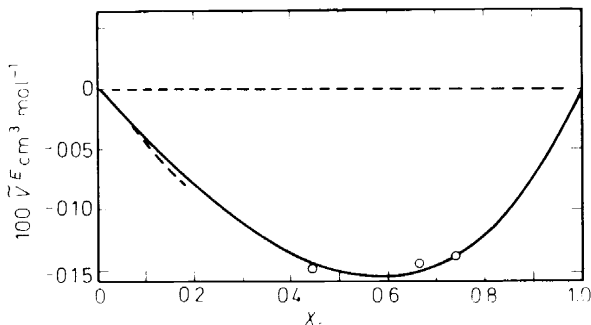


Figure 2. Excess volume of mixing for polyisobutylene-cyclohexane solutions. The curve is theoretical, for  $r_{\sigma} = 0.505$ ,  $K' = 0$ ,  $v_{\Delta} = -0.89 \text{ cm}^3 \text{ mol}^{-1}$ . Data points from Eichinger and Flory<sup>39</sup> (25°). The straight line (dashed) shows the limiting slope, as deduced from data by Cuniberti and Bianchi<sup>44</sup> at 30°.

A further approximate check is obtained from the value of the limiting slope of the  $\tilde{V}^E$  vs.  $x_2$  curve, for which Cuniberti and Bianchi<sup>44</sup> give the value  $-0.46$  at 30°. The dashed curve in Figure 2 has this slope. Differentiating equation 19 gives

$$\left( \frac{d\tilde{V}^E}{dx_2} \right)_{x_2 \rightarrow 0} = v_{\Delta} r_{\sigma} \quad (21)$$

From this, if  $r_{\sigma} = 0.505$ ,  $v_{\Delta} = -0.91$ . The  $\tilde{V}^E$  curve for these parameters is just slightly below that shown in the figure, the difference being less than 0.003 at all concentrations.

### Polyisobutylene-benzene

Heats of mixing for this system are much larger than for the polyisobutylene-cyclohexane system; it is not justifiable to assume  $K = 1$ , requiring random mixing of the contacts. There are no  $\tilde{V}^E$  or  $\tilde{H}^E$  data adequate to determine the shapes of the curves showing their dependence on concentration, from which  $r_{\sigma}$  and  $K'$  could be derived. The first of these parameters, however, can be deduced from  $r_{\sigma}$  for the polyisobutylene-cyclohexane and benzene-cyclohexane systems, since

$$r_{\sigma, \text{PIB/B}} = \frac{\sigma_{\text{PIB}}^{\circ}}{\sigma_{\text{B}}^{\circ}} = \frac{\sigma_{\text{PIB}}^{\circ} \sigma_{\text{CH}}^{\circ}}{\sigma_{\text{CH}}^{\circ} \sigma_{\text{B}}^{\circ}} = r_{\sigma, \text{PIB/CH}} r_{\sigma, \text{CH/B}} \quad (22)$$



$r_{\sigma, \text{CH/B}}$  has been previously determined<sup>3</sup>, from  $\tilde{H}^E$  data by Díaz Peña and Martín<sup>45</sup>, as 1.112;  $r_{\sigma, \text{PIB/CH}}$  has been estimated (see above) as 0.505; hence  $r_{\sigma, \text{PIB/B}} \approx 0.562$ .

Eichinger and Flory<sup>46</sup> give  $\chi_h^0$  (designated  $\kappa_1$  by them) as 0.28, from measurements by Krigbaum and Flory<sup>47</sup>. Watters, Daoust and Rinfret<sup>37</sup> give heat of mixing data at low polymer concentrations. Plotting these against mole fraction yields a straight line, having a slope of 260 cal (Figure 3).

