unperturbed dimensions depend on such factors as bonding geometry, etc., than to attempt to obtain quantitative agreement between theory and experiment for particular molecules.

Characteristic ratios have previously been calculated for a variety of 1,4-linked homopolysaccharides, and it was noted that, in general, characteristic ratios were larger for equatorial–equatorial-linked systems than for axial–equatorial-linked systems and that, in both cases, the characteristic ratios decreased as the freedom of rotation about the glycosidic bonds increased. If we examine the results for 1,3-linked systems reported here, it is clear that the characteristic ratio is larger for axial–equatorial- than for equatorial–equatorial-linked systems and that, for each system, C_∞ decreases as Z increases.

For the 1,4-linked homopolysaccharides considered here, the results are in qualitative agreement with previous work.[5] Characteristic ratios decrease in the order a–a > e–e > e–a > a–e and for the e–e and a–e series, C_∞ decreases as Ω increases. Since Ω contains a contribution from the rotation about C5–C6, the results are not directly comparable with xylose or arabinose results.[5]

We can rationalize these results using the classification of Rees and Scott,[6] who noticed that 1,4-a–a, 1,4-e–e, and 1,3-a–e polymers are all of type A, while 1,4-e–a, 1,4-a–e, and 1,3-e–e polymers are all of type B. It appears that, in general, unperturbed dimensions of type A polymers are large and unperturbed dimensions of type B polymers are small, but that there are variations within these types depending on the details of the bonding geometry and on the degree of rotational freedom about the glycosidic bonds.

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Excluded Volume Expansion of a Polymer Chain in a Mixed Solvent

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ABSTRACT: A new theory of dilute solutions of polymers in mixed solvents has been developed. In this theory the solvent sea is divided into two regions, one consisting of the nearest neighbors of the segments of the polymer chain and the other the infinite sea beyond the isolated macromolecule. Expressions for the free energy and the Θ temperature for this model are obtained.

The theory of polymer solutions with a single solvent has been developed by many authors for both dilute solutions and concentrated solutions. Since the well-known lattice formulations of Flory[1] and Huggins[2] which were first published in the early 1940's, the subject has become highly developed and numerous treatments have appeared. The thermodynamic properties of a concentrated polymer solution have been more or less successfully explained by the lattice and the cell variant[3] of this theory, and some practical applications have been worked out. Another series of studies has been related to the characteristics of polymer molecules in a dilute solution, with the fundamental analysis being that of Flory.[4,5] The basic problem of dilute solutions is the calculation of the expansion factor α, which relates the true root-mean-square radius of gyration $\overline{s^2}$ of a swollen linear polymer molecule to that in the unperturbed state. According to Flory's theory,[5] this is given by

$$\alpha^5 - \alpha^3 = 2C_M\chi_1\left(1 - \frac{\Theta}{T}\right)M^{1/2} \tag{1}$$

where M is molecular weight, T is the temperature, and ψ_1 and Θ are functions of the solvent quality. When Θ equals T, the expansion factor must be unity, which, as Flory points out, is the criterion of incipient precipitation. The parameter Θ is called the Flory Θ temperature. Equation 1 has direct application to the theory of intrinsic viscosity, as one may write

$$[\eta] = \Phi'\frac{(\overline{s^2})^{3/2}}{M} = [\eta]_\Theta\alpha^3 \tag{2}$$

where $[\eta]_\Theta$ is the intrinsic viscosity under Θ conditions. More recent research[6-8] has been aimed at obtaining improved expressions for α.

In many practical applications, the system contains a mixture of two or more solvents rather than a single solvent. For example, in the process of fractional precipitation, a poor solvent is gradually added to a mixture of polymer and good solvent (at constant temperature). The apparent solvent power gradually decreases and the polymer molecules with high molecular weight begin to precipitate. A similar change

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(1) (a) P. J. Flory, *J. Chem. Phys.*, **10**, 51 (1942); **12**, 425 (1944); (b) "Principles of Polymer Chemistry," Cornell University Press, Ithaca, N. Y., 1953, pp 495–518 and 541–563.

(2) M. L. Huggins, *J. Phys. Chem.*, **46**, 151 (1942); *Ann. N. Y. Acad. Sci.*, **41**, 1 (1942); *J. Amer. Chem. Soc.*, **64**, 1712 (1942).

(3) I. Prigogine, N. Trappeniers, and V. Mathot, *J. Chem. Phys.*, **21**, 559, 560 (1953); A. Bellemans and C. Colin-Naar, *J. Polym. Sci.*, **15**, 121 (1955); D. Patterson, *Rubber Chem. Technol.*, **40**, 1 (1967).

(4) P. J. Flory, *J. Chem. Phys.*, **17**, 303 (1949).

(5) P. J. Flory, ref 1b, pp 519–539 and 595–602.

