A Revised Theory of High Polymer Solutions[1]

By Maurice L. Huggins

Received April 16, 1964

Theoretical equations, in closed form and as expansions in powers of the concentration, have been deduced for the enthalpy and entropy parts of the interaction coefficient for solutions of linear high polymers. These equations relate experimentally observable quantities to molecular and intermolecular properties. They furnish a reasonable basis for the approximately opposite concentration dependence of the enthalpy and entropy functions. It is expected that these results will prove useful in connection with various properties of polymer solutions and gels at intermediate and high concentrations.

Introduction

This paper reports an extension of the theory of the thermodynamic properties of solutions of long-chain polymers, previously deduced by the author.[2-7] Its chief aims are to relate experimentally measurable quantities as closely as possible to molecular structures and intermolecular interactions and to obtain equations which will give more quantitative agreement with experiment than do previous theoretical equations, especially at moderate and high concentrations of polymer. The present paper deals exclusively with the theory. Application of the results to experimental data is in progress and will be reported later.

Following previous theoretical developments by the writer,[2-7] Flory,[8-10] and others, the partial molal Gibbs free energy of mixing of the solvent, in a solution of linear polymer of a single type in a single solvent, is given by the equation

$$\Delta \bar{F}_1 = RT\left[\ln \phi_1 + \left(1 - \frac{\bar{V}_1}{\bar{V}_2}\right)\phi_2 + \chi\phi_2^2\right] \quad (1)$$

Here, $\bar{V}_1$ and $\bar{V}_2$ are the partial molal volumes of solvent and solute, respectively, ϕ_1 and ϕ_2 are their volume fractions in the solution, and χ is a parameter, which depends on the solute and solvent and the temperature, but not appreciably on the molecular weight of the polymer, as long as it is high. It does depend on the concentration, but approaches constancy as the concentration (i.e., ϕ_2) approaches zero. Various experimentally measurable quantities of interest can be related to $\Delta \bar{F}_1$ and so to χ. Considering χ as concentration dependent is of course equivalent to expanding eq. 1 into a series, with additional terms $\chi'\phi_2^3$, $\chi''\phi_2^3$, etc.

The problem to be solved is the quantitative evaluation of χ, including its concentration dependence, in terms of molecular and intermolecular properties.

(1) Except for minor changes and additions, this theory was developed while the author was on the staff of the Research Laboratories of the Eastman Kodak Co., Rochester, N. Y. He is now on the staff of Stanford Research Institute, Menlo Park, Calif. A preliminary report of this work was presented at the symposium honoring Prof. Joel H. Hildebrand on the occasion of his 80th birthday, Berkeley, Calif., Sept. 12, 1961.

(2) M. L. Huggins, J. Phys. Chem., 46, 151 (1942).

(3) M. L. Huggins, Ann. N. Y. Acad. Sci., 41, 1 (1942).

(4) M. L. Huggins, J. Am. Chem. Soc., 64, 1712 (1942).

(5) M. L. Huggins, J. Phys. Colloid Chem., 52, 248 (1948).

(6) M. L. Huggins, J. Polymer Sci., 16, 209 (1955).

(7) M. L. Huggins, "Physical Chemistry of High Polymers," John Wiley and Sons, Inc., New York, N. Y., 1958, Chapter 6.

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

(9) P. J. Flory, ibid., 12, 425 (1944).

(10) P. J. Flory, "Principals of Polymer Chemistry," Cornell University Press, Ithaca, N. Y., 1953.

It is known that χ is a function of both the enthalpy and the entropy of the solution. It is convenient for our purpose to write

$$\chi = \chi_h + \chi_s \quad (2)$$

and to consider the enthalpy contribution, χ_h, and the entropy contribution, χ_s, separately.

Theoretical Development: Enthalpy and Energy

Rather than dealing with the enthalpy of mixing directly, it is simpler to deal first with the energy of mixing, assuming zero volume change on mixing, and then, following Hildebrand and Scott,[11] to estimate the corrections for volume change by means of the relationships

$$\Delta \bar{F}_1 = \Delta \bar{A}_1 \quad (3)$$

$$\Delta \bar{H}_1 = \Delta \bar{E}_1(1 + \alpha_s T) \quad (4)$$

Here, $\Delta \bar{A}_1$ is the Helmholtz free energy of mixing and α_s is the coefficient of cubical expansion of the solution, approximated by

$$\alpha_s = \alpha_1\phi_1 + \alpha_2\phi_2 \quad (5)$$

We are concerned with the energy of molecular interactions in a solution of chain molecules, and with the dependence of that energy on the molecular properties and on the concentration. Except when Coulombic forces are involved, it seems reasonable to consider the molecular interaction energies as depending solely on the "contacts" between adjacent molecules. To put this concept on a quantitative basis, we consider that each molecule has a molecular surface of definite but unspecified area and that the interaction energy associated with contact between two adjacent molecules depends on the kinds of molecules and on the area' of mutual contact. It is of course necessary to deal with averages and to make allowance for intramolecular contacts and for the portions of the surface areas of molecules which are not in contact with surface areas of the same or other molecules, and to allow for departures from perfect randomness of mixing, resulting from differences in the interaction energies between different types of pairs of molecules.

