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The Thermodynamics of High-Polymer Solutions: I. The Free Energy of Mixing of Solvents and Polymers of Heterogeneous Distribution*

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The theories of Flory and Huggins for the free energy of mixing of a homogeneous chain polymer of uniform molecular weight with a single uniform solvent have been extended to the case of a polymer mixture of varying chain lengths with a mixture of solvents. By making the similar assumptions as those of Huggins, and utilizing familiar statistical mechanical methods, the partial molal free energy of mixing of the solvent is found to be

$$\bar{\Delta F}_0 = RT[\ln \phi_0 + (1 - \phi_0)(1 - 1/\bar{m}_N) + \mu(1 - \phi_0)^2],$$

where ϕ_0 is the volume fraction of solvent, \bar{m}_N a simple function of the number average molecular weight, and μ a constant characteristic of the polymer-solvent mixture (consisting largely of a heat term, but also including γ , the coordination number of the rubber segments). By assuming that a mixture of two solvents behaves like a new homogeneous liquid a method of calculating μ for such mixtures is developed. Applications of these formulas to solubility and fractionation are shown in a subsequent article.

INTRODUCTION

THE free energy relations of high-polymer solutions were first calculated independently by Flory¹ and Huggins² for the case of a homogeneous chain polymer of uniform molecular weight in a single uniform solvent. In practice, however, one is never dealing with a polymer sample in which all the molecules have the same molecular weight, but rather with a mixture of molecular weights, forming a virtually continuous distribution. If, on the other hand, one intends to extend the thermodynamic treatment of such solutions to the problems of fractionation and precipitation it is of interest to extend the treatment to a solvent medium consisting of a mixture of two pure solvents. The purpose of this and the following paper is to extend the theory to these two cases and to give a thermodynamic treatment of solubility, fractionation, and precipitation. Although the final results of Flory and Huggins are fairly analogous, we preferred to base our derivations upon the development of Huggins who, in our opinion, makes less, and more justifiable, assumptions concerning the nature of the rubber molecule than does Flory.

1. Entropy of Mixing of Chains of Varying Length with a Solvent

Suppose a mixture consisting of n_1 molecules of molecular weight m_1 (in units of arbitrary

submolecules, the density of all molecular weight fractions being taken as the same),³ n_2 molecules of molecular weight m_2 , n_3 of m_3 , etc. Then the total number of sites, for submolecules and solvent molecules is

$$N = N_0 + n_1 m_1 + n_2 m_2 + \cdots + n_j m_j, \quad (1)$$

where N_0 = the number of sites occupied by the solvent molecules.

In order to calculate the entropy of this system we have to determine the total number of configurations. We shall proceed in the same way as Huggins did for the binary system.⁴

Suppose now that n_1 molecules of the type m_1 , n_2 of the type m_2 , etc., up to n_{i-1} of the type m_{i-1} have already been put into the "lattice" as well as $K-1$ molecules of the type m_i .

Let $\nu_{i,K,l}$ be the number of alternative sites available for the l th segment of the K th molecule of the type m_i . Then for the first segment of the K th molecule of the m_i type

$$\nu_{i,K,1} = N(1 - f_j), \quad (2)$$

³ Each submolecule is considered as the same size as a molecule of solvent so that m_i is in reality the ratio of the molecular volume of the polymer molecule of molecular weight M_i and the molecular volume of the solvent V_0 or $m_i = M_i/\rho V_0$. If ρ , the density of the polymer, is considered as independent of the chain length, then m_i is, for any given solvent, directly proportional to and therefore a measure of the molecular weight.

⁴ There is, however, one difference between our treatment and that of Huggins. Huggins considers each molecule of molecular volume m as consisting of l freely orienting segments each of them composed of p submolecules. Since, however, in the final formulation l and p appear only as the product $lp = m$, we did not use this decomposition and consider simply the molecule as composed of m segments.

* The major portion of the following work was done on a grant from the Rubber Reserve Company for fundamental research in the field of synthetic rubber.

¹ P. J. Flory, *J. Chem. Phys.* **10**, 51 (1942).

