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The Thermodynamics of High-Polymer Solutions: II. The Solubility and Fractionation of a Polymer of Heterogeneous Distribution*

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The free energy relations for heterogeneous molecular weight distributions developed in Part I, are applied to problems of solubility and fractionation. Critical conditions for solubility are obtained. A rigorous expression for the solubility is derived, although certain approximations are made to facilitate calculation, and to permit extension to polymers which are part "gel." Following the same methods the thermodynamic equilibria involved in fractionation are described by mathematical expressions which permit a comparison of the extraction and precipitation methods. The effectiveness of fractionation is shown to be strongly dependent upon concentration.

INTRODUCTION

FLORY¹ and Huggins² first developed theories of the entropy of mixing of polymers of uniform molecular weight with solvents and soon thereafter^{3,4} extended their treatment to include the solubility of such homogeneous polymers. Later, using a modified form of the Flory theory, Gee⁵ attempted to give a rough treatment of fractionation. Until now, however, no systematic treatment has been given for polymers consisting of a heterogeneous distribution of chain lengths. Such distributions are to be found in both natural and synthetic rubbers and in all similar chain polymers.

It has been shown in Part I⁶ that in a mixture of solvent with such a heterogeneous polymer, the partial molal free energies of mixing of the solvent ΔF_0 and of the i th fraction of the polymer ΔF_i may be represented as:

$$\Delta F_0 = RT \left[\ln \phi_0 + (1 - \phi_0) \left(1 - \frac{1}{\bar{m}_N} \right) + \mu(1 - \phi_0)^2 \right], \quad (1)$$

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

where ϕ_0 and ϕ_i are the volume fractions of solvent and i th fraction respectively.

m_i is the ratio of the molecular volumes of the i th fraction V_i and that of the solvent V_0 and, assuming that the density of the polymers is independent of the chain length, a direct measure of the molecular weight.

$$m_i = V_i / V_0 = M_i / \rho_r V_0. \quad (3)$$

\bar{m}_N is the number average m , defined as

$$\bar{m}_N = \frac{\sum_i n_i m_i}{\sum_i n_i} = \frac{\sum_i m_i}{\sum_i m_i / \phi_i}, \quad (4)$$

and related to the number average molecular weight by a relation similar to Eq. (3).

μ is a constant for any given system, consisting of the heat of mixing and a term from the entropy, such that

$$\mu = 1/\gamma + K V_0 (\alpha_0 - \alpha_r)^2 / RT, \quad (5)$$

where γ = the coordination number of the segments (about 3-4), α_0 , α_r = constants for the rubber (polymer) and the solvent (the square root of the internal energy of vaporization per cc) and K an empirical constant relating to the polarity of the substances in the mixture.⁷

⁷ For a more comprehensive discussion of these constants, see Part I.

* 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. 9, 660 (1941).

² M. L. Huggins, J. Chem. Phys. 9, 440 (1941).

³ P. J. Flory, J. Chem. Phys. 10, 51 (1942).

⁴ M. L. Huggins, J. Phys. Chem. 46, 151 (1942); Ann. N. Y. Acad. Sci. 43, 1 (1942).

⁵ G. Gee, Trans. Faraday Soc. 38, 276 (1942).

⁶ R. L. Scott and M. Magat, J. Chem. Phys. 13, 172 (1945).

Equation (1) is identical with that for the free energy of the solvent in a binary system as derived by Huggins, with the exception that \bar{m}_N replaces m . Equation (2), however, is not identical with that of the rubber in the homogeneous system.

**A. Solubility of a Polymer of Distribution $f(m)$:
Distribution of a Fraction of Molecular
Weight m_i Between Solution
and Swollen Precipitate**

From Eqs. (1) and (2), one may deduce the solubility conditions and the distribution of the rubber between two phases.

If one plots ΔF_0 against decreasing ϕ_0 , one finds that for sufficiently small values of μ , ΔF_0 decreases uniformly, signifying complete miscibility of solvent and polymer. (Fig. 1.)⁸ With a larger value of μ (that is, a larger heat of mixing), however, the curve shows a minimum and a maximum indicating only partial miscibility. There will therefore be a critical value of μ , μ_c , at which the solution breaks into two phases. For this value the curve will show a point of inflection, and applying the familiar conditions that, here, the first and second derivatives of ΔF_0 with respect to ϕ_0 must vanish, one finds:

$$\mu_c = (1/\gamma) + (KV_0(\Delta\alpha)^2/RT) \\ = 1/2[1 + (1/\bar{m}_N)^2]. \quad (6)$$

This is identical with the similar equation,^{3,4} for a homogeneous polymer except that \bar{m}_N replaces m . In short, all the critical conditions are the same as those for a binary system if one utilizes the number average molecular weight. These critical conditions depend only on \bar{m}_N and not on the precise nature of the distribution function, which may correspond either to a fairly narrow, homogeneous fraction, or to a very broad distribution.