We designate by σ_1 and σ_2 the average "molecular surface areas" of solvent and solute (polymer) molecules, respectively. By σ_{11}, σ_{12}, and σ_{10} we designate the average surface areas per solvent molecule which are "in contact" with other solvent molecules, solute molecules, and nothing, respectively. By σ_{21}, $\sigma_{22,int}$, $\sigma_{22,ext}$, and σ_{20} we denote the average surface areas of a

(11) J. H. Hildebrand and R. L. Scott, "Solubility of Nonelectrolytes," 3rd Ed., Reinhold Publishing Corp., New York, N. Y., 1950.

solute molecule in contact with solvent molecules, other portions of the surface of the same solute polymer molecule, other solute molecules, and nothing, respectively. Then

$$\sigma_1 = \sigma_{11} + \sigma_{12} + \sigma_{10} \qquad (6)$$

$$\sigma_2 = \sigma_{21} + \sigma_{22,\text{int}} + \sigma_{22,\text{ext}} + \sigma_{20} \qquad (7)$$

We assume σ_1, σ_2, σ_{10}, and σ_{20} to be independent of concentration. Also, although it is likely that $\sigma_{22,\text{int}}$ varies with concentration in some instances, we neglect such variation and take it also as constant. We can then define the "effective surface areas," σ_1' and σ_2', by the equations

$$\sigma_1' = \sigma_1 - \sigma_{10} = \sigma_{11} + \sigma_{12} \qquad (8)$$

$$\sigma_2' = \sigma_2 - \sigma_{20} - \sigma_{22,\text{int}} = \sigma_{21} + \sigma_{22,\text{ext}} \qquad (9)$$

If N_1 and N_2 are the numbers of solvent and solute molecules in the solution, respectively

$$N_1\sigma_{12} = N_2\sigma_{21} \qquad (10)$$

Leaving out of consideration all the internal energies of the molecules which should be independent of concentration, the energy of the solution is the sum of the energies of intermolecular contact. We designate by ϵ_{11}, ϵ_{22}, and ϵ_{21} the average interaction energies per unit area of contact, for the three types of intermolecular contact. These should each be independent of concentration at a given temperature. (For intermolecular attraction, these are negative.)

Let p_{21} and $p_{22,\text{ext}}$ be the probabilities that a small area of the surface of a polymer molecule, which is in contact with another molecule, is in contact with a solvent and with another solute molecule, respectively. If the two types of molecule were similar in size, shape, rigidity, and intermolecular contact energy (i.e., $\epsilon_{21} = \epsilon_{22}$), we should expect these probabilities to be proportional to the available molecular surface areas of the two types. Hence

$$\frac{\sigma_{22,\text{ext}}}{\sigma_{21}} = \frac{p_{22,\text{ext}}}{p_{21}} = \frac{N_2\sigma_2'}{N_1\sigma_1'} \qquad (11)$$

If, however, the solute molecules are flexible linear polymer molecules, the presence of one contact between such molecules increases the probability of two or more contacts. To allow for this we may insert a "multiple contact factor," k_{mc}, in the numerator on the right side of eq. 11. (This factor corresponds to $(1 - f)^{-1}$ in ref. 7. For a fuller discussion, see ref. 6, pp. 216–217.) For present purposes, we assume k_{mc} to be independent of concentration.

For high polymer solutions, another factor, f_{sh}, should be included in the numerator of eq. 11 to allow for the fact that the interior segments of a convoluted molecule are partially shielded from contact with interior segments of other polymer molecules. This may be very important in dilute solutions, but the shielding should be negligible in concentrated solutions when the polymer molecules interpenetrate each other to a large extent. Tentatively, we shall assume the shielding factor to depend on concentration according to the equation

$$f_{sh} = 1 - (1 - k_{sh})\phi_1{}^m = k_{sh} + (1 - k_{sh})m\phi_2 -$$
$$\frac{(1 - k_{sh})m(m - 1)}{2!}\phi_2{}^2 + \cdots \qquad (12)$$

Here, m is an empirical constant and k_{sh} is a constant for a given system at a given temperature, approximately unity for low polymers and decreasing as the average molecular weight increases. The volume fraction of solvent in the solution is related to the molecular volumes (v_1, v_2) by the equation

$$\phi_1 = \frac{N_1v_1}{N_1v_1 + N_2v_2} \qquad (13)$$

At infinite dilution, f_{sh} equals k_{sh}; in pure polymer, f_{sh} is unity.

