AN ASSOCIATED SOLVENT THEORY OF POLYMER SOLUTIONS

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ABSTRACT

This paper describes an association theory of the thermo-
dynamic properties of mixtures of a non-polar polymer with a polar
solvent, based on the Flory-Huggins equation. The solvent molecules
are assumed to associate to linear complexes which form an athermal
Flory-Huggins mixture, while the polymer and the solvent complexes
form a Flory-Huggins mixture with a single interchange energy
parameter.

The experimental dilution properties of mixtures of
polypropylene with diethylketone and with di-isopropyl ketone,
obtained from vapour pressure measurements, are shown to be
satisfactorily described by the theory. The volumes of mixing
exhibit the cubic type of dependence on composition possible
theoretically, but the value of the Flory-Huggins parameter required
is inconsistent with the other dilution properties.
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1. Introduction

The Flory-Huggins theory accounts very well on the whole for the mixing properties of some non-polar polymers in non-polar solvents[1]. However, it is not so successful for polar solvents, and neither is the more sophisticated version of the lattice theory developed by Huggins, Guggenheim and Miller. One of the characteristic features of a polymer solution containing a polar solvent is its abnormally high vapour pressure when only small amounts of solvent are present, and the rapid drop in the free energy of dilution as more solvent is added. This behaviour is almost certainly due to the orientationally dependent polar forces between the solvent molecules, and a statistical theory which should be applicable to these systems has been given by Barker[2] and by Tompa[3]. However, the detailed lattice model on which the theory is based, and the complexity of the resulting equations, deterred the authors from attempting to apply it to the experimental results obtained by them in collaboration with Gee[4]. The present theory was therefore developed in the attempt to find a simpler and more flexible way of describing the difference between polar and non-polar solvents.

The basic idea is simply to treat the solvent as an associated liquid in the chemical sense. Such association theories occur frequently in the literature of physical chemistry[5], and although they are really only applicable to hydrogen-bonded liquids, they should also give a rough description of polar liquids generally.

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One novel feature of the theory presented here is that instead of making the usual postulate that the associated complexes form an ideal mixture it is assumed that they form an athermal Flory-Huggins mixture. This assumption is made primarily in order to simplify the theory, which is based on the Flory-Huggins equation for a non-polar polymer solution. It has been shown by Prigogine and his colleagues[5] that the assumption is a bad one for solvents with hydroxyl groups, which mainly form dimer and trimer complexes, but it should be more reasonable for polar liquids which do not involve hydrogen bonding.

2. Assumptions

(a) The solvent consists of linear complexes S_ν $(\nu = 2, 3, \ldots$ ad inf.) formed by the association of polar monomer molecules S_1 in a chemical fashion, so that

$$\nu S_1 \rightleftharpoons S_\nu \qquad (\nu = 2, 3, \ldots).$$
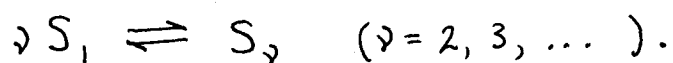
(b) The Gibbs free energy of association of S_1 with any complex S_ν is the same for all values of ν.

(c) The complexes S_ν form an athermal Flory-Huggins mixture.

(d) The polymer and the solvent complexes form a Flory-Huggins mixture with the same interchange energy parameter χ.

(e) Any volume changes on mixing can be neglected in calculating free energies and heats of mixing.

3. Gibbs Free Energy and Potentials

Consider a mixture containing n_s moles of solvent and n_p moles of polymer, with volume fractions ϕ_s and $\phi_p = 1 - \phi_s$. In accordance with assumption (a) let the solvent consist of n_ν moles of complex S_ν with volume fraction ϕ_ν, so that

$$n_s = \sum_1^\infty \nu n_\nu \ , \qquad \phi_s = \sum_1^\infty \phi_\nu \ , \qquad (3.1)$$

and the molar mass of the complexes and unassociated molecules is

$$n = \sum_1^\infty n_\nu \ .$$

If the solvent complex S_ν interacts with the polymer with an energy parameter $\chi_{\nu p}$, then the total Gibbs free energy on the Flory-Huggins theory is

$$G = \sum_1^\infty n_\nu \mu_\nu^i + n_p \mu_p^{ii} + RT\left[\sum_1^\infty n_\nu \ln \phi_\nu + n_p \ln \phi_p + \sum_1^\infty n_\nu \phi_p \chi_{\nu p} \right], \qquad (3.2)$$

where μ_ν^t is the potential of pure S_ν at the given temperature and pressure, and μ_p^o is that of the pure polymer.

The potential of S_ν in solution can be obtained by differentiating (3.2) with respect to n_ν and is

$$\mu_\nu = \mu_\nu^t + RT\left[\ln \phi_\nu + \phi_s(1 - \nu/\bar\nu) + \phi_p(1 - \nu/p) + \right.$$
$$\left. + \chi_{\nu p} - \nu \sum_1^\infty \phi_\lambda \chi_{\lambda p}/\lambda \right], \qquad (3.3)$$

where p is here the ratio of the molar volume of the polymer to that of the solvent monomer S_1 , and $\bar{\nu} = n_s/n$ is the average degree of association. The corresponding potential for the pure solvent is

$$\mu_\nu^o = \mu_\nu^\dagger + RT\left[\ln \phi_s^o + 1 - \nu/\bar{\nu}_o\right], \qquad (3.4)$$

where all the quantities referrring to the pure solvent have been distinguished by the superscript or suffix 0 .