² M. L. Huggins, *Ann. N. Y. Acad. Sci.* **43**, 1 (1942).

where f_j = the fraction of the total number of sites already occupied.

$$f_j = \frac{\sum_{i=1}^{i-1} n_i m_i + (K-1)m_i}{N} \quad (3)$$

Once the first submolecule is placed in a site S_0 , the position of the other submolecule is greatly limited. Huggins points out that if the immediately adjacent site S_1 is occupied, two of the sites immediately adjacent to S_1 must also be occupied, provided S_1 is not the end of the chain.⁵ Hence the probability that both S_1 and S_0 are occupied by adjacent molecules of a previous chain is:

$$P = 2f_j/\gamma, \quad (4)$$

where γ is the "coordination number," i.e., the

number of neighbor sites around each site. But in our case S_0 cannot have been occupied by a submolecule of a previous chain since we assumed that it is occupied by a first submolecule of the present chain. Hence the probability that S_1 is unoccupied and free for the second submolecule is greater than (4) and is

$$P = [1 - f_j]/[1 - (2f_j/\gamma)], \quad (5)$$

and the number of sites available for the second submolecule is

$$\nu_{j,K,2} = \gamma(1 - f_j)/[1 - (2f_j/\gamma)], \quad (6)$$

and similarly for the third submolecule

$$\nu_{j,K,3} = (\gamma - 1)(1 - f_j)/[1 - (2f_j/\gamma)], \quad (7)$$

and so on.

Hence for the K th chain of the i th type the total number of distinguishable configurations is

$$\nu_{i,K} = (N/\sigma)(1 - f_j)\gamma(\gamma - 1)^{m_i-2}[1 - f_j]/[1 - (2f_j/\gamma)]^{m_i-1}, \quad (8)$$

where σ is the symmetry number of the chain (i.e., 2 if the ends are interchangeable), or introducing the definition of f_j (3)

$$\nu_{i,K} = \frac{\gamma(\gamma - 1)^{m_i-2}}{\sigma} \frac{(N - \sum_{i=1}^{i-1} n_i m_i - (K-1)m_i)^{m_i}}{(N - 2/\gamma[\sum_{i=1}^{i-1} n_i m_i - (K-1)m_i])^{m_i-1}}.$$

Then, the total number of configurations for the n_i molecules of the i th type may be written as:

$$\prod_{k=1}^{n_i} \nu_{i,k} = x \left[\frac{\gamma(\gamma - 1)^{m_i-2}}{\sigma} \right]^{n_i} \frac{\prod_{k=0}^{n_i-1} (N - \sum_{i=1}^{i-1} n_i m_i - k m_i)^{m_i}}{\prod_{k=0}^{n_i-1} (N - 2/\gamma[\sum_{i=1}^{i-1} n_i m_i + k m_i])^{m_i-1}}. \quad (9)$$

Taking the logarithm and replacing the summations by integrals (equivalent to the approximation of Sterling's formula),

$$\ln \prod_{K=1}^{n_i} \nu_{i,K} = n_i \ln \left(\frac{\gamma(\gamma - 1)^{m_i-2}}{\sigma} \right) + m_i \int_0^{n_i} \ln (N - \sum_{i=1}^{i-1} n_i m_i - K m_i) dK - (m_i - 1) \int_0^{n_i} \ln (N - 2/\gamma[\sum_{i=1}^{i-1} n_i m_i + K m_i]) dK. \quad (10)$$

⁵ For long molecules, as Huggins has shown, this possibility introduces only a negligible correction.

Integrating

$$\begin{aligned} \ln \prod_{K=1}^{n_i} \nu_{i,K} = n_i \ln \left(\frac{\gamma(\gamma-1)^{m_i-2}}{\sigma} \right) - n_i m_i - (N - \sum_{i=1}^i n_i m_i) \ln (N - \sum_{i=1}^i n_i m_i) \\ + (N - \sum_{i=1}^{i-1} n_i m_i) \ln (N - \sum_{i=1}^{i-1} n_i m_i) + \frac{(m_i-1)}{2m_i} \gamma [(N - 2/\gamma \sum_{i=1}^i n_i m_i) \ln (N - 2/\gamma \sum_{i=1}^i n_i m_i) \\ - (N - 2/\gamma \sum_{i=1}^{i-1} n_i m_i) \ln (N - 2/\gamma \sum_{i=1}^{i-1} n_i m_i) + 2/\gamma n_i m_i]. \quad (11) \end{aligned}$$