If the attraction, per unit surface area, between like molecules is greater than that between unlike molecules, the ratio of eq. 11 should be increased. It seems reasonable to approximate this increase by insertion of a factor

$$W = \exp\left(\frac{k_\sigma\Delta\epsilon}{k_BT}\right) = 1 + \frac{k_\sigma\Delta\epsilon}{k_BT} + \cdots \qquad (14)$$

where

$$\Delta\epsilon = 2\epsilon_{21} - \epsilon_{11} - \epsilon_{22} \qquad (15)$$

k_B is Boltzmann's constant, T is the absolute temperature, and k_σ is a factor that depends on chain flexibility and other structural features. We thus have, for polymer solutions

$$\frac{\sigma_{22,\text{ext}}}{\sigma_{21}} = \frac{N_2\sigma_2'k_{mc}f_{sh}W}{N_1\sigma_1'} \qquad (16)$$

From this and eq. 9, one readily obtains

$$\sigma_{21} = \frac{\sigma_2'N_1\sigma_1'}{N_1\sigma_1' + N_2\sigma_2'k_{mc}f_{sh}W} \qquad (17)$$

The energy of mixing N_1 molecules of solvent with N_2 molecules of solution is

$$\Delta E_{mix} = E_{solution} - E_{solvent} - E_{solute}$$

$$= \frac{1}{2}\{[N_1(\sigma_{11}\epsilon_{11} + \sigma_{12}\epsilon_{12}) + N_2(\sigma_{22,\text{ext}}\epsilon_{22} +$$
$$\sigma_{21}\epsilon_{21})] - N_1(\sigma_1'\epsilon_{11}) - N_2(\sigma_2'\epsilon_{22})\} \qquad (18)$$
$$= \frac{N_2\sigma_{21}\Delta\epsilon}{2}$$

Substitution of eq. 17 into eq. 18 gives

$$\Delta E_{mix} = \frac{N_1N_2\sigma_1'\sigma_2'}{2(N_1\sigma_1' + N_2\sigma_2'k_{mc}f_{sh}W)} \qquad (19)$$

The partial molal energy of the solvent is related to the energy of mixing by the equation

$$\Delta\bar{E}_1 = N_A\left(\frac{\partial\Delta E_{mix}}{\partial N_1}\right)_{N_2} \qquad (20)$$

where N_A is Avogadro's number.

Performing the indicated differentiation yields the result

$$\Delta\bar{E}_1 = \frac{N_Av_1{}^2\sigma_2'{}^2k_{mc}W\Delta\epsilon\phi_2{}^2[f_{sh} + m(1 - f_{sh})\phi_2]}{2v_2{}^2\sigma_1'\left[1 - \left(1 - \frac{v_1\sigma_2'}{v_2\sigma_1'}k_{mc}f_{sh}W\right)\phi_2\right]^2} \qquad (21)$$

The ratio of molecular volumes, v_1/v_2, can reasonably be taken equal to the ratio of partial molal volumes and to the ratio of contacted molecular surface areas

$$\frac{v_1}{v_2} = \frac{\bar{V}_1}{\bar{V}_2} = \frac{\sigma_1'}{\sigma_2' + \sigma_{22,\text{int}}} \qquad (22)$$

Then

$$\Delta\bar{E}_1 = \frac{N_A \bar{V}_1 \sigma_2 k_{\text{ext}} k_{\text{mc}} W \Delta\epsilon \phi_2{}^2 [f_{\text{sh}} + m(1 - f_{\text{sh}})\phi_2]}{2\bar{V}_2[1 - (1 - k_{\text{ext}} k_{\text{mc}} f_{\text{sh}} W)\phi_2]^2} \qquad (23)$$

or

$$\Delta\bar{E}_1 = \Delta\bar{E}_1{}^0 \frac{f_{\text{sh}}}{k_{\text{sh}}} \left\{ \frac{\left[1 + m\left(\frac{1 - f_{\text{sh}}}{f_{\text{sh}}}\right)\phi_2 \right]}{[1 - (1 - k_{\text{ext}} k_{\text{mc}} f_{\text{sh}} W)\phi_2]^2} \right\} \qquad (24)$$

with

$$\Delta\bar{E}_1{}^0 = \frac{N_A \bar{V}_1 \sigma_2' k_{\text{ext}} k_{\text{mc}} k_{\text{sh}} W \Delta\epsilon \phi_2{}^2}{2\bar{V}_2} \qquad (25)$$

and

$$k_{\text{ext}} = \frac{\sigma_2'}{\sigma_2 - \sigma_{20}} \qquad (26)$$

which equals the average fraction of contacted polymer molecule surface which is in contact with portions of other molecules.