The critical point corresponds also to a critical value of ϕ_0 and of ϕ_r (the volume fraction of the total rubber.)

⁸ For identical curves for polymers of homogeneous distribution, see M. L. Huggins, *Cellulose and Cellulose Derivatives*, edited by Ott (Interscience Publishers, Inc., New York), p. 893.

$$(\phi_0)_c = \frac{\bar{m}_N}{1 + \sqrt{\bar{m}_N}} = \frac{1}{1 + (1/\sqrt{\bar{m}_N})}; \quad (7a)$$

$$(\phi_r)_c = \left(\sum_i \phi_i \right)_c = \frac{1}{1 + \sqrt{\bar{m}_N}}. \quad (7b)$$

Similarly one may speak of a critical solution temperature T_c or a critical value of $(\alpha_0 - \alpha_r)$, $(\Delta\alpha)_c$.

$$T_c = \{KV_0(\Delta\alpha)^2\} / \{R[1/2(1 + (1/\sqrt{\bar{m}_N}))^2 - (1/\gamma)]\}; \quad (8)$$

$$(\Delta\alpha)_c = \{RT[1/2(1 + (1/\sqrt{\bar{m}_N}))^2 - (1/\gamma)]\} / KV_0. \quad (9)$$

Certain consequences follow immediately from these equations: (1) As pointed out above, the critical point is dependent only upon the number average molecular weight. Since, for values of μ less than μ_c , no separation of a rubber phase is possible, it is clear that the presence of low molecular weight material in the polymer tends to keep the high molecular weight material in solution by decreasing the value of \bar{m}_N . In short, *low molecular weight material actually makes the higher fractions more soluble*. This factor is crucial

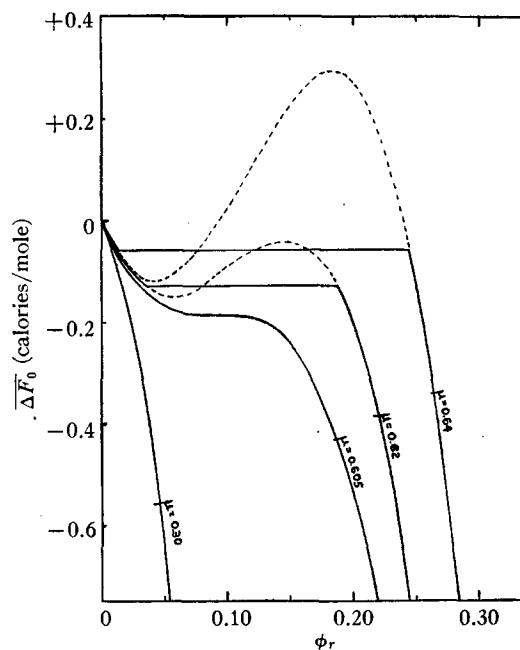


FIG. 1. Partial molal free energy of solvent ΔF_0 as a function of μ and ϕ_r , the volume fraction of rubber. $\bar{m}_N = 100$ ($\bar{m}_N \leq 10,000$).

in any consideration of fractionation or precipitation curves. (2) Since μ_c is inversely proportional to T (Eq. (5)), the solubility increases with an increase in temperature. (3) If for a given rubber-solvent system, $(\alpha_0 - \alpha_r)$ is less than the critical $(\Delta\alpha)_c$ in Eq. (9), the rubber and solvent are necessarily completely miscible in all proportions.

To determine the solubility at any other point than at the critical point, one must utilize the equilibrium conditions between the two phases:

$$\overline{\Delta F_0} = \overline{\Delta F_0'}, \quad (10)$$

$$\overline{\Delta F_i} = \overline{\Delta F_i'}, \quad (11)$$

where the prime represents the swollen rubber phase.

There are, of course, i simultaneous equations of the type of Eq. (11), one for each distinct fraction.

In other words

$$\begin{aligned} \ln \phi_0 + 1 - \phi_0 - \frac{1 - \phi_0}{\bar{m}_N} + \mu(1 - \phi_0)^2 \\ = \ln \phi_0' + 1 - \phi_0' - \frac{1 - \phi_0'}{\bar{m}_N'} + \mu(1 - \phi_0')^2; \end{aligned} \quad (12)$$

$$\begin{aligned} \ln \phi_i + 1 - \frac{m_i}{\bar{m}_N}(1 - \phi_0) - m_i\phi_0 + m_i\mu\phi_0^2 \\ = \ln \phi_i' + 1 - \frac{m_i}{\bar{m}_N'}(1 - \phi_0') - m_i\phi_0' + m_i\mu\phi_0'^2. \end{aligned} \quad (13)$$

Note that the distribution functions in the two phases are presumed to be different; hence \bar{m}_N' is not the same as \bar{m}_N .