4. Association Equilibrium

For chemical equilibrium between the species S_1 , S_2 , etc.,

$$\mu_\nu - \nu\mu_1 = 0 \qquad (\text{all } \nu). \qquad (4.1)$$

When equation (3.3) is substituted into this relation it becomes

$$\mu_\nu^\dagger - \nu\mu_1^\dagger = RT\left[\ln(\phi_1^\nu/\phi_\nu) + \nu - 1 + \phi_p(\nu\chi_{1p} - \chi_{\nu p})\right]. \qquad (4.2)$$

Introducing assumption (b), that is

$$\mu_\nu^\dagger - \nu\mu_1^\dagger = (\nu-1)g^\dagger, \qquad (4.3)$$

and assumption (d), that is

$$\chi_{\nu p} = \chi \qquad (\text{all } \nu),$$

and putting

$$g^\dagger - RT = -RT \ln K_0, \qquad (4.4)$$

$$K = K_0 \exp(\chi \phi_p), \qquad (4.5)$$

equation (4.2) can be written in the form

$$\phi_\nu = \phi_1^\nu K^{\nu-1}.$$

Eliminating ϕ_1, by means of (3.1) we get

$$\phi_\nu = \frac{1}{K} \left(\frac{K \phi_s}{1 + K \phi_s} \right)^\nu, \quad (\text{all } \nu). \qquad (4.6)$$

The distribution of complexes is thus a geometric one for mutual equilibrium.

The average degree of association $\overline{\nu}$ is given by

$$1/\overline{\nu} = \sum_1^\infty \phi_\nu / \nu \phi_s.$$

Substituting from (4.6) for ϕ_ν and summing leads to

$$\bar{\nu} = K\phi_s / \ln(1 + K\phi_s).$$
(4.7)

It follows that $\bar{\nu} > 1$ except for the pure polymer $(\phi_s \to 0)$ or no association $(K_0 = 0)$ when $\bar{\nu} = 1$. It can easily be seen that the degree of association has a maximum at $\phi_s = 1/\chi$ if $\chi > 1$, where the solvent is more associated than when it is pure. The physical interpretation of this is that when χ is large enough the tendency for mixing with the polymer to dissociate the solvent by dilution is overcome by the reduced heat of mixing of the associated complexes as compared with the dissociated monomers; the comparison is between an S_ν complex with heat parameter χ and νS_1 molecules with heat term $\nu\chi$.

5. Pure Solvent

It is evident that the potential of the pure solvent, μ_s^0, is equal to that of the monomer, μ_1^0, and is therefore given by equation (3.4). The free energy of association of the solvent, $\Delta^0\mu_s$, can be obtained by substituting from the equations of §4 into (3.4), and is given by

$$\Delta^0\mu_s = \mu_s^0 - \mu_1^\tau = -RT \zeta_0 ,$$
(5.1)

where ζ_0 is the ratio of the number of complexes to the number of unassociated molecules, given by

$$\zeta_0 = (n^\circ - n_1^\circ)/n_1^\circ,$$

$$= (1 + 1/K_0)\ln(1+K_0) - 1. \qquad (5.2)$$

When the standard free energy of association $g^\dagger$ is large and positive, so that K_0, given by equation (4.5), is small and association is slight, (5.2) can be expanded to give

$$\zeta_0 = \tfrac{1}{2}K_0 - \tfrac{1}{6}K_0^2 + O(K_0^3), \qquad (5.3)$$

On the other hand, when $g^\dagger$ is large and negative

$$\Delta^\circ \mu_s \cong g^\dagger,$$

which corresponds to complete association.

6. Solvent in Solution

The Gibbs free energh of mixing of the solution may be written in the form

$$\Delta G = \Delta G^{FH} + \Delta^* G$$

where ΔG^{FH} is the Flory-Huggins term given by[1]

$$\Delta G^{FH} = RT \left[n_s \ln \phi_s + n_p \ln \phi_p + n_s \phi_p \chi \right], \qquad (6.1)$$

and $\Delta^* G$ is a term due to association of the solvent. It follows from the equations of §§ 3 and 4 that

$$\Delta^* G = n_s RT (\zeta_0 - \zeta) \qquad (6.2)$$

where ζ is the ratio of the number of complexes to the number of unassociated solvent molecules in solution, and is given by

$$\zeta = (n - n_1) / n_1,$$

$$= (1 + 1/\kappa \phi_s) \ln (1 + \kappa \phi_s) - 1. \qquad (6.3)$$

$\Delta^* G$ is positive or negative depending on whether association in the solution is less than or greater than that in the pure solvent; the condition for $\Delta^* G$ to be negative is

$$\zeta > \zeta_0 \qquad \text{or} \qquad \phi_s \exp(\chi \phi_p) > 1,$$

which is only possible if $\chi > 1$.