Expansion of eq. 24 in powers of ϕ_2 gives the series

$$\Delta\bar{E}_1 = \Delta\bar{E}_1{}^0 \left\{ 1 + \left[2 - 2m + \frac{2m}{k_{\text{sh}}} - \right. \right.$$
$$2k_{\text{ext}} k_{\text{mc}} W k_{\text{sh}} \left] \phi_2 + \left[\frac{-\frac{3}{2}m^2 + \frac{9}{2}m}{k_{\text{sh}}} + \right. \right.$$
$$\left(\frac{3}{2}m^2 - \frac{9}{2}m + 3 - 6m k_{\text{ext}} k_{\text{mc}} W\right) + (6m - $$
$$\left. \left. 6)k_{\text{ext}} k_{\text{mc}} W k_{\text{sh}} + 3k_{\text{ext}}{}^2 k_{\text{mc}}{}^2 W^2 k_{\text{sh}}{}^2 \right] \phi_2{}^2 + \ldots \right\} \qquad (27)$$

From eq. 4 and 24, the enthalpy contribution to the interaction coefficient χ is deduced to be

$$\chi_{\text{h}} = \frac{\Delta\bar{H}_1}{RT V_2{}^2} = \chi_{\text{h}}{}^0 \left\{ \frac{f_{\text{sh}}\left[1 + m\left(\frac{1 - f_{\text{sh}}}{f_{\text{sh}}}\right)\phi_2 \right]}{k_{\text{sh}}[1 - (1 - k_{\text{ext}} k_{\text{mc}} f_{\text{sh}} W)\phi_2]^2} \right\} \qquad (28)$$

$$= \chi_{\text{h}}{}^0 + \chi_{\text{h}}'\phi_2 + \ldots \qquad (29)$$

where

$$\chi_{\text{h}}{}^0 = \frac{\bar{V}_1}{2\bar{V}_2} KWL(1 + \alpha_s T) \qquad (30)$$

$$\chi_{\text{h}}' = 2\chi_{\text{h}}{}^0(1 + \alpha_{\text{sh}} - KW) \qquad (31)$$

$$\chi_{\text{h}}'' = 3\chi_{\text{h}}{}^0 \left[\left(1 + \frac{3}{2}\alpha_{\text{sh}} - \frac{m\alpha_{\text{sh}}}{2} \right) - 2(1 + \alpha_{\text{sh}})KW + (KW)^2 \right] \qquad (32)$$

$$K = k_{\text{ext}} k_{\text{mc}} k_{\text{sh}} \qquad (33)$$

$$L = \frac{\sigma^{2'}\Delta\epsilon}{k_{\text{B}} T} = \frac{\alpha_L}{T} \qquad (34)$$

and

$$\alpha_{\text{sh}} = m\left(\frac{1}{k_{\text{sh}}} - 1\right) \qquad (35)$$

The function $\chi_{\text{h}}{}^0$ is the same as Flory's "heat parameter," κ_1 (see ref. 10, p. 522).

Theoretical Development: Entropy

The entropy with which we are concerned is related to the randomness of placing of the molecules and molecular segments in the solution. It is convenient to consider each polymer molecule as composed of n_r like rigid segments. We imagine these molecules as being placed in the volume, V, to be occupied by the solution, one segment at a time for the first molecule, then one segment at a time for the second molecule, and so on until all the N_2 polymer molecules have been placed. The N_1 solvent molecules (presumed to be rigid) are then hypothetically inserted one at a time.

The entropy (S) of the solution is related to the randomness of placing of the polymer segments and solvent molecules by the equation

$$\frac{S}{k_{\text{B}}} = \ln\left\{ \frac{\prod_{i=1}^{N_2} \nu_{i1} \cdot \prod_{i=1}^{N_2} \prod_{j=2}^{n_r} \nu_{ij} \prod_{l=1}^{N_1} \nu_l}{N_2! \; N_1!} \right\} \qquad (36)$$

Here, ν_{i1} designates the randomness of placing the first rigid segment of the ith solute molecule, ν_{ij} denotes the randomness of placing the jth rigid segment (with $j > 1$) of the ith polymer molecule, and ν_l represents the randomness of placing the lth solvent molecule.

The randomness of placing the first segments can be expressed by the relationship

$$\nu_{i1} = \frac{V}{v_r}\left[1 - k_2 v_2 \frac{i}{V} \pm \text{higher terms} \left(\text{involving} \; \frac{v_2{}^2 i^2}{V^2}, \frac{v_2{}^3 i^3}{V^3}, \text{etc.} \right) \right] \qquad (37)$$

with v_r representing the volume of the segment, equal to v_2/n_r if all segments are alike, and with k_2 a constant, of the order of magnitude of a small integer, which represents the average ratio of the volume excluded from occupancy by the center of the segment being placed, as a result of the presence of an already placed polymer molecule, to the volume actually occupied by that placed molecule.