The total number of distinguishable configurations for the whole system is

$$W = [(\prod_{i=1}^i \prod_{K=1}^{n_i} \nu_{i,K}) (\prod \nu_0)] / [(\prod_i n_i!) (n_0!)] = [\prod_i \prod_{K=1}^{n_i} \nu_{i,K}] / [\prod_i n_i!], \quad (12)$$

and the entropy of the system

$$S/k = \ln W = \sum_i \ln \prod_{K=1}^{n_i} \nu_{i,K} - \sum_i n_i \ln n_i + \sum_i n_i. \quad (13)$$

Substituting (11) in (13) and simplifying

$$\begin{aligned} S/k = \sum_i n_i \ln \left[\frac{\gamma(\gamma-1)^{m_i-2}}{\sigma} \right] - \sum_i n_i \ln n_i / N - N_0 \ln N_0 / N + \gamma/2 (N - 2/\gamma \sum_i n_i m_i) \\ \times \ln \left(1 - 2/\gamma \frac{\sum_i n_i m_i}{N} \right) - \gamma/2 \sum_i [N/m_i] [(1 - 2/\gamma N \cdot \sum_{i=1}^i n_i m_i) \ln (1 - 2/\gamma N \cdot \sum_{i=1}^i n_i m_i) \\ - (1 - 2/\gamma N \cdot \sum_{i=1}^{i-1} n_i m_i) \ln (1 - 2/\gamma N \cdot \sum_{i=1}^{i-1} n_i m_i)]. \quad (14)^6 \end{aligned}$$

So far no new assumption or approximation has been made beyond the ones used in Huggins' theory. However, in order to go further than Eq. (14) one has to make the following simplification: the last term of the Eq. (14) is very small since it involves essentially a difference of sums extended once to the i th molecule type, once to the $(i-1)$ th type. If we now assume that any given molecular weight fraction is small, $n_i m_i \ll \sum n_i m_i$ it is legitimate to expand the logarithms in series and cancel all but the first term. Then this term becomes

$$\begin{aligned} -\gamma/2 \cdot \sum_i N/m_i [(1 - 2/\gamma N \cdot \sum_{i=1}^i n_i m_i) \ln (1 - 2/\gamma N \cdot \sum_{i=1}^i n_i m_i) \\ - (1 - 2/\gamma N \cdot \sum_{i=1}^{i-1} n_i m_i) \ln (1 - 2/\gamma N \cdot \sum_{i=1}^{i-1} n_i m_i)] \cong + \sum_i n_i. \quad (15) \end{aligned}$$

Equation (14) has taken then the simplified form:

$$\begin{aligned} S/k \cong \sum_i n_i \ln \left[\frac{\gamma(\gamma-1)^{m_i-2}}{\sigma} \right] - \sum_i n_i \ln n_i / N - N_0 \ln N_0 / N \\ + \gamma/2 (N - 2/\gamma \sum_i n_i m_i) \ln (N - 2/\gamma \sum_i n_i m_i) + \sum_i n_i. \quad (16) \end{aligned}$$

⁶ If one now assumes that only molecules of one chain length are present, $n_1 = N_r$, $n_2 = n_3 = \dots = 0$ then Eq. (14) reduces to:

$$S/k = N_r \ln \left[\frac{\gamma(\gamma-1)^{m-2}}{\sigma} \right] - N_r \ln \frac{N_r}{N_0 + m N_r} - N_0 \ln \frac{N_0}{N_0 + m N_r} + (m-1) [\gamma/2 m \cdot N_0 + (\gamma/2 - 1) N_r] \ln \left[\frac{N_0 + (1-2/\gamma) m N_r}{N_0 + m N_r} \right],$$
 which is identical with the equation derived by Huggins.

The entropy of mixing is of course

$$\Delta S_{\text{mix}} = S - S_0 - \sum S_i, \quad (17)$$

where S_0 and S_i are the entropies of pure solvent and pure rubber fraction respectively. Substituting in Eq. (16) the conditions $n_1 \neq 0$ and $n_2 = n_3 = n_4 = \dots = 0$; $n_2 \neq 0$ and $n_1 = n_3 = n_4 = \dots = 0$, etc., and $N_0 = 0$ separately one finds

$$S_0 = 0, \quad (18)$$

$$S_i/k = n_i \ln [\gamma(\gamma-1)^{m_i-2}]/\sigma + n_i \ln m_i + (\gamma/2-1)n_i m_i \ln (1-2/\gamma) + n_i. \quad (19)^7$$

After subtraction one obtains the entropy of mixing.