It is clear that the effective solvent potential in solution, μ_s, is equal to that of the unassociated molecules μ_1. The free energy dilution of the solvent can therefore be found from the equations of the previous sections, and split into two parts:

$$\Delta\mu_s = \Delta\mu_s^{FH} + \Delta^*\mu_s , \qquad (6.4)$$

where the Flory-Huggins term is

$$\Delta\mu_s^{FH} = RT\left[\ln\phi_s + \phi_p(1-1/p) + \chi\phi_p^2\right] \qquad (6.5)$$

and the association term is given by

$$\Delta^*\mu_s/RT = \zeta_0 - \zeta - \phi_p(1-1/\bar{\nu})(1-\chi\phi_s) . \qquad (6.6)$$

For the pure solvent $\Delta^*\mu_s$ vanishes, while for the pure polymer we find that

$$\Delta^*\mu_s = -\Delta^0\mu_s \qquad (\phi_s = 0) ,$$

where $\Delta^0\mu_s$ is the free energy of association of the pure solvent, given by (5.1). This means that dissociation is initially complete when an associated solvent is added to pure polymer.

Rather than consider $\Delta^{*}\mu_s$ itself it is more interesting to introduce an effective Flory-Huggins parameter χ_{eff} by means of the equation

$$\Delta\mu_s = RT\left[\ln\phi_s + \phi_p(1-1/p) + \chi_{eff}\phi_p^2\right],$$

so that

$$\chi_{eff} = \chi + \Delta^{*}\mu_s/RT\phi_p^2 . \qquad (6.7)$$

The behaviour of χ_{eff} as a function of composition is shown in Figure 1 for various values of χ and K_o. It can be seen that for the pure polymer

$$\chi_{eff}^{p} = \chi + \zeta_o \qquad (\phi_p = 1), \qquad (6.8)$$

and for the pure solvent

$$\chi_{eff}^{s} = \tfrac{1}{2} + \phi_1^{o}(\tfrac{1}{2}\zeta_o\chi^2 + \chi - \tfrac{1}{2}) \qquad (\phi_p = 0), \qquad (6.9)$$

where $\phi_1^{o} = 1/(1+K_o)$ is the volume fraction of unassociated molecules in the pure solvent. When the degree of association is very high then

$$\chi^{p}_{eff} \cong -g^{\dagger}/RT \quad \text{and} \quad \chi^{s}_{eff} \cong \frac{1}{2} \quad (k_{0} \to \infty). \quad (6.10)$$

χ^{p}_{eff} is always greater than χ , but whether χ^{s}_{eff} is greater or less than χ depends on the values of χ and K_{0} . If K_{0} is very large it lies between χ and $\frac{1}{2}$; if K_{0} is very small it is less than χ when

$$2 + \sqrt{2} > \chi > 2 - \sqrt{2} = 0.585.$$

The second virial coefficient A_{2} for a polymer in the solvent is proportional to $\frac{1}{2} - \chi^{s}_{eff}$. It follows from equation (6.9) that the effect of association is always to lower A_{2} .

7. Phase Separation and Critical Mixing

For solutions of high polymers ($p \gg 1$) phase separation will occur if, on adding solvent, the potential of the solvent in solution, μ_{s} , rises above the value for the pure solvent, μ^{0}_{s} . The condition for saturation is therefore

$$\Delta \mu_{s} = 0.$$

If $\Delta \mu_{s}$ is written in the form (6.7), this condition gives χ_{eff} as a function of the saturation composition; the relation is shown as a dashed line in Figure 1 . For given values of χ and K_{0}

the saturation composition (if any) is given by the intersection of the χ_{eff} curve with the dashed curve.

The critical mixing composition for polymers of high molecular weight is almost that of the pure solvent, and the condition for critical mixing becomes simply that χ_{eff} for this composition is equal to $1/2$, or by (6.9)

$$\mathcal{S}_0 \chi^2 + 2\chi - 1 = 0. \qquad (7.1)$$

Since $\mathcal{S}_0$ and χ will depend on temperature, this condition determines the critical mixing temperature T^c for infinitely high polymers (the Flory temperature). It is of interest to see how association affects the value of χ^c, which is $1/2$ for a non-associating solvent. As an equation in χ (7.1) has two roots, of which one is always negative and may be ignored since the theory cannot be expected to cover cases of specific attraction between solvent and polymer molecules. The positive root is

$$\chi^c = \left[1 + (1 + \mathcal{S}_0)^{\frac{1}{2}} \right]^{-1} \leq \frac{1}{2}, \qquad (7.2)$$

and shows that the effect of association is to lower the critical value of χ and therefore to raise the Flory temperature in general above the value predicted by the Flory-Huggins equation. In the limit of complete association $\chi^c = 0$.