Equation 37 can also be written

$$\nu_{i1} = \frac{N_2 n_r}{\phi_2}\left[1 - \left(\frac{k_2 \phi_2}{N_2}\right)i \pm \text{terms involving} \; \left(\frac{\phi_2 i}{N_2}\right)^2, \text{etc.} \right] \qquad (38)$$

From this

$$\ln \prod_{i=1}^{N_2} \nu_{ii} = N_2 \ln N_2 + N_2 \ln n_r - N_2 \ln \phi_2 +$$

$$\sum_{i=1}^{N_2} \ln \left(1 - \frac{k_2 \phi_2 i}{N_2} \pm \ldots \right) \quad (39)$$

For large N_2

$$\sum_{i=1}^{N_2} \ln \left(1 - \frac{k_2 \phi_2}{N_2} i \pm \ldots \right) =$$

$$\int_0^{N_2} \ln \left(1 - \frac{k_2 \phi_2}{N_2} i \pm \ldots \right) \mathrm{d}i \quad (40)$$

It can be shown that for flexible high polymers the higher terms in the expansion are negligible. Then

$$\sum_1^{N_2} \ln \left(1 - \frac{k_2 \phi_2}{N_2} i \right) = -N_2 -$$

$$\frac{N_2(1 - k_2 \phi_2)}{k_2 \phi_2} \ln (1 - k_2 \phi_2) \quad (41)$$

$$= -\frac{k_2 N_2}{2} \phi_2 \pm \text{ terms involving}$$

$$\phi_2{}^2, \text{ etc.} \quad (42)$$

For the solvent molecules, to a sufficient degree of approximation

$$\nu_l = \frac{V - N_2 v_2}{v_1} \left(1 - \frac{l-1}{N_1}\right) =$$

$$N_1 \left(1 - \frac{l-1}{N_1}\right) = N_1 - l + 1 \quad (43)$$

Hence

$$\ln \prod_{l=1}^{N_1} \nu_l = \ln N_1! = N_1 \ln N_1 - N_1 \quad (44)$$

The randomness of location of each rigid polymer segment, other than the first, is just its randomness of orientation relative to the preceding segment. This randomness is, of course, reduced by blocking by solvent molecules, other segments of the same polymer molecule, and other polymer molecules. Let us define ν^0 as the average randomness of orientation of a rigid segment of a solute molecule in infinitely dilute solution, i.e., in contact only with solvent molecules and other portions of the same polymer molecule. (It will be recalled that we have assumed that the chance of contact with another portion of the same molecule does not change with the concentration). The averaging is over all values of j, as well as over all configurations of the polymer molecule, all distributions and orientations of neighboring solvent molecules, etc.

At finite concentrations the average randomness of orientation is changed (usually reduced) from the value ν_i by the presence in the vicinity of (i.e., blocking by) other polymer molecules. It seems reasonable to assume that the blocking effect (averaged for any segment of the ith molecule) is proportional to the fraction of noninternally contacted surface which is in contact with other polymer molecules, that is, to the

ratio $\sigma_{22,\text{ext}}/\sigma_2'$, computed from eq. 9 and 17 with substitution of i for N_2. Thus

$$\nu_{ij} = \nu_i{}^0(1 - k_s p_i) \quad (45)$$

$$p_i = \left(\frac{\sigma_{22,\text{ext}}}{\sigma_2'}\right)_i = \left(\frac{\sigma_2' - \sigma_{21}}{\sigma_2'}\right)_i = 1 - \left(\frac{\sigma_{21}}{\sigma_2'}\right)_i$$

$$= \frac{\sigma_2' k_{\text{mc}} f_{\text{sh}} Wi}{N_1 \sigma_1' + \sigma_2' k_{\text{mc}} f_{\text{sh}} Wi} = \frac{K_p \left(\dfrac{i}{N_1}\right)}{1 + K_p \left(\dfrac{i}{N_1}\right)} \quad (46)$$

where k_s is a proportionality constant and

$$K_p = \frac{\sigma_2'}{\sigma_1'} k_{\text{mc}} f_{\text{sh}} W \quad (47)$$

Hence

$$\ln \prod_{i=1}^{N_2} \prod_{j=2}^{n_r} \nu_{ij}$$

$$= (n_r - 1) N_2 \ln \nu^0 + (n_r - 1) \sum_{i=1}^{N_2} \ln (1 - k_s p_i)$$

$$= (n_r - 1) N_2 \ln \nu^0 +$$

$$(n_r - 1) \int_{i=0}^{N_2} \ln \left[1 - \frac{k_s \dfrac{K_p}{N_1} i}{1 + \dfrac{K_p}{N_1} i}\right] \mathrm{d}i$$

$$= (n_r - 1) N_2 \ln \nu^0 + (n_r - 1) \left\{ \left[N_2 + \frac{N_1}{(1 - k_s) K_p}\right] \ln \left[1 + (1 - k_s) \frac{K_p N_2}{N_1}\right] - \left[N_2 + \frac{N_1}{K_p}\right] \ln \left[1 + \frac{K_p N_2}{N_1}\right] \right\} \quad (48)$$

For large N_2 and N_1

$$\ln N_2! = N_2 \ln N_2 - N_2 \quad (49)$$

$$\ln N_1! = N_1 \ln N_1 - N_1 \quad (50)$$

Substitution of eq. 39, 41, 44, 48, 49, and 50 into eq. 36 gives

$$\frac{S}{k_{\text{B}}} = N_2 \ln n_r - N_2 \ln \phi_2 - \frac{N_2(1 - k_2 \phi_2) \ln (1 - k_2 \phi_2)}{k_2 \phi_2} +$$

$$(n_r - 1) N_2 \ln \nu^0 + (n_r - 1) \left[N_2 + \frac{N_1}{(1 - k_s) K_p}\right] \ln \left[1 + (1 - k_s) \frac{K_p N_2}{N_1}\right] -$$

$$(n_r - 1) \left(N_2 + \frac{N_1}{K_p}\right) \ln \left(1 + \frac{K_p N_2}{N_1}\right) \quad (51)$$