Solving Eq. (13) for $\ln \phi_i'/\phi_i$ and substituting from Eq. (12), one obtains

$$\ln \frac{\phi_i'}{\phi_i} = m_i \left[2\mu(\phi_0 - \phi_0') - \ln \frac{\phi_0}{\phi_0'} \right], \quad (14)$$

or

$$\phi_i'/\phi_i = \exp(Am_i), \quad (15)$$

where

$$A = 2\mu(\phi_0 - \phi_0') - (\ln \phi_0/\phi_0').$$

A relation similar to Eq. (14) is given by Schulz:⁹

$$C = Ke^{-P(A+B\gamma)/R\theta}, \quad (16)$$

where C = solubility of material of molecular

weight M ; P = degree of polymerization of polymer = M/M_0 ; M_0 = molecular weight of monomer; γ = concentration of precipitant (not the γ of Part I of this paper⁶); θ = a temperature function; A, B, K = constants.

This equation yields the same exponential dependence of the solubility on the molecular weight as in Eq. (15), but in our opinion, the assumptions made in the derivation are faulty, and the significance of the constants uncertain. Schulz's work is important, however, as the first attempt to treat the problem of solubility and fractionation from a thermodynamic standpoint.

Equation (15) represents the fundamental basis of the theory of solubility and fractionation presented in the following pages. For any given system, A is a constant; and, therefore, Eq. (15) may be used as a strictly valid relation, showing the distribution of material of different molecular weights between the solution and the rubber phases.

We may now undertake to express the solubility. Let the actual distribution of molecular weights be represented by a distribution function:

$$dw_i = f(m)dm_i, \quad (17)$$

where dw_i is the fraction¹⁰ of the total rubber of molecular weight m_i and $f(m)$ is a normalized function, such that

$$\int_0^\infty f(m)dm = 1. \quad (18)$$

What is the solubility if a certain volume v_r of this rubber is placed in a volume v_0 of a certain solvent? The total amount of rubber, v_i in any given fraction is the sum of the amounts in the solution phase and in the swollen rubber phase.

$$v_i = \phi_s v_s + \phi_i' v_p, \quad (19)$$

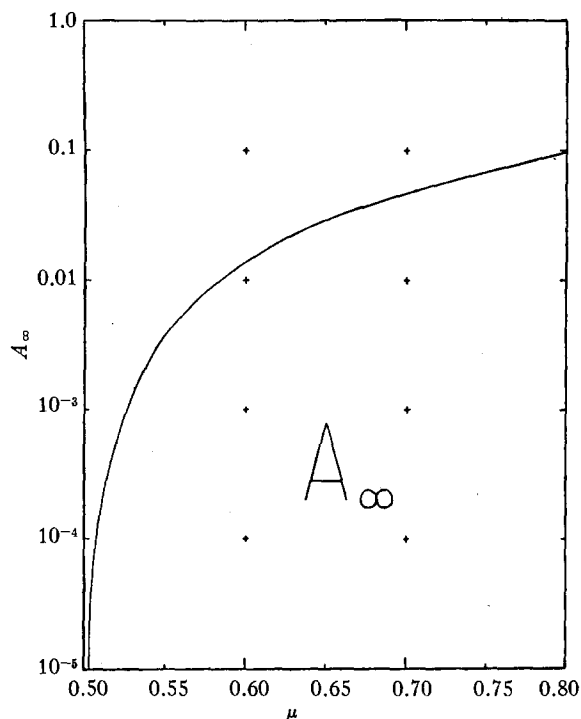
where $v_i = v_r dw_i = v_r f(m)dm_i$; v_s = volume of solution phase; v_p = volume of swollen rubber phase. Substituting the condition of Eq. (15),

$$v_i = \phi_s v_s + \phi_i v_p \exp(Am_i); \quad (20)$$

$$\phi_i = v_i/(v_s + v_p e^{Am_i}) = v_r f(m)dm_i/(v_s + v_p e^{Am_i}). \quad (21)$$

¹⁰ Either weight fraction or volume fraction, since the density of the rubber is presumed to be uniform, independent of molecular weight. This assumption however, is only approximate. It means in reality that we neglect the end atoms when compared to the length of the chain. For high molecular weights, this is obviously justified.

⁹ G. V. Schulz, Zeits. f. physik. Chemie A179, 321 (1937).

FIG. 2. The approximation constant A_∞ as a function of μ .

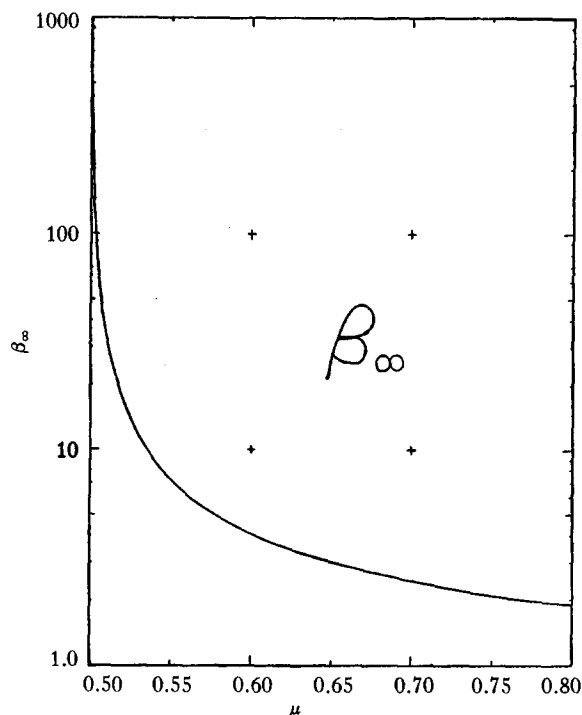
The total solubility in terms of volume fraction of rubber is therefore