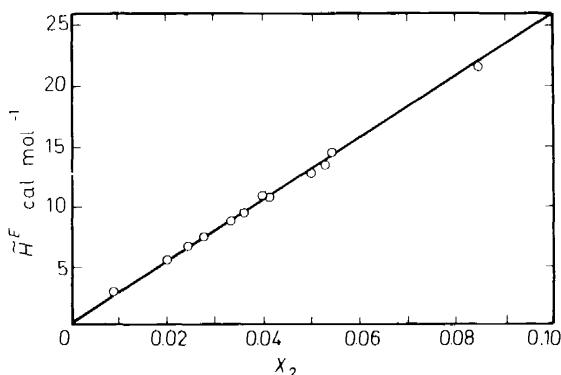


Figure 3. Excess enthalpy of mixing for polyisobutylene-benzene solutions at 25°. Data by Watters, Daoust and Rinfret<sup>37</sup>. The slope corresponds to  $r_{\sigma} = 0.562$ ,  $\epsilon_{\Delta} = 463 \text{ cal mol}^{-1}$ .

According to the present theory, this slope is given by the equation

$$\left( \frac{d\tilde{H}^E}{dx_2} \right)_{x_2 \rightarrow 0} = r_{\sigma} \epsilon_{\Delta}.$$

Hence,  $\epsilon_{\Delta} = 260/0.562 = 463 \text{ cal}$ .

From equation 7, the enthalpy contribution to the interaction parameter, at  $\phi_2 = 0$ , is deduced to be

$$\chi_h^0 = \frac{r_{\sigma}^2 \epsilon_{\Delta}}{KRT r_v^2}$$

where  $r_v$  is the ratio of the mer volumes, in this case equal to 0.685. With all the other quantities known,  $K$  is computed to be 1.88, from which, by equation 8,  $K' = -1.87$ .

All the needed parameters have now been evaluated. Using them, equations 7, 9 and 10 give the concentration dependence of  $\chi_h$ . The curve obtained (Figure 4) agrees with the measurements of Eichinger and Flory<sup>46</sup> within the large error limits given by them, as represented by the vertical lines through the data points in the figure.

$\chi$  values from high pressure osmometry by Flory and Daoust<sup>41</sup> (24.5°) and by Eichinger and Flory<sup>46</sup> (25°), and from vapour pressure data by Eichinger and Flory (25°), by Bawn and Patel<sup>40</sup> (25°), and by Jessup<sup>48</sup> (26.9°) are also shown in Figure 4. From the Flory and Daoust measurements,  $\chi_{x_2=0} = 0.50$ , and from the Jessup and Eichinger and Flory measurements

$\chi_{x_2=0.5} = 0.694$ . From these  $\chi$  values one can calculate the two remaining parameters:  $\sigma_\alpha^0 = 8.99$ , needed for  $\chi_{s,cc}$  and  $k'_s = -0.03$ , needed for  $\chi_{s,or}$ .

The curves for  $\chi$  and its components, calculated from these parameters, are shown in Figure 4. They are in reasonable agreement with the experimental data points, except for some departures at high polymer concentrations. Similar departures were found for the poly(propylene oxide)-carbon tetrachloride system. Eichinger and Flory state: 'The values of  $\chi$  for concentrations  $\phi_2 > 0.5$  are subject to greater uncertainties than those at lower concentrations.' On the other hand, the differences between the theoretical curves and the experimental data points may be due to departures from the assumptions of the theory or to inaccuracy of the parameter estimates.