The partial molal entropy of mixing of the solvent is given by the equation

$$\Delta \bar{S}_1 = N_A \left(\frac{\partial}{\partial N_1} [S - S_{N_1 = 0} - S_{N_2 = 0}]\right)_{N_2} =$$

$$R \left(\frac{\partial S}{\partial N_1}\right)_{N_2} \quad (52)$$

where R is the molal gas constant. Making use of the relation

$$\left(\frac{\partial \phi_2}{\partial N_1}\right)_{N_2} = -\frac{v_1 \phi_2{}^2}{v_2 N_2} = -\frac{\bar{V}_1 \phi_2{}^2}{\bar{V}_2 N_2} \qquad (53)$$

we deduce

$$\frac{\Delta S_1}{R} = -\frac{\bar{V}_1 \ln (1 - k_2 \phi_2)}{k_2 \bar{V}_2} +$$

$$(n_r - 1)\frac{\bar{V}_1 \phi_2}{\bar{V}_2 \phi_1}\left[1 + m\left(\frac{1 - f_{sh}}{f_{sh}}\right)\phi_2\right] \times$$

$$\left\{\frac{\ln [1 + (1 - k_s)k_{ext}k_{mc}f_{sh}W\phi_2/\phi_1] -}{(1 - k_s) \ln (1 + k_{ext}k_{mc}f_{sh}W\phi_2/\phi_1)}\right\} \qquad (54)$$

Expansion in powers of ϕ_2 leads to

$$\frac{\Delta S_1}{R} = \left(\frac{\bar{V}_1}{\bar{V}_2}\right)\phi_2 + \left[\frac{k_2 \bar{V}_1}{2\bar{V}_2} + (n_r - 1)\frac{\bar{V}_1 k_s}{\bar{V}_2 2}KW\right]\phi_2{}^2 +$$

$$\left\{\frac{k_2{}^3 \bar{V}_1}{3\bar{V}_2} + (n_r - 1)\frac{\bar{V}_1 k_s}{\bar{V}_2 2}KW\left[2 - 2m + \frac{2m}{k_{sh}} + \right.\right.$$

$$\left.\left.\left(\frac{2k_s}{3} - \frac{4}{3}\right)KW\right]\right\}\phi_2{}^3 + \cdots \quad (55)$$

One would expect k_2 to be of the same order of magnitude as KW. Therefore, for large n_r, the terms involving k_2 can be neglected. Also, $n_r - 1$ can be replaced by n_r. Hence we put

$$\frac{\Delta S_1}{R} = \frac{\bar{V}_1}{\bar{V}_2}\phi_2 + \frac{n_r \bar{V}_1 \phi_2}{\bar{V}_2 \phi_1}\left[1 + m\left(\frac{1 - f_{sh}}{f_{sh}}\right)\phi_2\right] \times$$

$$\left\{\frac{\ln [1 + (1 - k_s)k_{ext}k_{mc}f_{sh}W\phi_2/\phi_1] -}{(1 - k_s) \ln (1 + k_{ext}k_{mc}f_{sh}W\phi_2/\phi_1)}\right\} \quad (56)$$

Referring back to eq. 1 and 2, we can relate ΔS_1 to χ_s by means of the equation

$$\Delta S_1 = -R\left[\ln \phi_1 + \left(1 - \frac{\bar{V}_1}{\bar{V}_2}\right)\phi_2 + \chi_s \phi_2{}^2\right] \quad (57)$$

It is now convenient to define an "entropy parameter," ψ_s, by means of the relationship

$$\psi_s = \frac{1}{\phi_2{}^2}\left(\frac{\Delta S_1}{R} - \frac{\bar{V}_1}{\bar{V}_2}\phi_2\right) = \left(\frac{-\ln \phi_1 - \phi_2}{\phi_2{}^2}\right) - \chi_s$$

$$= \left(\frac{1}{2} + \frac{\phi_2}{3} + \frac{\phi_2{}^2}{4} + \cdots\right) - \chi_s \quad (58)$$

This parameter is equivalent to Flory's "entropy parameter," ψ_1 (see ref. 10, p. 522), if all terms except the first, in the series expansion in eq. 58, are negligible.