$$\phi_r = \sum \phi_i = \int_0^\infty v_r f(m) dm / (v_s + v_p e^{Am}). \quad (22)$$

Equation (22), while rigorously correct is not very helpful when it comes to actual calculation. Given the distribution function $f(m)$, either explicitly or graphically, the ratio of v_r to v_0 and the value of μ for the mixture, one can make the calculation, for v_s and v_p are functions of the above variables—but the computation may be exceedingly long and tedious.

Exact calculation of A is extremely difficult, since both ϕ_0 and ϕ_0' are functions not only of \bar{m}_N and \bar{m}_N' but also of the distribution function itself. It is to be noted, however, that the values of ϕ_r (i.e., $1 - \phi_0'$), calculated for various m 's, approach the limiting curve for $m = \infty$ asymptotically as μ increases. Hence, for values of μ sufficiently above the critical point, one may take for A , the value A_∞ calculated for $m = \infty$. For $m = \infty$, $\phi_0 = 1$, since the rubber is completely insoluble above the critical point, so that

$$A_\infty = \mu(\phi_r')_{m=\infty} + \ln [1 - (\phi_r')_{m=\infty}]. \quad (23)$$

FIG. 3. The approximation constant β_∞ as a function of μ .

Since, when $m = \infty$ in Eq. (1) $(\phi_r')_{m=\infty}$ is a function of μ alone:

$$\ln [1 - (\phi_r')_{m=\infty}] + (\phi_r')_{m=\infty} + \mu(\phi_r')_{m=\infty}^2 = 0, \quad (24)$$

one may calculate A_∞ as a function of μ . The results of these calculations are shown graphically in Fig. 2. Actually, these calculations of A are accurate virtually to the critical point, thanks to compensating errors.

Certain other approximations may also be made: For dilute solutions, where the swollen rubber phase is small in comparison to the solution, v_s may be taken as approximately equal to v_0 , the amount of solvent added.

Further, one may write v_p as a function of the amount of rubber in the precipitate, v_r' and the percentage of the precipitate which is rubber, ϕ_r' .

$$v_p = v_r' / \phi_r' = v_r' / (1 - \phi_0'), \quad (25)$$

and hence the solubility

$$\phi_r = \int_0^\infty \frac{v_r f(m) dm}{v_0 + (v_r' / \phi_r') \exp(Am_i)}. \quad (26)$$

We may, however, determine an approximate limiting value of ϕ_r' by taking the value for

$\bar{m}_N = \infty$, which is the asymptote for all finite values of \bar{m}_N as μ increases. The asymptotic value $1/(\phi_r')_{m=\infty}$, which we shall henceforth call β_∞ is a function of μ only, and may be calculated from Eq. (24).

Values of β_∞ are shown graphically in Fig. 3.

A further approximation may be made in cases where μ is appreciably greater than the critical μ_c . Then the solubility will be small and nearly all the rubber will be in the precipitate, and one may write

$$v_r' \cong v_r. \quad (27)$$

Nearer the critical point, the solubility is considerable, and v_r' is appreciably smaller than v_r . Here also, however, ϕ_r' is less than $(\phi_r')_{m=\infty}$, and partially compensates. Since this deviation of ϕ_r' is not usually as marked¹¹ as that of v_r , one may say as a general rule

$$\beta v_r' = v_r' / \phi_r' \cong v_r / (\phi_r')_{m=\infty} = \beta_\infty v_r. \quad (28)$$

Therefore one may write as a final approximate form for the solubility

$$\phi_r \cong \int_0^\infty \frac{f(m)dm}{(v_0/v_r) + \beta_\infty \exp(A_\infty m)}. \quad (29)$$

Because of the condition of Eq. (28), one will expect that the actual solubility will be greater than that calculated from Eq. (29). Errors in determining A are distinctly second order compared to those involving β .

B. Solubility of "Gel" Rubbers

One further point must be noted—Eq. (29) as it stands applies only to rubber which is 100 percent soluble in "good" solvents ($\mu < 0.50$)—the so-called "sol rubber." Actually much rubber consists of more or less highly cross-linked material which is completely insoluble in all solvents—the so-called "gel rubber"—all vulcanized rubber is of this type. This gel can swell greatly so that the rubber phase may be very voluminous, but none of the cross-linked material will be found in the solution phase.