8. Heat and Entropy of Dilution

The heat of mixing ΔH can be derived from equations (6.1) and (6.2) for ΔG by differentiating with respect to temperature, and is given by

$$\Delta H = (n^{\circ} - n)h^{\dagger} + n\phi_p RT\chi_H ,   (8.1)$$

where $h^{\dagger}$ is the standard heat of association of the solvent defined by

$$h^{\dagger} = - T^2 \partial(g^{\dagger}/T)/\partial T   (8.2)$$

and χ_H is the Flory-Huggins "heat" parameter defined by

$$\chi_H = - T\partial\chi/\partial T .   (8.3)$$

Both terms in equation (8.1) have a direct physical interpretation. Since $h^{\dagger}$ is negative, the first term is positive or negative depending on whether the solvent is more or less associated in the solution than when pure. The second term has the same sign as χ_H (which is normally positive) but is always less than the corresponding Flory-Huggins heat term

$$\Delta H^{FH} = n_s \phi_p RT \chi_H .$$

The heat of dilution of the solvent due to association can be obtained by differentiating either $\Delta^* \mu_s$ with respect to temperature or $\Delta^* H$ with respect to n_s, and is given by

$$\Delta^* H_s = (\eta_0 - \eta) h^\dagger + \phi_p (\eta - \phi_1/\phi_s)(1 - \chi \phi_s)(h^\dagger - RT\chi_H \phi_p)$$
$$- (1 - \eta) RT\chi_H \phi_p^2 , \qquad (8.4)$$

where for convenience we have put $\eta = n/n_s = 1/\bar{\nu}$. This expression vanishes for the pure solvent and for the pure polymer has the value

$$\Delta^* H_s = - \Delta^0 H_s \qquad (\phi_p = 1),$$

$$= - (1 - \eta_0) h^\dagger , \qquad (8.5)$$

where $\Delta^0 H_s$ is the heat of association of the pure solvent.

It is useful to introduce an effective Flory-Huggins heat parameter $(\chi_{eff})_H$ given by

$$(\chi_{eff})_H = \chi_H + \Delta^* H_s / RT \phi_p^2 . \qquad (8.6)$$

Its value for the pure polymer is

$$(\chi_{eff})_H = \chi_H - (1-\gamma_0)h^\dagger/RT \qquad (\phi_p = 1),$$

which is positive and greater than χ_H. Heat is therefore always absorbed initially when solvent is added to the polymer.

An effective Flory-Huggins entropy parameter $(\chi_{eff})_S$ may be defined by

$$\chi_{eff} = (\chi_{eff})_H + (\chi_{eff})_S.$$

Since the standard entropy of association

$$s^\dagger = (h^\dagger - g^\dagger)/T$$

will be negative, corresponding to the loss of translational and orientational freedom of the solvent monomers on associating, the contribution of association to $(\chi_{eff})_S$ will be negative.

9. Standard Free Energy of Association

If a non-polar (unassociated) reference liquid can be found whose properties are the same as those of the unassociated solvent S_1, then by comparing the vapour pressure of the associated solvent with that of the reference liquid it is possible to calculate the standard free-energy of association $g^\dagger$ at any temperature. Thus the potential of the reference liquid is

$$\mu_r^o = \mu_1^\dagger$$

and if it is assumed that the solvent is not associated in the vapour phase, then

$$\Delta^{\circ}\mu_s = \Delta_e\mu_r - \Delta_e\mu_s , \qquad (9.1)$$

where

$$\Delta_e\mu = {}^g\mu - {}^L\mu$$

is the difference between the gaseous and liquid states. If the vapours of the solvent and reference liquid are perfect, then

$$\Delta_e\mu(T,P) = \Delta_e H - T\Delta_e S^{\ddagger} + RT\ln(P/P^{\ddagger}), \qquad (9.2)$$

where the heat of evaporation, $\Delta_e H$, is assumed independent of temperature. It follows from (9.1) and (9.2) that

$$\Delta^{\circ}\mu_s = (\Delta_e H_r - \Delta_e H_s) - T(\Delta_e S^{\ddagger}_r - \Delta_e S^{\ddagger}_s), \qquad (9.3)$$

$$= RT\ln(p_s/p_r), \qquad (9.4)$$

where $p_s(T)$ and $p_r(T)$ are the vapour pressures of the solvent and reference liquid at temperature T . The ratio $\mathcal{I}_o$ can therefore be obtained from the simple equation

$$\xi_o = \ln(p_r/p_s), \tag{9.5}$$

and the constant K_o and the standard free energy of association $g^\dagger$ can be calculated from (5.2) and (4.4). The standard heat of association $h^\dagger$ can then be obtained from the heats of evaporation of the solvent and reference liquid by means of the equations

$$\Delta^o H_s = \Delta_e H_r - \Delta_e H_s,$$

$$= (1 - \eta_o) h^\dagger \tag{9.6}$$

Note that if $\Delta_e H_r$ and $\Delta_e H_s$ are independent of temperature, then so is $\Delta^o H_s$, and $\Delta^o \mu_s$ is then linearly dependent on temperature according to (9.3).

The major and obvious difficulty with this method of obtaining $g^\dagger$ is to formulate practical criteria for choosing the reference liquid appropriate to a particular solvent.