$$\begin{aligned} \Delta S_{\text{mix}}/k = & - \sum_i n_i \ln n_i m_i / N - N_0 \ln N_0 / N \\ & + \gamma/2(N-2/\gamma \sum_i n_i m_i) \ln (N-2/\gamma \sum_i n_i m_i) - (\gamma/2-1) \ln (1-2/\gamma) \cdot \sum_i n_i m_i. \end{aligned} \quad (20)$$

After partial differentiation and some simplifications, Eq. (20) yields the partial molal entropies.

$$\frac{\overline{\Delta S}_0}{R} = \frac{\partial(\Delta S_{\text{mix}}/R)}{\partial N_0} = + \sum_i \frac{n_i}{N} - \ln \frac{N_0}{N} - \frac{N_0}{N} + \frac{\gamma}{2} \left[\ln \left(1 - \frac{2}{\gamma N} \sum_i n_i m_i \right) + \frac{2}{\gamma N} \sum_i n_i m_i \right], \quad (21a)$$

$$\begin{aligned} \frac{\overline{\Delta S}_i}{R} = \frac{\partial(\Delta S_{\text{mix}}/R)}{\partial n_i} = & + m_i \sum_i \frac{n_i}{N} - \ln \frac{n_i m_i}{N} - 1 + \frac{m_i N_0}{N} \\ & + \left(\frac{\gamma}{2} - 1 \right) \ln \left[\frac{1 - \frac{2}{\gamma N} \sum_i n_i m_i}{\frac{2}{1 - \frac{2}{\gamma}}} \right] - m_i \left(1 - \frac{\sum_i n_i m_i}{N} \right). \end{aligned} \quad (21b)$$

If we introduce now measurable values, e.g., volume fractions, one has the relation

$$N_0/N = \phi_0, \quad n_i m_i / N = \phi_i, \quad \sum_i n_i m_i / N = \sum_i \phi_i = 1 - \phi_0.$$

Further, the number average molecular weight (in units of submolecules) is:

$$\bar{m}_N = \sum_i n_i m_i / \sum_i n_i = (\sum_i \phi_i) / [\sum_i (\phi_i / m_i)] \quad (22)$$

and hence

$$\sum_i n_i / N = 1 - \phi_0 / \bar{m}_N. \quad (23)$$

Introducing this definition in Eq. (21), expanding the logarithms in the last term and neglecting the terms in ϕ^3 or higher, one obtains finally:

$$\overline{\Delta S}_0 = -R[\ln \phi_0 + (1 - 1/\bar{m}_N)(1 - \phi_0) + 1/\gamma(1 - \phi_0)^2]; \quad (24)$$

$$\overline{\Delta S}_i = -R[\ln \phi_i + 1 - m_i \phi_0 - (m_i / \bar{m}_N)(1 - \phi_0) + (m_i / \gamma) \phi_0^2]. \quad (25)$$

Several remarks can be made concerning Eqs. (24) and (25). (1) It is not apparent why the last term in Eq. (25) is $m_i/\gamma \cdot \phi_0^2$ and not $m_i \phi_0^2/(\gamma-2)$

as would follow from the calculation given above. This substitution is made by analogy to Huggins, who gives no justification for it. Actually, the denominator has to be γ and not $\gamma-2$ if Eqs. (24) and (25) are to be consistent and satisfy the Gibbs

⁷ This is what Flory calls the disorientation entropy of the polymer mixture.

relation. Presumably this substitution corrects for the fact that the expansions in Eqs. (21a) and (21b) are not exactly equivalent, the terms in (21a) being all positive while the terms in (21b) are alternately positive and negative. Hence when the higher terms are neglected, the same degree of approximation is not reached. (2) For a binary system $m_i = \bar{m}_n = m$ and this reduces to the familiar equations of Huggins:

$$\overline{\Delta S}_0 = -R[\ln \phi_0 + (1 - 1/m)\phi_r + (1/\gamma)\phi_r^2]; \quad (26a)$$

$$\overline{\Delta S}_r = -R[\ln \phi_r - (m - 1)\phi_0 + (m/\gamma)\phi_0^2]. \quad (26b)$$

(3) The partial molal entropy of the solvent does not depend on the molecular weight distribution of the high polymer but only on the number average molecular weight \bar{m}_N , while the partial molal entropy of the polymer depends on both \bar{m}_N and the molecular weight distribution. This is important because it shows that the colligative properties (osmotic pressure, vapor pressure lowering, freezing point lowering) are independent of the actual molecular weight distribution of the polymer and always permit determination of the number average molecular weight.