(6) E. Teramoto, *Busseiron Kenkyu*, **39**, 1 (1951); **40**, 18 (1951); **41**, 14 (1951); **42**, 24 (1951); **44**, 36 (1951); R. J. Rubin, *J. Chem. Phys.*, **20**, 1940 (1952); N. Saito, *J. Phys. Soc. Jap.*, **9**, 750 (1954).

(7) M. Kurata, W. H. Stockmayer, and A. Roig, *J. Chem. Phys.*, **33**, 151 (1960); W. H. Stockmayer and M. Fixman, *J. Polym. Sci., Part C*, **No. 1**, 137 (1963); H. Yamakawa, A. Aoki, and G. Tanaka, *J. Chem. Phys.*, **45**, 1938 (1966).

(8) T. Kato, *Rep. Progr. Polym. Phys. Jap.*, **12**, 1 (1969); Y. Chikahisa, manuscript in preparation.

in the solvent power due to the mixing of two or more solvents occurs in the Baker–Williams precipitation chromatograph. Solutions of polymers in mixed solvents exhibit some rather striking characteristics. There are many examples of polymers which are insoluble in either of two solvents but soluble in a mixture of them[9] (the most famous is cellulose nitrate, which is insoluble in ether or ethyl alcohol but dissolves in their mixture to form collodion). Another phenomenon is the selective absorption of a good solvent by swollen rubber vulcanizates (*Tompkins effect;*[10] compare the experimental studies of Krigbaum and Carpenter[11] and Bristow[12]). Undoubtedly, if such a phenomenon occurs in swollen network polymers, an individual macromolecule in solution will have a local environment rich in good solvent. This has already been observed by Ewart and his colleagues[13] in connection with light-scattering measurements. A number of authors, notably Gee,[9] Scott and Magat,[14] and Flory,[1] have discussed lattice theories of polymers dissolved in mixed solvents. Shultz and Flory[15] have developed a theory of dilute polymer solutions involving mixed solvents, in which they have considered the solvent within the coil to have a different composition from that in the solvent sea beyond it. This theory represents essentially an extension of an analysis of Krigbaum and Carpenter[11] for vulcanizates. More recently, a thermodynamic treatment of the dilute polymer solution–mixed solvent problem has been published by Pouchly, Zivny, and Solc[16] who note the analogy of the problem to preferential adsorption and treat the problem using the methodology of the Gibbs adsorption isotherm.

In the present paper, we will analyze the character of a dilute solution of a polymer in mixed solvent and, in particular, we will calculate the Flory Θ temperature for a new model. In our model the good solvent region consists of the nearest neighbors of the polymer segments and the remaining region is considered a solvent sea even within the sphere of polymer segments. A previous paper[17] applied this model to concentrated solutions.

Theoretical Section

Gathering Effect and Partition Function. Let us consider a canonical ensemble of systems consisting of a single polymer chain possessing M segments suspended in a mixed solvent containing N_1 "1" solvent molecules and N_2 "2" solvent molecules. First of all, we presume that a segment and a molecule of both solvents have a same volume, and we can apply the lattice model with a cell size just containing a segment or a molecule. The effect of molecular size of solvents will be considered later. We divide the solvent into a coating of N_s' molecules adjacent to the polymer chain and a sea of N_s'' molecules. These will in general possess different compositions. The total number of nearest-neighbor lattice sites of a polymer molecule with M units in its fully stretched conformation, or the total number of contacts of polymer chain, is

$$N_0' = (z-2)M + 2 \tag{3}$$

where z is the number of nearest neighbors of a unit or the lattice coordination number. If the polymer molecule has a completely stretched conformation, all of these contacts are free to be with solvent molecules. In an equilibrium situation, however, this is not the case, and a polymer molecule has a random-coil conformation, so that some of these nearest-neighbor sites are occupied by the polymer segments themselves, and a number of these contacts are intramolecular. The number of such internal contacts is approximately given by $\phi_p'N_0'$, where ϕ_p' is the fraction of the polymer segments in the neighborhood of the polymer molecule. Therefore, the number of remaining free contacts is $(1-\phi_p')N_0'$.

Making use of the so-called quasichemical method, ϕ_p' is given by[18]

$$\phi_p' = \phi_p\left[1 + \frac{1-\phi_p}{\phi_p}\frac{\beta-1}{\beta+1}\right] \tag{4}$$

with the average concentration ϕ_p of segments in the "polymer region," the spherical region having the radius equal to the radius of gyration of the polymer chain, being $\phi_p = M/N_0$. N_0 is the total number of lattice sites in the polymer region and β is given by

$$\beta^2 = 1 + 4\phi_p(1-\phi_p)(\eta^2 - 1) \tag{5}$$

$$\eta = \exp(\Delta\epsilon_{sp}/kT) \tag{6}$$

in this calculation $\Delta\epsilon_{sp}$ is the random average interaction energy between polymer segments and molecules of solvents, and we assume the relation