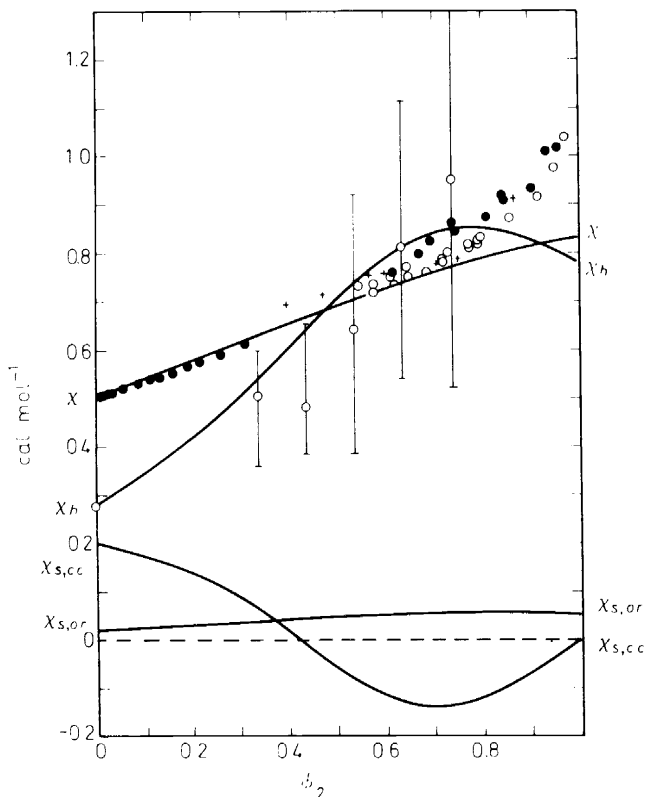


Figure 4.  $\gamma$  and its components for polyisobutylene-benzene solutions. Data points for  $\gamma_h$ :

○ Krigbaum and Flory<sup>47</sup>

○ Eichinger and Flory<sup>46</sup>

Data points for  $\gamma$ :

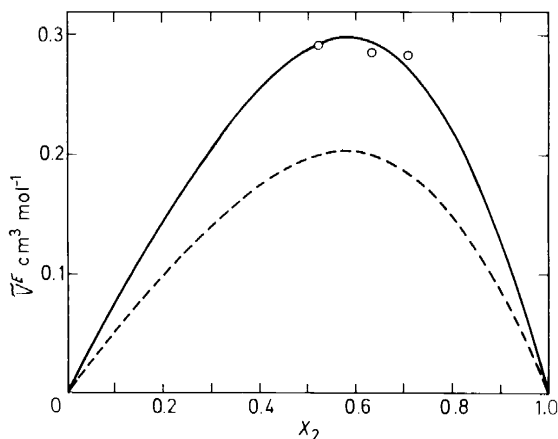
● Flory and Daoust<sup>41</sup> (24.5°)

○ Eichinger and Flory<sup>46</sup> (25°)

○ Jessup<sup>48</sup> (26.9°)

+ Bawn and Patel<sup>40</sup> (25°)

Eichinger and Flory<sup>46</sup> have reported three measurements of the excess volume of mixing. Assuming  $r_\sigma = 0.562$  and  $K' = -1.87$ , the average of the three  $v_\Delta$  values, calculated by equation 19, is 1.407. The dependence of  $\bar{V}^E$  on concentration, using these parameters, is shown by the upper curve in *Figure 5*. The experimental points fall reasonably close to the curve.



*Figure 5.* Excess volume of mixing for polyisobutylene-benzene solutions. Data points from Eichinger and Flory<sup>46</sup> (24.5°).

— Theoretical curve for  $r_\sigma = 0.56$ ,  $K' = -1.87$ ,  $v_\Delta = 1.407$

--- Theoretical curve for  $r_\sigma = 0.56$ ,  $K' = -1.87$ ,  $v_\Delta = 0.96$

The lower (dashed) curve in this figure is drawn for the same  $r_\sigma$  and  $K'$  values, but with  $v_\Delta = 0.96$ , required to give agreement with Cuniberti and Bianchi's<sup>44</sup> value of 0.54 for  $(d\bar{V}^E/dx_2)_{x_2 \rightarrow 0}$  at 30°. The disagreement between this curve and Eichinger and Flory's 24.5° data points may be due to inaccuracy of the assumed  $r_\sigma$  and  $K'$  parameters or of the experimental data or to temperature dependence of the parameters or the measured properties.

## DISCUSSION OF THE PARAMETERS

*Table 1* compares the parameters (rounded) for the two systems dealt with in this paper, together with those previously reported for two other polymer-solvent systems.