This swelling may be calculated, as was shown by Flory and Rehner.¹² By assuming the cross-

¹¹ It can be shown mathematically that, even at the critical point, ϕ_r' is greater than $\frac{1}{3}(\phi_r')_{m=\infty}$. Hence $\beta_\infty < \beta < 3\beta_\infty$.

¹² P. J. Flory and J. Rehner, *J. Chem. Phys.* 11, 521 (1943).

linked gel to be an infinite three-dimensional network of chains and deriving a suitable expression for the entropy of elastic stretching, they obtain, as the condition for swelling equilibrium

$$\ln(1 - \phi_r) + \phi_r + \mu \phi_r^2 + \frac{\rho_r V_0 \phi_r^{\frac{1}{3}}}{M_c} = 0, \quad (30)$$

where V_0 = molecular volume of solvent; ρ_r = density of rubber; M_c = average molecular weight of chains between cross links.

For gels which are not highly cross-linked, M_c is very large (of the order of 100,000) and the last term of Eq. (30) is negligibly small. If this last term is neglected, the equation is identical with Eq. (18). Hence for loosely cross-linked networks, such as found in unvulcanized rubbers, the degree of swelling may be taken as roughly the same as that of the sol for the range in which we are interested.¹³

We may therefore write as the generalized case:

$$\phi_r \cong K \int_0^\infty \frac{f(m)dm}{(v_0/v_r) + \beta e^{Am}}, \quad (31)$$

where K is the fraction of the rubber which is "sol."

The solubility may also be expressed as the fraction of the rubber dissolved, S . In this case one may write

$$S = \text{fraction dissolved} = \frac{\phi_r v_s}{v_r} \cong K \int_0^\infty \frac{f(m)dm}{1 + (v_r/v_0)\beta e^{Am}}. \quad (32)$$

C. Fractionation

(1) Methods of Fractionation

For a long time, at least two different methods have been in general use for fractionation of high polymers:

(a) *Precipitation method.*—The raw polymer is dissolved in a good solvent, and then successive amounts of a non-solvent are added to the solution, producing fractional precipitation. The highest molecular weights are the first to precipitate, then the next highest, and so forth.

¹³ For lower values of μ (below 0.50), the sol is completely soluble, but the gel is never soluble.

(b) *Extraction method*.—The raw polymer is successively extracted with mixtures of a good solvent and a non-solvent, increasing the relative proportion of solvent with each extraction. In this case, the lowest molecular weights are extracted first, and then higher molecular weights and so on.

Both of these methods can be interpreted in terms of the same theory, based essentially on Eq. (15). In both cases, each step consists of the establishment of thermodynamic equilibrium between a swollen rubber phase and a solution containing varying quantities of solvent and non-solvent.

(2) Theory of Fractionation

In a polymer of a given distribution $f(m)$ (Eq. (19)), the equilibrium distribution of any fraction of molecular weight m between solution and precipitate phase is expressed by Eq. (15).

We may then develop equations in a similar manner as before. The actual amounts of the i th fraction in each phase w_i (solution) and w_i' may be written as

$$v_i = \phi_i v_s + \phi_i' v_p = w_i + w_i'; \quad (33)$$

$$w_i'/w_i = \phi_i' v_p / \phi_i v_s = (v_p/v_s) \exp(Am_i). \quad (34)$$

Solving Eqs. (33) and (34) for w_i and w_i' and utilizing the approximations of Eq. (29)

$$w_i' = \frac{v_i}{1 + (v_s/v_p) \exp(-Am_i)} \approx \frac{v_i}{1 + (v_0/v_r'\beta) \exp(-Am_i)}; \quad (35)$$

$$w_i = \frac{v_i}{1 + (v_p/v_s) \exp(Am_i)} \approx \frac{v_i}{1 + (v_r'/v_0)\beta \exp(Am_i)}. \quad (36)$$

In all our further considerations, we shall assume that the solvent-non-solvent mixture may be considered as a homogeneous liquid, the same in both phases,¹⁴ and with an interaction with the

rubber characterized by a μ_m calculated from Eq. (44) of Part I.

From this μ_m , which depends on the relative proportions of solvent and non-solvent, one may calculate A and β as before. v_r'/v_0 is nothing more than the concentration c (in units of volume fraction) of the precipitated rubber in the total mixture.