From eq. 56 and 58, we obtain

$$\psi_s = n_r \frac{\bar{V}_1}{\bar{V}_2}\frac{1}{\phi_1 \phi_2}\left[1 + m\left(\frac{1 - f_{sh}}{f_{sh}}\right)\phi_2\right] \times$$

$$\left\{\frac{\ln [1 + (1 - k_s)k_{ext}k_{mc}f_{sh}W\phi_2/\phi_1] -}{(1 - k_s) \ln (1 + k_{ext}k_{mc}f_{sh}W\phi_2/\phi_1)}\right\} \quad (59)$$

Expanding into a series in powers of the volume fraction of polymer

$$\psi_s = \psi_s{}^0 + \psi_s{}'\phi_2 + \psi_s{}''\phi_2{}^2 + \cdots \quad (60)$$

with

$$\psi_s{}^0 = \frac{\bar{V}_1 KW k_s n_r}{2\bar{V}_2} \quad (61)$$

$$\psi_s{}' = 2\psi_s{}^0\left[1 + \alpha_{sh} + \left(\frac{k_s - 2}{3}\right)KW\right] \quad (62)$$

and

$$\psi_s{}'' = 3\psi_s{}^0\left[\left(1 + \frac{3}{2}\alpha_{sh} - \frac{m\alpha_{sh}}{2}\right) + \frac{2}{3}\left(-2 - 2\alpha_{sh} + \right.\right.$$

$$\left.\left. k_s\alpha_{sh} + 2k_s\right)KW + \left(\frac{1}{2} - \frac{k_s}{2} + \frac{k_s{}^2}{6}\right)(KW)^2\right] \quad (63)$$

The Interaction Coefficient and Its Temperature Dependence

It has been customary to assume that one can separate the interaction coefficient into a temperature independent part and a temperature dependent part, according to the equation

$$\chi = a_\chi + \frac{b_\chi}{T} \quad (64)$$

and then to identify these parts with the entropy and enthalpy contributions, χ_s and χ_h (see eq. 2). From the theory presented here, however, ψ_s, and hence χ_s, should depend on temperature, since the factor W, which enters into the expressions for $\psi_s{}^0$, $\psi_s{}'$, etc., is temperature dependent (see eq. 14). Of course, if the product $k_\sigma \Delta \epsilon$ is sufficiently small relative to $k_B T$, the temperature dependence of χ_s may be negligible. Nevertheless, it would seem worthwhile to transfer the temperature dependent part of χ_s to the other component part, so obtaining theoretical expressions for the temperature independent and temperature dependent components, which can be readily measured experimentally. This has been done, neglecting all terms in powers of $1/T$ higher than the first, with the following results.

$$a_\chi = \frac{-\ln \phi_1 - \phi_2}{\phi_2{}^2} - \psi_a \quad (65)$$

$$\psi_a = \psi_a{}^0 + \psi_a{}'\phi_2 + \psi_a{}''\phi_2{}^2 + \cdots \quad (66)$$

$$\psi_a{}^0 = \frac{\bar{V}_1 K k_s n_r}{2\bar{V}_2} \quad (67)$$

$$\psi_a{}' = 2\psi_a{}^0\left[(1 + \alpha_{sh} + \left(\frac{k_s - 2}{3}\right)K\right] \quad (68)$$

$$\psi_a{}'' = 3\psi_a{}^0\left[\left(1 + \frac{3}{2}\alpha_{sh} - \frac{m\alpha_{sh}}{2}\right) + \frac{2}{3}\left(-2 - 2\alpha_{sh} + \right.\right.$$

$$\left.\left. k_s\alpha_{sh} + 2k_s\right)K + \left(\frac{1}{2} - \frac{k_s}{2} + \frac{k_s{}^2}{6}\right)K^2\right] \quad (69)$$

$$b_\chi = b_\chi{}^0 + b_\chi{}'\phi_2 + b_\chi{}''\phi_2{}^2 + \cdots \quad (70)$$

$$b_\chi{}^0 = \frac{\bar{V}_1 K}{2\bar{V}_2}\alpha_L(1 - \beta)(1 + \alpha_s T) \quad (71)$$

$$b_\chi{}' = 2b_\chi{}^0\left\{1 + \alpha_{sh} - K\left[\frac{1 - \left(\frac{4}{3} - \frac{2k_s}{3}\right)\beta}{1 - \beta}\right]\right\} \quad (72)$$

$$b_\chi'' = 3b_\chi^0 \Bigg\{ \left(1 + \frac{3}{2}\alpha_{\text{sh}} - \frac{m\alpha_{\text{sh}}}{2}\right) - 2(1 + \alpha_{\text{sh}})K \times$$

$$\left[1 + \frac{2}{3}\frac{\left(\dfrac{-2 - 2\alpha_{\text{sh}} + k_{\text{s}}\alpha_{\text{sh}} + 2k_{\text{s}}}{1 + \alpha_{\text{sh}}}\right)\beta}{1 - \beta}\right] +$$

$$K^2 \left[\frac{1 - 3\left(\dfrac{1}{2} - \dfrac{k_{\text{s}}}{2} + \dfrac{k_{\text{s}}^2}{6}\right)\beta}{1 - \beta}\right] \Bigg\} \quad (73)$$

The β in eq. 71–73 is defined by the equation

$$\beta = \frac{n_{\text{r}}k_{\text{s}}k_\sigma}{\sigma_2'} \quad (74)$$

It is possible that some of the quantities assumed in the foregoing derivations to be independent of temperature do in fact vary with the temperature. If so, appropriate adjustments must be made in these relationships.