For a close-packed arrangement of contacting spherical molecules, the molecular surface area is proportional to the two-thirds power of the molecular volume. For close-packing of rodlike molecules, the molecular surface area is approximately proportional to the first power of the molecular volume. For other shapes and other arrangements and especially for mixtures, the relationships are more complicated. Comparing the ratios,  $r_\sigma$ , of the *contacting* mer surface areas, for the four polymer-solvent systems here considered, with the ratios,  $r_v$ , of their mer volumes, it is seen (*Figure 6*) that  $r_\sigma$  is roughly proportional both to  $r_v$  and to  $r_v^{\frac{2}{3}}$ . It appears likely that it will be possible to estimate approximate  $r_\sigma$  values from  $r_v$  values (hence from

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Table 1. Parameters (rounded)

Components	Temp. °C	$r_s$	$r_v$	$K'$	$K$	$\epsilon_{\Delta}$ cal mol <sup>-1</sup>	$\sigma_{\alpha}^0$	$k'_s$	$v_{\Delta}$ cm <sup>3</sup> mol <sup>-1</sup>
Rubber-benzene <sup>4,5</sup>	25	0.74	0.908	-1.40	1.54*	268*	5.0	-0.05	0.32
Poly(propylene oxide)-CCl <sub>4</sub> <sup>4,5,7</sup>	5.5	0.54	0.609	0	1	-500		-0.36	1.12
Polyisobutylene -cyclohexane	25	0.51	0.563	0	1	-18		-0.22	-0.9
Polyisobutylene -benzene	25	0.56	0.685	-1.87	1.88	463	9.0	-0.03	1.41

\* As a result of copying errors,  $K$  and  $\epsilon_{\Delta}$  for rubber-benzene were incorrectly given as 0.74 and 2.68 in refs. 4 and 5.

the densities of the pure components), at least when these ratios are known for systems having components of similar (mer) shapes.

As can be seen from equation 5,  $K$  measures the relative tendencies to form unlike and like contacts between the components. For the poly(propylene oxide)-carbon tetrachloride and the polyisobutylene-cyclohexane systems the two types of contact are approximately equally likely: the relative numbers of unit contacts of the three types are as they would be for perfect randomness. For the other two systems, however, there is some preference for polymer-solvent contacts, rather than polymer-polymer and solvent-solvent contacts.

The parameter  $\epsilon_{\Delta}$  is defined<sup>4</sup> by the equation

$$\epsilon_{\Delta} = \frac{1}{2}\sigma_{\alpha}^0\Delta E = \frac{1}{2}\sigma_{\alpha}^0(2\epsilon_{\alpha\beta} - \epsilon_{\alpha\alpha} - \epsilon_{\beta\beta}) \quad (25)$$

where  $\epsilon_{\alpha\beta}$ ,  $\epsilon_{\alpha\alpha}$  and  $\epsilon_{\beta\beta}$  represent energies per unit contact area. (The  $\epsilon$ 's are all negative, since the energies are attractions.) The positive  $\epsilon_{\Delta}$  values found

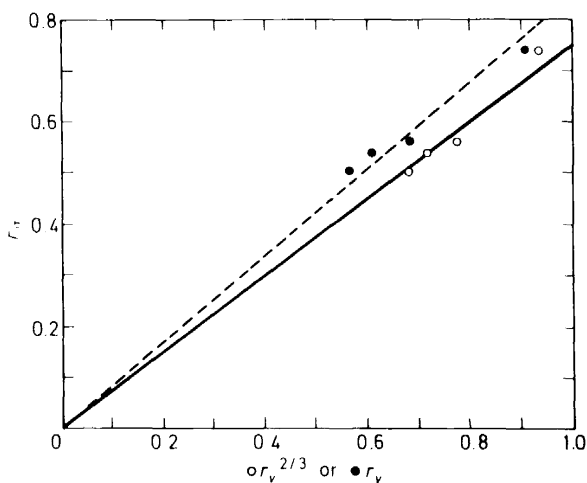


Figure 6.  $r_s$  plotted against  $r_v$  (●) and against  $r_v^{2/3}$  (○) for four polymer-solvent systems. Data from Table 1.

for the rubber-benzene and polyisobutylene-benzene systems thus mean that the attraction energy per unit contact area is greater for like contacts than for unlike contacts. For the other systems the opposite relation holds. Obviously there is no parallelism, in these systems, between the relative attraction energies and the relative probabilities of contact. This is because of the large difference between the entropies of mixing in the different systems.