We may therefore express the distribution functions of the rubber in the solution and in the precipitate as follows:

Precipitate:

$$f_p(m_i) = [f(m_i)]/1 + [\exp(-Am_i)]/\beta c, \quad (37)$$

Solution:

$$f_s(m_i) = [f(m_i)]/[1 + \beta c \exp(Am_i)], \quad (38)$$

where of course:

$$f_p(m_i) + f_s(m_i) = f(m_i). \quad (39)$$

The actual amounts in precipitate and solution are therefore:

$$w_p = v_r \int_0^\infty \frac{f(m)dm}{1 + (e^{-Am})/\beta c}, \quad (40)$$

$$w_s = v_r \int_0^\infty \frac{f(m)dm}{1 + \beta c e^{Am}}. \quad (41)$$

It is apparent immediately¹⁵ from the above equation that in any such distribution of the rubber between the two phases, most of the high molecular weight material will be in the precipitate, and most of the low molecular weight material in the solution. There is no sharp division since there will be some of every fraction in both phases. In the case of the high molecular weights, the amount in the solution may well be negligible since

$$\lim_{m \rightarrow \infty} 1/(1 + \beta c e^{Am}) = 0, \quad (42)$$

but there will always be at least βc of the low molecular weight material in the precipitate,

¹⁴ This is not strictly true, for the solution will actually be slightly richer in non-solvent and the precipitate in solvent, but treatment of such a condition leads to tremendous complications, and the above assumptions seem to introduce no errors of great significance, when compared with unpublished experimental results of the author.

¹⁵ All of the following qualitative conclusions are quite rigorous. Actually Eqs. (40) and (41) are precise until one makes simplifying assumptions in order to calculate β and A . The dependence on molecular weight is quite accurate, however.

since

$$\lim_{m \rightarrow 0} \frac{1}{1 + (e^{-Am}/\beta c)} = \frac{\beta c}{1 + \beta c} = \frac{v_p}{v_p + v_s} \cong \beta c. \quad (43)$$

This last fact is important, for in the precipitation method of fractionation, a finite amount of the low molecular weight material will always be in the precipitate, a fact which is well known empirically. That this should be is to be seen from a consideration of the interaction between the molecules. If the interaction between the rubber molecule and the solvent is the same as the interaction between it and the rest of the rubber, then it is completely indifferent as to its distribution, in which case, its concentration will be the same in both phases. In general however, the rubber molecule interacts more strongly with molecules of its own kind than with the solvent (and more so with increasing discrepancies between the molecular weights of rubber and solvent); and therefore the concentration in the rubber phase, even of the lowest molecular weight fractions, will always be higher than that in the solution phase, which is essentially solvent.

As indicated above, this is a purely thermodynamic effect, and is not caused by mechanical co-precipitation or occlusion as has been suggested in the past.

With increasing values of μ , A increases,¹⁶ so that the tendency for the rubber to be in the precipitate phase increases; hence one obtains fractionation by systematically varying μ in one direction or the other, taking advantage of the fact that the distribution between the two phases is strongly dependent on the molecular weight.

$$f_s^n(m) = \frac{f(m)}{(1 + \beta_a c \exp(A_a m))(1 + \beta_b c \exp(A_b m)) \cdots (1 + \beta_n c \exp(A_n m))}; \quad (46)$$

$$f_p^n(m) = \frac{f(m)}{(1 + \beta_a c \exp(A_a m))(1 + \beta_b c \exp(A_b m)) \cdots \left(1 + \frac{\exp(-A_n m)}{\beta_n c}\right)}. \quad (47)$$

The distribution function of the n th fraction is therefore represented by $f_p^n(m)$. Actually, this may be very nearly represented by neglecting all but the last two terms in the denominator.

¹⁶ β decreases with increasing μ , but this is more than offset by the increase in A .

(3) Comparison of the Precipitation and Extraction Methods

It is now desirable to consider more in detail the two different methods of fractionation.

In the precipitation method, the polymer is dissolved in a good solvent and then small increments of a non-solvent or precipitant (such as methyl alcohol) added until the solution breaks into two phases, with the formation of a swollen rubber phase or precipitate. This, of course, cannot occur until sufficient of the non-solvent is added to increase μ_m beyond the critical value defined by Eq. (6).

The original rubber of distribution function $f(m)$ has now distributed itself between the two phases, and the distributions in the two phases are defined by $f_p(m)$ and $f_s(m)$ in Eqs. (37) and (38). The solution is then decanted and fractionation continued on it by adding more non-solvent and so increasing μ_m further. Two phases exist again, with similar equations holding:

$$f_s'(m) = \frac{f_s(m)}{1 + \beta' c \exp(A' m)} = \frac{f(m)}{(1 + \beta' c' e^{A' m})(1 + \beta c e^{A m})}; \quad (44)$$

$$f_p'(m) = \frac{f_s(m)}{1 + [\exp(-A' m)]/\beta' c} = \frac{f(m)}{\{1 + [\exp(-A' m)]/\beta' c\} \{1 + \beta c e^{A m}\}}. \quad (45)$$

More generally one may express the distribution in the n th fraction as:

$$f_p^n(m) \cong \frac{f(m)}{(1 + \beta_m c \exp(A_m m)) \left(1 + \frac{\exp(-A_n m)}{\beta_n c}\right)}. \quad (48)$$

This function starts out at a very small value

for $m=0$, increases to a maximum and then decreases to zero for $m=\infty$.

$$\lim_{m \rightarrow 0} \frac{1}{(1 + \beta_m c \exp(A_m m)) \left(1 + \frac{\exp(-A_n m)}{\beta_n c} \right)} = \frac{\beta_n c}{(1 + \beta_m c)(1 + \beta_n c)} \approx \beta_n c; \quad (49)$$

$$\lim_{m \rightarrow \infty} \frac{1}{(1 + \beta_m c \exp(A_m m)) \left(1 + \frac{\exp(-A_n m)}{\beta_n c} \right)} = 0. \quad (50)$$

In the extraction method, the polymer is extracted with a blend of solvent and non-solvent, such that a small fraction of the total polymer—largely low molecular weight material—is re-

moved. Here again the distribution between the solution and the swollen rubber is defined by Eqs. (37) and (38). The solution is decanted, and the precipitate is further fractionated by extraction with a solvent mixture of lower μ_m .