10. <u>Volume of Mixing</u>

One of the assumptions of this treatment, assumption (e) of § 2, is that any volume change on mixing can be neglected in calculating free energies and heats of mixing, so that the Flory-Huggins equation, which is theoretically appropriate to constant volume conditions, can be used as a basis. However, there is bound to

be some change in volume on mixing polar and non-polar substances at constant pressure, since association of the solvent is almost certain to be accompanied by a contraction. Assuming that the volumes of the complexes S_γ and the polymer are additive, the total volume change is

$$\Delta V = \sum_1^\infty (n_\gamma - n_\gamma^o) V_\gamma^o ,$$

(10.1)

where V_γ^o is the molar volume of S_γ . Let us assume the change of volume (contraction) is $v^\dagger$ for each act of association, so that

$$V_\gamma^o - \gamma V_1^o = (\gamma - 1) v^\dagger .$$

(10.2)

Then by substitution

$$\Delta V = (n^o - n) v^\dagger .$$

(10.3)

This equation is consistent with (6.1) et seq., for ΔG , and can be derived from it, assuming that only $g^\dagger$ depends on pressure, by means of the relations

$$\Delta V = (\partial \Delta G / \partial P)_T , \qquad v^\dagger = (\partial g^\dagger / \partial P)_T .$$

The proportional volume change is approximately

$$\Delta V/V = \phi_s (\eta_0 - \eta)(v^{\dagger}/V_1^o). \qquad (10.4)$$

For $0 \leqslant \chi \leqslant 1$ the volume always increases due to the dissociation of complexes on dilution, but if $\chi > 1$ then ΔV changes sign at $\phi_s = 1/\chi$ and becomes negative. This "cubic" type of behaviour is actually observed with the systems compared with theory in the next section, but it is not clear that this behaviour is entirely due to association of the solvent.

11. Comparison of Theory and Experiment

The theory has been applied to the systems polypropylene + diethyl ketone and polypropylene + di-isopropylketone[4]. Although it is not to be supposed that such ketones are literally associated liquids, nevertheless it is interesting to see how far the association theory can describe the essential differences between polar and non-polar solvents.

The values of $g^{\dagger}/RT$ and χ were chosen to fit the experimental vapour pressure results at 25^oC. The calculated curves of χ_{eff} against ϕ_p are compared with the experimental points in Figure 2. The agreement is seen to be satisfactory, except near the pure polymer end of the range. This region has been further investigated[6], with the conclusion that the sharp rise in χ_{eff} is

due to the crystallinity of polypropylene.

In view of the fact that these ketones are certainly not associated liquids in the literal sense, it is of interest to see if the $g^\dagger$ values which fit the polymer solution results are reasonable in comparing the ketones to similar non-polar liquids. We have therefore used the theory of section 9 to compare the ketones with reference hydrocarbons having about the same critical volume. Thus 2,4-dimethylpentane was used as reference liquid for di-isopropylketone. The results are:

Diethylketone: $\qquad g^\dagger/RT \; = \; -0.5 \;$ (solution)

$\qquad\qquad\qquad\qquad\qquad\qquad -1.7 \;$ (reference)

Di-isopropylketone: $g^+/RT \; = \; 0 \qquad$ (solution)

$\qquad\qquad\qquad\qquad\qquad\qquad -1.4 \;$ (reference) .

The only thing to be said for the comparison is that the values parallel each other roughly. It is clear that the comparison puts too great a strain on the model.

The theoretical heat of dilution in section 8 involves two further parameters χ_H and $h^\dagger$. These have been chosen to give the best fit of the calculated curve and experimental points. The comparison is shown in Figure 3. With two extra parameters, it is difficult to assess the significance of the good agreement which is obtained. However, the best values of the heats of

association $h^{\dagger}$ are comparable with those obtained by comparing the pure solvents with reference liquids, according to the equations of section 8 :

Diethyl ketone:	$h^{\dagger}/RT$	=	-4.2	(solution)
		=	-4.0	(reference)
Di-isopropylketone:	$h^{\dagger}/RT$	=	-3.3	(solution)
		=	-4.2	(reference)

Figure 4 shows some unpublished experimental results[7] for the volume change on mixing of these systems. The measurements were made because the association theory predicted a cubic dependence on composition, as shown in section 10. The cubic form of the experimental results was therefore very gratifying. However, ΔV only changes sign theoretically if $\chi > 1$, and since the values of χ giving the best fits to the vapour pressure results are both less than unity, association cannot be the whole story.

CONCLUSION

The association model proposed to account for the differences in behaviour between polar and non-polar solvents in interaction with polymers has been shown to be capable of describing these differences. However, the model is clearly not realistic for the

ketones to which it has been applied. Nevertheless, it may prove
useful for solvents which do associate through hydrogen bonding.
In defence of the theory, it may claim to have satisfied the touch-
stone of a true scientific hypothesis, in predicting an effect
(the cubic ΔV) which was subsequently verified by experiment.

ACKNOWLEDGEMENT

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Legends for Figures

Figure 1. Theoretical curves of χ_{eff} as a function of ϕ_p for various values of $g^\dagger/RT$ and χ . The dashed line is the saturation curve.

Figure 2. Comparison of theoretical curves and experimental points (25°C) for χ_{eff} against ϕ_p : ✗ Diethylketone + polypropylene, $g^+/RT = -0.5$, $\chi = 0.6$.

⊙ Di-isopropylketone + polypropylene, $g^\dagger/RT = 0$, $\chi = 0.35$.

Figure 3. Comparison of theoretical curves and experimental points (25°) for $\Delta H_s/RT$ against ϕ_p .

✗ Diethylketone + polypropylene, $h^+/RT = -4.2$, $\chi_H = 0.95$.

⊙ Di-isopropylketone + polypropylene, $h^+/RT = -3.27$, $\chi_H = 0.45$.