The functions deduced for χ_{h} and ψ_{s} show a very similar dependence on concentration. (Compare eq. 28 with eq. 59, also 31 with 62 and 32 with 63). Therefore χ_{h} and χ_{s} should vary oppositely, a behavior that has often been noted empirically. In certain systems the relationship is approximately a rectilinear one.[7,12,13] The accuracy of the rectilinearity probably depends on the magnitudes of certain of the parameters.

Correlation with Experiment

From precise experimental data one can determine χ and its dependence on concentration and temperature, hence values of ψ_a^0, b_χ^0, and the ratios ψ_a'/ψ^0, ψ_a''/ψ_a^0, b_χ'/b_χ^0, and b_χ''/b_χ^0. If β is negligible, one

(12) H. Takenaka, J. Polymer Sci., 24, 321 (1957).
(13) G. Rehage and H. Meys, ibid., 30, 271 (1958).

can use these ratios and eq. 68, 69, 72, and 73 (putting $\beta = 0$) to deduce the remaining four unknowns in these equations: K, α_{sh}, k_{s}, and m. From eq. 35, one can obtain k_{sh}. Equation 12 will then give f_{sh} as a function of the concentration. Equation 67 will yield n_{r} and eq. 71 will give α_{L} (assuming that α_{s} has been estimated by means of eq. 5). From K and k_{sh}, one can (eq. 33) determine the product $k_{\text{ext}}k_{\text{mc}}$, but not the individual values of these two factors. Likewise, from eq. 34, one can obtain the product $\sigma_2'\Delta\epsilon$, but not σ_2' and $\Delta\epsilon$ separately.

In this way, one can determine, from experimental data, all the constants needed for substitution into the closed-form equations for $\Delta\bar{H}_1$ and $\Delta\bar{S}_1$ (eq. 28 and 54).

If β is not negligible, the more complicated equations, containing this quantity, must be used; another experimental quantity, such as ψ_a'''/ψ_a^0 or b_χ'''/b_χ^0, is needed, unless one or more of the "unknowns" can be determined or estimated in another way.

Testing of the equations presented in this paper, using published experimental data, has been begun. The results will be reported in due course. If the theory and its equations should prove satisfactory, it will be possible, from a relatively small amount of experimental data, to deduce curves for the variation of the thermodynamic properties of polymer solutions up to quite high concentrations. (At very high concentrations certain other factors[6] not considered in the present development may become important.) It is hoped, moreover, that the theory will lead to the determination of the various molecular constants which affect the thermodynamic solution properties and so eventually to a better understanding of the phenomena and an ability to predict the properties of new systems.

An extension of this theory to solutions of graft and block copolymers has already been published.[14]

(14) M. L. Huggins, ibid., C1, 445 (1963).

Viscometric Tests of Excluded Volume Theories

By G. C. Berry and T. G Fox

Some aspects of viscometric tests for excluded volume theories are discussed. Attention is confined to those systems for which the intrinsic viscosity and the molecular weight are known, possibly as a function of temperature. It is concluded that definitive evaluation of the various theories requires data at higher molecular weights than normally studied or over a large temperature span.

Introduction

It is our purpose here to comment briefly on some aspects of viscometric tests for the various theories of the excluded volume effect in polymer coils. We will restrict our attention to studies for which *only* [η] *and M are known*, possibly as a function of temperature. Viscometric studies have recently received renewed interest because of new theoretical developments in both the hydrodynamic and thermodynamic aspects of the problem. It is an over-simplification to consider these aspects separately, but the theoretical developments which attempt to include both effects simultaneously are still at an early stage.[1-3]

(1) M. Kurata and H. Yamakawa, J. Chem. Phys., 29, 311 (1958).
(2) O. B. Ptitsyn and I. E. Eizner, Zh. Fiz. Khim., 32, 2464 (1958).

Thermodynamic Effects on the Intrinsic Viscosity

The molecular description of the hydrodynamic flow has been understood in terms of equivalent models advanced by Debye and Bueche,[4] Kirkwood and Riseman,[5] and others,[6,7] and this description has been utilized to form the basis of approximations to include thermodynamic (excluded volume) effects.[1,2,8,9] A principle result of the hydrodynamic calculations

(3) See, for example, the review: A. Peterlin, Makromol. Chem., 34, 89 (1959).
(4) P. Debye and A. M. Bueche, J. Chem. Phys., 16, 565 (1948).
(5) J. G. Kirkwood and J. Riseman, ibid., 16, 565 (1948).
(6) H. C. Brinkman, Physica, 13, 447 (1947).
(7) B. H. Zimm, J. Chem. Phys., 24, 269 (1956).
(8) T. G Fox and P. J. Flory, J. Am. Chem. Soc., 73, 1904 (1951).
(9) M. Kurata and W. H. Stockmayer, Advan. Polymer Sci., 3, 196 (1963).