2. Heat of Mixing

No exact formula exists for the time being for the computation of the partial molal heats of mixing. However, at least in the case of non-polar polymers, it was shown by the experiments of Gee and Treloar⁸ and by some unpublished experiments of the authors that the total heat of mixing can be fairly well represented by a Scatchard-Hildebrand formula, i.e.,

$$\Delta H_{\text{mix}} = V_m(\alpha_0 - \alpha_r)^2 \phi_0 \phi_r, \quad (27a)$$

where α_0 and α_r are the square roots of the cohesive energies (internal heats of vaporization) per unit volume:⁹

$$\begin{aligned} \alpha_0 &= (E_{0(\text{coh})}/V_0)^{\frac{1}{2}} = (\lambda_0 - RT/V_0)^{\frac{1}{2}}, \\ \alpha_r &= (E_{r(\text{coh})}/V_r)^{\frac{1}{2}} = (\lambda_r - RT/V_r)^{\frac{1}{2}}, \end{aligned} \quad (28)$$

and V_m the molecular volume of the mixture

$$V_m = X_0 V_0 + X_r V_r = V_0 V_r / (\phi_0 V_r + \phi_r V_0). \quad (29)$$

In order to expand the Scatchard-Hildebrand formula to mixtures of polymers and solvents, let us recall at this point the basic assumptions from which the formula (27) is derived. The cohesive energy of a mixture is supposed to be the sum of three types of interaction, writing each in terms of the volume fraction

$$(E_{\text{coh}})_{\text{mix}} = (A_{11}\phi_1^2 + 2A_{12}\phi_1\phi_2 + A_{22}\phi_2^2) V_m, \quad (30)$$

where A_{11} , A_{12} and A_{22} are constants characteristic of the interaction between the molecules, A_{11} and A_{22} between molecules of the same type, A_{12} between molecules of different types.

For the pure components,

$$\begin{aligned} (E_{\text{coh}})_1 &= A_{11}V_1; & (E_{\text{coh}})_2 &= A_{22}V_2; \\ &= \alpha_1^2 V_1; & &= \alpha_2^2 V_2. \end{aligned} \quad (31)$$

For the interaction of two different type molecules, it is now assumed

$$A_{12} = (A_{11}A_{22})^{\frac{1}{2}}. \quad (32)$$

This assumption was first made by van der Waals. The quantum mechanical treatment¹⁰ of the intermolecular forces of non-electrostatic nature corrected this formula to

$$A_{12} \leq (A_{11}A_{22})^{\frac{1}{2}}. \quad (33)$$

Assuming Eq. (32) to be valid, Eq. (30) can hence be written

$$(E_{\text{coh}})_{\text{mix}} = [(A_{11})^{\frac{1}{2}}\phi_1 + (A_{22})^{\frac{1}{2}}\phi_2]^2 V_m, \quad (34)$$

which, after subsequent transformation, under the additional assumption that the mixture is ideal in the sense that volumes of the components are additive, leads to Eq. (27).

In the case when one of the components is polar the relation of Eq. (32) can no longer be expected to hold even approximately. Nevertheless, experiments have shown that, in this case, the total heat of mixing can be roughly represented by

$$\Delta H_{\text{mix}} = K V_m(\alpha_0 - \alpha_r)^2 \phi_0 \phi_r, \quad (27b)$$

where K is a constant somewhat larger than unity and correcting for the fact that always in this case $A_{12} < (A_{11}A_{22})^{\frac{1}{2}}$. For mixtures of non-polar compounds $K = 1$.

It must be emphasized that the cohesive energy is essentially a localized affair determined by the

⁸ G. Gee and L. R. G. Treloar, Trans. Faraday Soc. **38**, 147 (1942).

⁹ The subscript 0 represents the solvent, and r the rubber (polymer).

¹⁰ F. London, Zeits. f. physik. Chemie **B11**, 222 (1930).

interactions between adjacent atoms and groups of atoms belonging to the several components. It is essentially the interaction between the sub-molecules of the polymer and the molecules of the solvent, and is independent of the actual chain length.

Let us apply now Eq. (27a) or (27b) to the complex system of a mixture of a solvent and of polymer molecules of differing chain length. From the outset we can assume that α_r is the same for all the different rubber molecules and that therefore there is no heat of mixing from this source. The only heat of mixing developed is that between the solvent and the polymer which we may treat for our purposes as one component.