Figure 4. Experimental volume change on mixing (cc/g) against weight fraction of polymer (25°C).
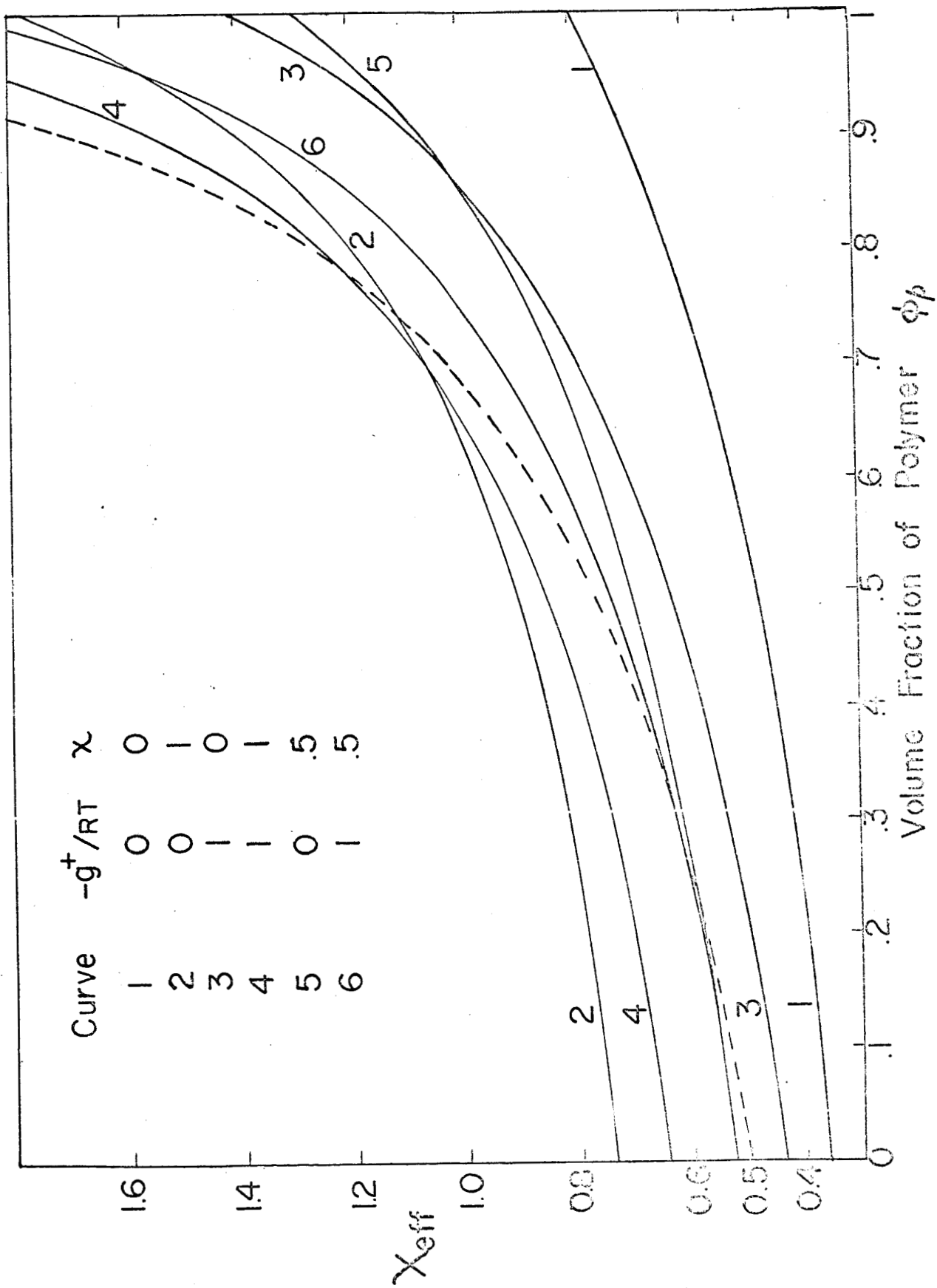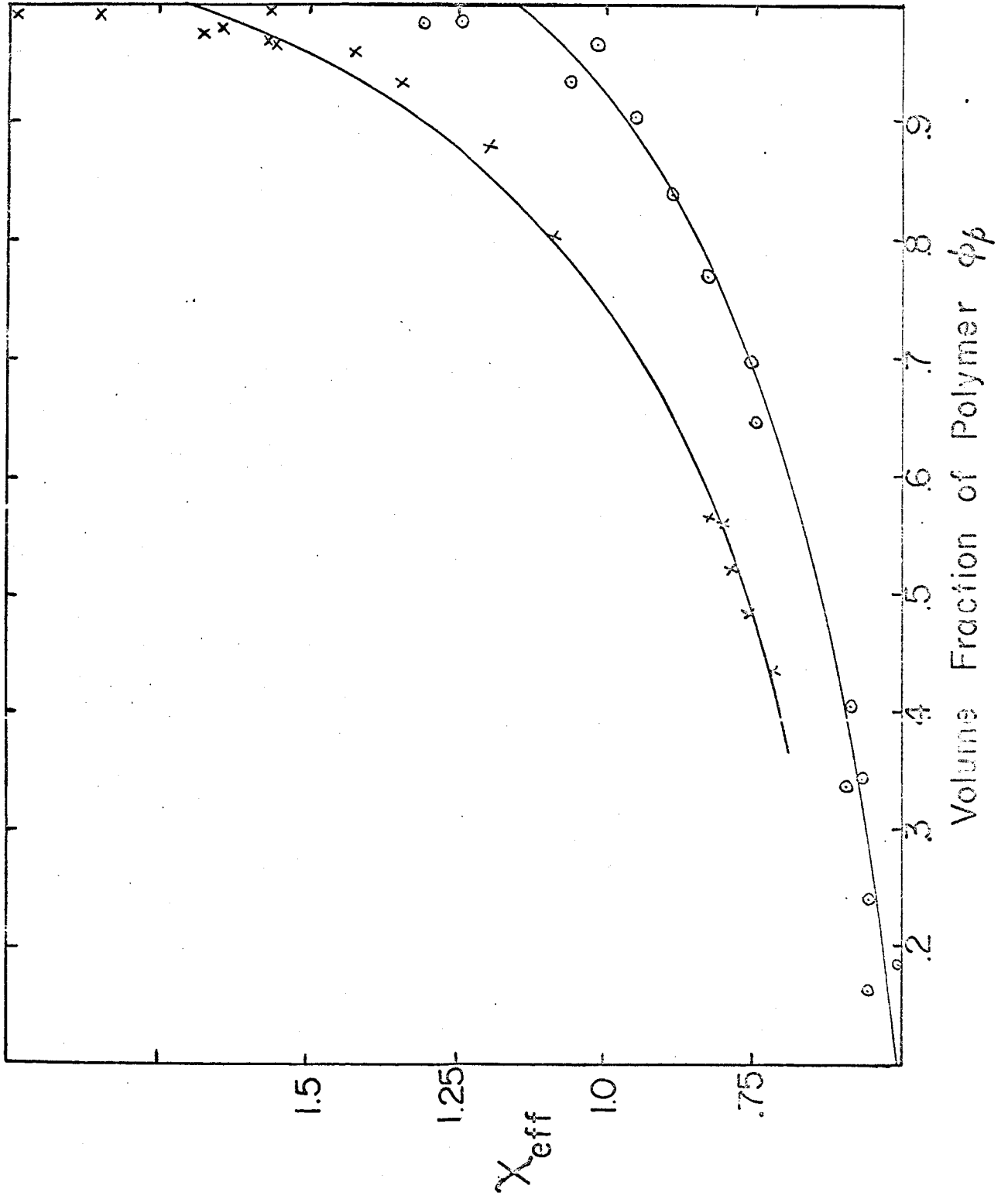
✗ Diethylketone + polypropylene