The  $\sigma_\alpha^0$  values are determined from the corrections to the entropy of mixing measuring the randomness of placing the molecules in the total volume, for systems in which  $K$  is not equal to unity.  $\sigma_\alpha^0 = 5$  (or 9) means that the randomness of making intersegment contacts is the same as it would be for a hypothetical system in which, on the average, each  $\alpha$  segment makes 5 (or 9) contacts, these contacts all being made independently, without mutually influencing each other. The numbers, 5 and 9, appear reasonable. (They need not be integers.) The maximum number of contacts for a regular assemblage of spheres of uniform size is 12. The type of contact at each site would be expected to be influenced somewhat by the types of contact at neighbouring sites (see ref. 18, p. 3536), thus decreasing the number of contacts in the equivalent hypothetical system containing only independent contacts.  $\sigma_\alpha^0$  can be considered to be determined in part by the segment geometries and in part by the degree to which contact types are affected by the types of neighbouring contacts.

The parameter  $k'_s$  is related to the average changes in orientational and vibrational randomness ( $v$ ) for the component segments (here, solvent molecules and polymer mers) as the concentration changes. Mathematically expressed,

$$k'_s = \frac{v_{1,x_2 \rightarrow 0} - v_{1,x_2 \rightarrow 1}}{v_{1,x_2 \rightarrow 1}} + \frac{v_{2,x_2 \rightarrow 0} - v_{2,x_2 \rightarrow 1}}{v_{2,x_2 \rightarrow 1}} \quad (26)$$

$k'_s$  is thus *minus* (the fractional change in orientational and vibrational randomness per segment of type 1 *plus* the same per segment of type 2, as  $x_2$  changes from 1 to 0). For solutions of flexible polymers, the randomness to be considered is probably chiefly that of the orientation of the rigid segment in the polymer molecules relative to neighbouring segments. Note that it is not the magnitude of this randomness related to the flexibility, but the *change* in its magnitude as the segment environment changes. It should also be noted that the theoretical equations were derived on the assumption of a straight-line relationship between this change and the average composition of the shell of contacting neighbours around each segment. Departures from the assumed straight-line relationship might well cause disagreement, especially at high polymer concentration, between the experimental Gibbs free energies (or the  $\chi$  values) and those predicted from the theoretical equations.

It seems premature to discuss further the relative magnitudes of the  $k'_s$  values deduced for these systems.

The parameter  $v_\Delta$  is defined by the equation

$$v_\Delta = \frac{1}{2}\sigma_\alpha^0 \Delta v = \frac{1}{2}\sigma_\alpha^0 (2v_{\alpha\beta} - v_{\alpha\alpha} - v_{\beta\beta}) \quad (27)$$

(compare equation 25). The positive  $v_{\Delta}$  values found for the rubber-benzene and polyisobutylene-benzene systems mean that a contact between like segments contributes more to the total volume than the average contributions of contacts between like segments. For the other two systems, having negative  $v_{\Delta}$  values, the reverse relationship holds. The magnitudes of these contributions, and so of  $v_{\Delta}$ , must be related in a complicated way to the geometries of the molecules. Further discussion does not seem warranted at this time.

### SUMMARY AND CONCLUSION

For the two polymer-solvent systems discussed in detail here, the theoretical equations appear to be applicable, giving good agreement with the available experimental data, except for some departures at high polymer concentrations for the polyisobutylene-benzene system. Similar results have been previously reported for two other systems.

The parameters obtained for these four systems have been interpreted in terms of molecular and intermolecular properties. It is to be expected that, as parameters for more systems become available, more precise interpretations can be made and, hopefully, predictions of parameters for new systems will become possible.

### ACKNOWLEDGEMENTS

Since a new theory, such as this one, must be evaluated by comparison between the theoretical predictions and experimental measurements, the theoretician must rely heavily on the availability of good data. Since the writer is not in a position to obtain new data himself, he must depend on literature sources. He feels very grateful to those authors who have published accurate data of the kinds suitable for his purpose. He is also grateful to the many other scientists with whom he has discussed aspects of the new theory during its development.

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