The following two items are the two essential differences in the two methods: (1) In the precipitation method, μ is systematically increased; in the extraction method, μ is systematically decreased. (2) In the precipitation method, the fraction removed is in the precipitate, and the solution is further fractionated while in the extraction method, the fraction removed is in the solution, and the precipitate is further fractionated.

Following the same line of reasoning as in Eqs. (44) to (47), except in the reverse direction, one finds that for the m th fraction, in the case of the extraction method

$$f_s^m(m) = \frac{f(m)}{\left(1 + \frac{\exp(-A_z m)}{\beta_z c} \right) \left(1 + \frac{\exp(-A_y m)}{\beta_y c} \right) \cdots (1 + \beta_m c \exp(A_m m))}; \quad (51)$$

$$f_p^m(m) = \frac{f(m)}{\left(1 + \frac{\exp(-A_z m)}{\beta_z c} \right) \left(1 + \frac{\exp(-A_y m)}{\beta_y c} \right) \cdots \left(1 + \frac{\exp(-A_m m)}{\beta_m c} \right)}. \quad (52)$$

The distribution function for this fraction is therefore represented by $f_s^m(m)$ which may be closely represented by

$$f_s^m(m) \approx \frac{f(m)}{(1 + \beta_m c \exp(A_m m)) \left(1 + \frac{\exp(-A_n m)}{\beta_n c} \right)}. \quad (53)$$

It is to be seen that to this degree of approximation, this fraction of the extraction method has the same distribution as the n th fraction in the precipitation method, since Eq. (53) is the same as Eq. (48).

We may therefore say that, to the first approximation, the results of the two methods are identical, and that essentially the same fractions are obtained in both ways.

This is not exactly true, however, for the exact Eqs. (47) and (51) are not identical. In the first place, A and β are actually dependent on the actual distributions in the mixture, which are

quite different for the two methods. Therefore

$$(A_m)_{\text{extraction}} \neq (A_m)_{\text{precipitation}}; \quad (54)$$

$$(\beta_m)_{\text{extraction}} \neq (\beta_m)_{\text{precipitation}}. \quad (55)$$

This of course will introduce differences, but this effect is distinctly secondary compared with a second factor which we may call the tail effect.

If we take the limiting cases of Eqs. (47) and (51) for low molecular weights, we find that

Precipitation:

$$\lim_{m \rightarrow 0} f_p^n(m) = \frac{\beta_n c}{(1 + \beta_a c) \cdots (1 + \beta_n c)}; \quad (56)$$

Extraction:

$$\lim_{m \rightarrow 0} f_s^m(m) = \frac{(\beta_n c) \cdots (\beta_z c)}{(1 + \beta_n c) \cdots (1 + \beta_z c)}. \quad (57)$$

Hence, we see that since $\beta c \ll 1$ the most significant difference is that in the extraction method, far less low molecular weight material will be found in the higher fractions than is the case for the precipitation method.

It would seem therefore that, normally, the extraction method of fractionation should be preferable to the precipitation method. Certain objections to such a choice might be raised:

(1) Because of the large and compact nature of the rubber phase, equilibrium is reached much more slowly in the extraction method.

(2) If insoluble gel is present, its great swelling will cause a tremendous overlapping in the higher fractions.

(3) Because of the great sensitivity of the solubility to slight changes in μ , it is very difficult to choose solvent mixtures properly in the extraction method.

It remains for the individual investigator to choose between the methods. In the opinion of the author, the precipitation method, if modified to the extent of washing the precipitate or reprecipitating the fraction (in order to remove the "tail"), is adequate for all ordinary purposes.

(4) Effect of Temperature

The temperature has no effect upon the general considerations of fractionation in the preceding pages. However, since μ is known both theoretically and experimentally, to be a function of temperature, decreasing as T increases,¹⁷ it follows that the temperature is involved in any fractionation in practice. In general, during the process of fractionation, by either method, the temperature should be kept relatively constant or anomalous results may be found.

A variation of the precipitation method is that of inducing precipitation by cooling. Since μ increases with decreasing temperatures, this is thoroughly consistent with the theory developed above.

¹⁷ See Eq. (5), and for further discussion of the dependence of μ on various factors, see M. L. Huggins, *Ann. Acad. Sci.* **44**, 431 (1943).