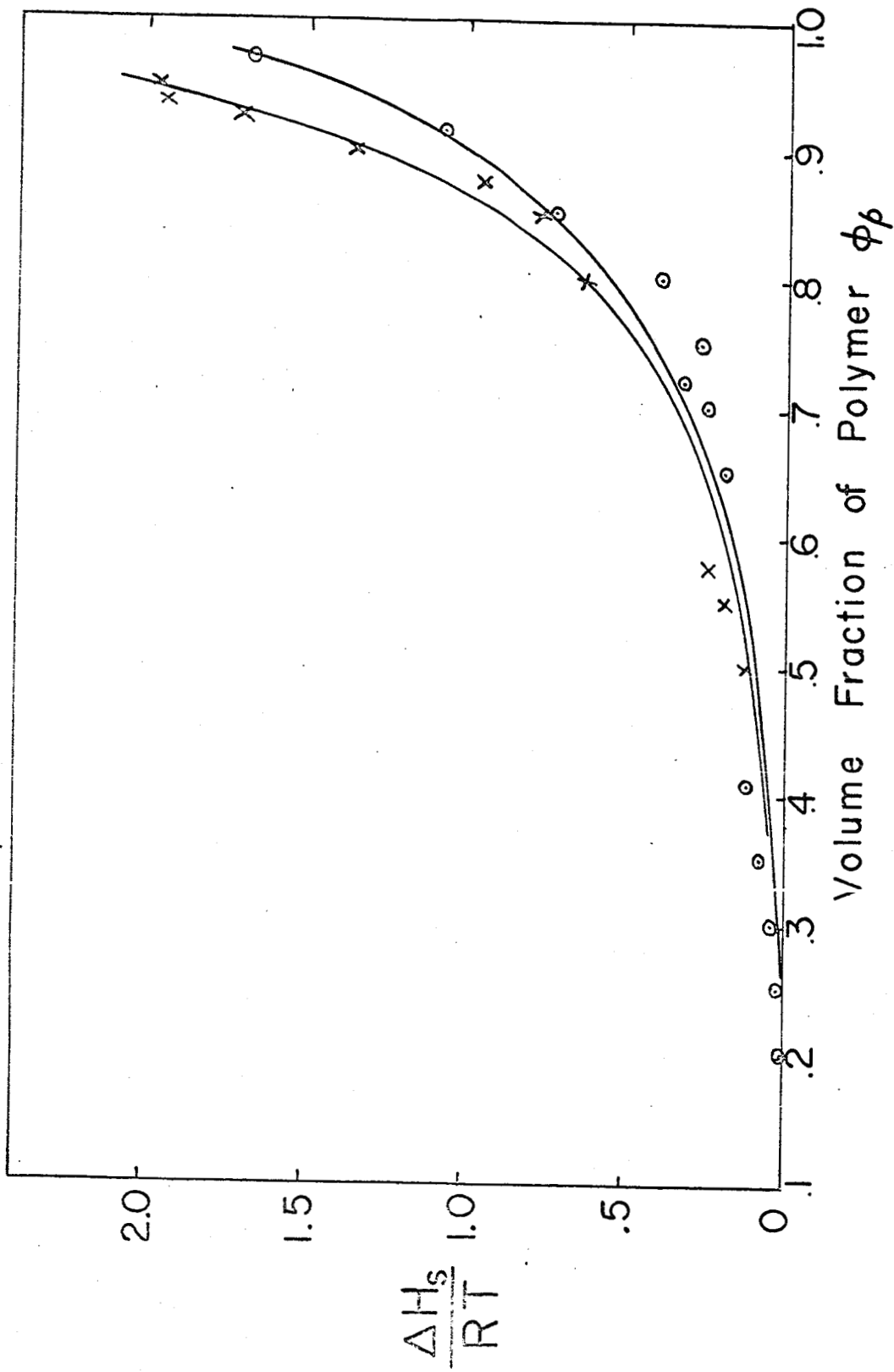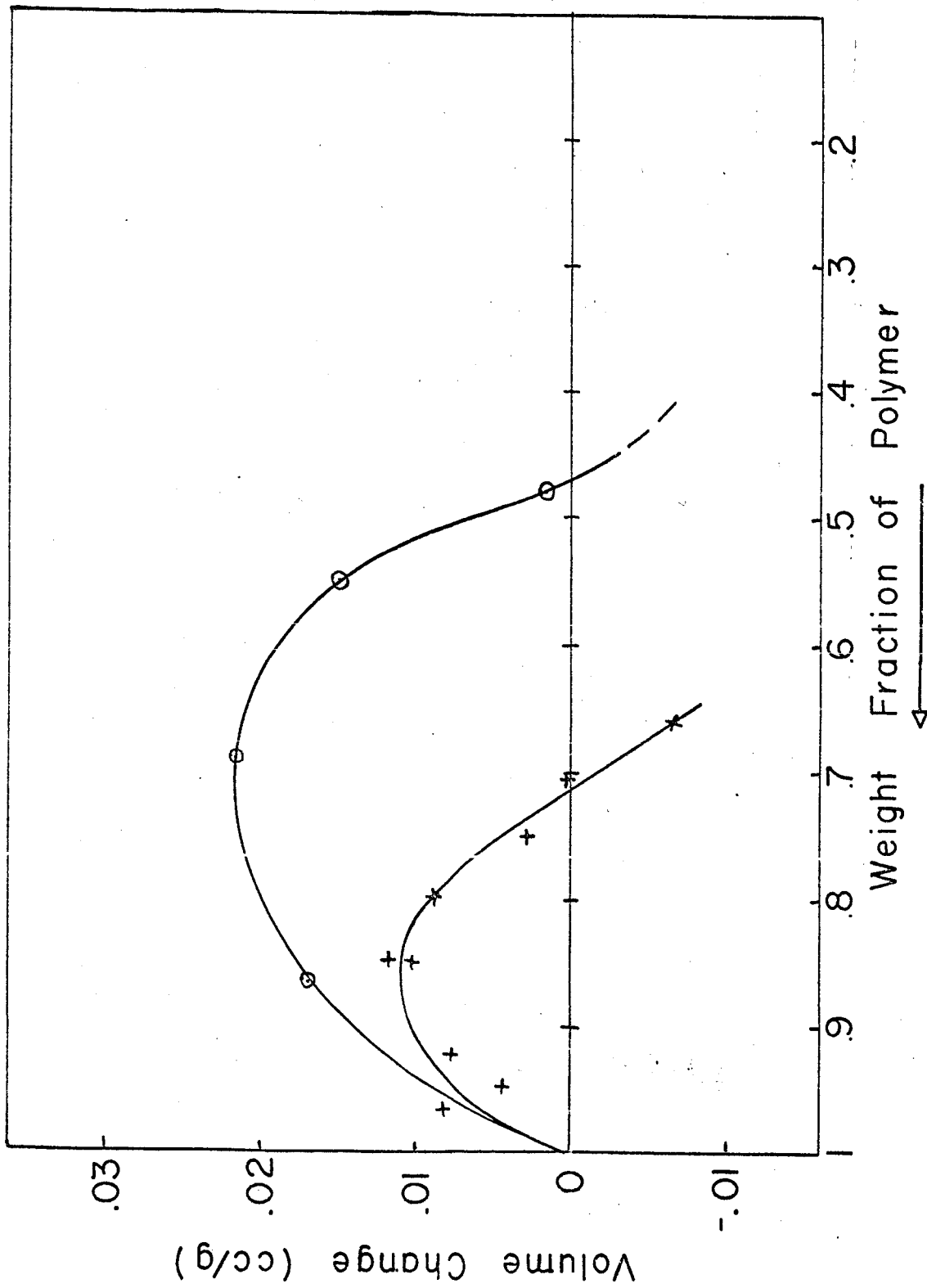⊙ Di-isopropylketone + polypropylene

Figure 1

Figure 2

Figure 3

Figure 4