Introducing the molar fractions, Eq. (27a) becomes

$$\begin{aligned} H_{\text{mix}} &= (X_0 V_0 + \sum_i X_i m_i V_0)(\alpha_0 - \alpha_r)^2 \\ &\quad \times \frac{X_0 V_0 (\sum_i X_i m_i V_0)}{(X_0 V_0 + \sum_i X_i m_i V_0)^2} \\ &= V_0 (\alpha_0 - \alpha_r)^2 \frac{X_0 \sum_i X_i m_i}{(X_0 + \sum_i X_i m_i)}. \end{aligned} \quad (35)$$

The partial molar heats of mixing are obtained by differentiation of Eq. (35).

$$\begin{aligned} \overline{\Delta H}_0 &= \left(\frac{\partial H_{\text{mix}}}{\partial X_0} \right) \\ &= V_0 (\alpha_0 - \alpha_r)^2 \frac{(\sum_i X_i m_i)^2}{(X_0 + \sum_i X_i m_i)^2} \\ &= V_0 (\alpha_0 - \alpha_r)^2 (1 - \phi_0)^2; \end{aligned} \quad (36)$$

$$\begin{aligned} \overline{\Delta H}_i &= \left(\frac{\partial H_{\text{mix}}}{\partial X_i} \right) \\ &= V_0 (\alpha_0 - \alpha_r)^2 \frac{m_i (X_0)^2}{(X_0 + \sum_i X_i m_i)^2} \\ &= m_i V_0 (\alpha_0 - \alpha_r)^2 \phi_0^2. \end{aligned} \quad (37)$$

In order to be able to treat the solubility and other properties of a polymer in a mixture of two solvents, we have to extend the formula for the heat of mixing in order to include this case. We

found that solvent mixtures can be treated with a fair degree of accuracy assuming the mixture of the two solvents to behave as a homogeneous liquid,¹¹ with respect to the polymer, this new "liquid" having characteristic values of α and V , α_m and V_m . The values of α_m and V_m can be obtained from the theory of heat of mixing developed above (Eq. 34).

$$(E_{\text{coh}})_m / V_m = \alpha_m^2 = ((A_{11})^{\frac{1}{2}} \phi_1 + (A_{22})^{\frac{1}{2}} \phi_2), \quad (38)$$

or

$$\alpha_m = \phi_1 \alpha_1 + \phi_2 \alpha_2 = \alpha_1 + \phi_2 (\alpha_2 - \alpha_1), \quad (39)$$

while

$$\begin{aligned} V_m &= V_1 V_2 / \phi_1 V_2 + \phi_2 V_1 \\ &= V_1 [(1 + \phi_2 V_2 / (V_1 - V_2))]. \end{aligned} \quad (40)$$

3. Partial Molal Free Energy

We are now able to express the partial molal free energies of the system considered: a mixture of polymer molecules of different molecular weight and of one or two solvents.

Combining Eqs. (24) and (25) with (36) and (37) respectively, we obtain

$$\overline{\Delta F}_0 = RT [\ln \phi_0 + (1 - \phi_0)(1 - 1/\bar{m}_N) + \mu(1 - \phi_0)^2], \quad (41)$$

$$\Delta F_i = RT [\ln \phi_i + 1 - m_i \phi_0 - (m_i / \bar{m}_N)(1 - \phi_0) + m_i \mu \phi_0^2], \quad (42)$$

where $\mu = 1/\gamma + K V_0 (\alpha_0 - \alpha_r)^2 / RT$ in the case of a simple solvent and

$$\begin{aligned} \mu_m &= 1/\gamma + \frac{K V_1 (\alpha_1 - \alpha_r)^2}{RT} \\ &\quad \times \left[1 + \phi_2 \left(\frac{\alpha_2 - \alpha_1}{\alpha_1 - \alpha_r} \right) \right]^2 / \left[1 + \phi_2 \frac{V_1 - V_2}{V_2} \right], \end{aligned} \quad (43)$$

in the case of a mixture of solvents (1) and (2).

In the following paper these expressions will be applied to the problems of solubility and fractionation of a rubber-like polymer.

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¹¹ This can be true only if the interaction of the solvents with the polymer is of second order in comparison with the interaction between the two solvents.