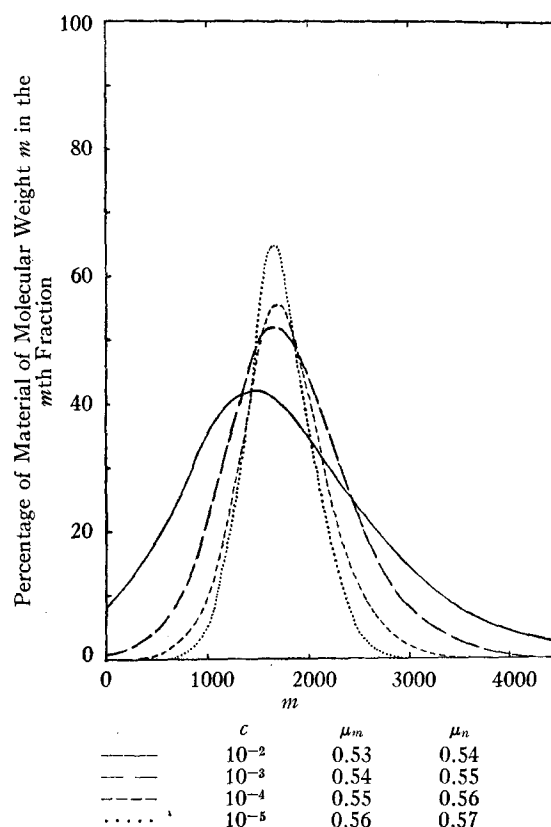


FIG. 4. The effect of concentration on the sharpness of concentration.

(5) Effect of Concentration

The influence of concentration is illustrated most effectively by the approximate Eqs. (48) (53). If this function is plotted against c , the "concentration" of the fraction¹⁸

$$c = v_r' / v_0, \quad (58)$$

the curves of Fig. 4 result. The curves represent the percentage of material of molecular weight m in a fraction taken between μ_m and $(\mu_m + .01)$, for four different concentrations, 10^{-2} , 10^{-3} , 10^{-4} , and 10^{-5} , the values of μ chosen so that the maximum for each concentration lies in approximately the same range.

¹⁸ This term "concentration" is a trifle unclear. It is the volume of the rubber in the precipitate as compared with the total solution. If, for example, one is fractionally precipitating a 1 percent solution of polymer into ten equal fractions, each fraction is 0.1 percent and $c = 0.001$. In the case of the extraction method, c varies in the course of the extraction, since, at the beginning of fractionation, the precipitate phase contains the whole polymer.

Figure 4 shows that there are two factors involved in varying c .

(a) For smaller values of c , the fractionation is sharper; there is less "tail" effect, and the maximum is higher.¹⁹ Had a fraction in the lower molecular weight range been chosen, the curve would have been still sharper.

(b) With higher dilutions, that is, smaller values of c , the value of μ necessary for precipitation of a given fraction is greater. For example, a dilution of 10-fold requires an increase of μ_n (and μ_m) by 0.01 unit. In the case of the lowest fractions, this shift is more appreciable.

From the foregoing discussion it is clear that from a theoretical point of view, c should be kept as small as possible to obtain the sharpest fractionation. Practically, however, one cannot carry such a solution too far. Not only does this entail working with great quantities of solution, but, because of the shift of μ with concentration, it may be next to impossible to separate the lowest fractions without adding tremendous quantities of precipitant.²⁰

¹⁹ The fact that the maxima in Fig. 4 correspond to only about 60 percent of the material of $m = 1700$ ($MW = 170,000$) is not significant. Had a wider range been taken (i.e., $\mu_n - \mu_m = 0.02$), such that the fraction was larger, the maxima would have approached 100.

²⁰ It would seem that, since the lowest fractions are fairly sharp, even when precipitated from a concentrated solution, the best procedure would be to start fractionation in a very dilute solution, but after separation of the higher fractions, to concentrate the material to facilitate separation of the lower fractions. This is, however, a complicated procedure.

In practice, one must strike a compromise. Most fractionations are carried out from solutions where the initial concentration of the total polymer is about 1 percent. For a fractionation into ten equal fractions, this corresponds roughly to $c = 10^{-3}$. This seems to give fairly good results, judging both from the experimental results, and from the $c = 10^{-3}$ curve in Fig. 4.

(6) Effectiveness of Fractionation

Some idea of the effectiveness of fractionation can be seen from Fig. 4. The distribution of each fraction is fairly broad especially for fractionation carried out at high concentrations. Especially objectionable is the "tail" effect, for the presence of even a small amount of low molecular weight material can alter the number average molecular weight appreciably.

A better fractionation can be obtained either by refractionating or by washing the precipitate with a fresh sample of the precipitating mixture; either procedure serves to remove the lowest sub-fractions, while not materially affecting the rest of the fraction. This solution may then be added to the decanted supernatant solution and fractionation continued. Experiments show that these methods are reasonably effective in eliminating the "tail."

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