$$\Delta\epsilon_{sp} = \chi_1'\Delta\epsilon_{1p} + \chi_2'\Delta\epsilon_{2p} \tag{7}$$

where $\Delta\epsilon_{ip}$ ($i = 1, 2$) is the excess interaction energy between segment and molecule of "i" solvent

$$\Delta\epsilon_{ip} = \epsilon_{ip} - \frac{1}{2}(\epsilon_{ii} + \epsilon_{pp}) \tag{8}$$

and χ_i' is the concentration of the i solvent molecules in the coating

$$\chi_i' = N_i'/(N_1' + N_2') = N_i'/N_s' \tag{9}$$

with N_i' being the total number of i solvent molecules in the coating. We denote the number of solvent molecules which are nearest-neighbor sites of the polymer molecule as N_s'. Each N_s' may have more than one contact with the polymer chain. It may be shown that on the average each solvent molecule has $1 + (z-1)\phi_p'$ contacts with polymer segments. Thus polymer–solvent contacts (N_{PS}) may be expressed

$$N_{PS} = [1 + (z-1)\phi_p']N_s' = (1-\phi_p')N_0'$$

$$N_s' = \frac{(1-\phi_p')[(z-2)M+2]}{1+(z-1)\phi_p'} \tag{10}$$

The basic problem of statistical mechanics is the computation of the partition function Q which allows us to evaluate the Helmholtz free energy. We now evaluate Q for the model described in the preceeding paragraphs. Factoring

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(9) G. Gee, *Trans. Faraday Soc.*, **40**, 468 (1944).

(10) H. K. Tompkins in "The Physics and Chemistry of Colloids," Appendix II, Report of a General Discussion held jointly by the Faraday Society and the Physical Society of London, His Majesty's Stationery Office, London, 1921; published with *Trans. Faraday Soc.*, **16** (1921).

(11) W. R. Krigbaum and D. K. Carpenter, *J. Polym. Sci.*, **14**, 241 (1954).

(12) G. M. Bristow, *Trans. Faraday Soc.*, **55**, 1246 (1959).

(13) R. H. Ewart, C. P. Roe, P. Debye, and J. R. McCartney, *J. Chem. Phys.*, **14**, 687 (1946).

(14) R. L. Scott and M. Magat, *ibid.*, **13**, 172 (1945).

(15) A. R. Shultz and P. J. Flory, *J. Polym. Sci.*, **15**, 231 (1955).

(16) J. Pouchly, A. Zivny, and K. Solc, *ibid.*, *Part C*, **No. 23**, 245 (1968).

(17) M. Yamamoto, J. L. White, and D. L. MacLean, *Polymer*, **12**, 290 (1971).

(18) N. Saito, "High Polymer Physics," revised ed, Shokabo, Tokyo, 1968, p 156.

out the internal partition functions, as is usually done in lattice formulations, allows us to write

$$Q = q_1^{N_1}q_2^{N_2}q_p\sum\Omega_j e^{-E_j/kT}$$
$$A = -kT\ln Q \qquad (11)$$

where Ω_j is the number of configurations possessing energy E_j.

If the numbers of solvent 1 and solvent 2 molecules in the coating are N_1' and N_2' and those in the sea beyond the monolayer are N_1'' and N_2'', respectively, the number of ways to arrange all molecules is

$$\Omega = \frac{N_s'!}{N_1'!N_2'!}\frac{N_s''!}{N_1''!N_2''!}\Omega_p \qquad (12)$$

where

$$N_s' = N_1' + N_2' \qquad (13a)$$

and

$$N_s'' = N_1'' + N_2'' \qquad (13b)$$

Ω_p is the number of possible conformations of the polymer chain. This is made up of two parts, (1) the number of conformations that it may have on a statistical basis and (2) a factor correcting for the fact that no two segments of the polymer chain may overlap and for the inhibitions of a lattice coordination number. If the polymer chain is swollen by the solvent beyond its normal unperturbed radius of gyration by some factor α, it is suggested from considerations of the theory of deformation of a rubber network that the possible number of conformations is decreased by a factor[19, 20]

$$e^{-(^3/_2)[\alpha^2-1]} \qquad (14)$$

(If we were to follow Flory's approach, this expression should be multiplied by a factor α^3). It follows that we may write

$$\Omega_p = [N_0\prod_{i=2}^{M}(z_p - 1)p_i]e^{-^3/_2[\alpha^2-1]} \qquad (15)$$

where z_p is the coordination number of the polymer sublattice and p_i is the probability of vacancy of a site. From eq 13 and 15, we have

$$\Omega = \frac{N_s'!}{N_1'!N_2'!}\frac{N_s''!}{N_1''!N_2''!}\frac{N_0!}{(N_0 - M)!}\frac{(z_p - 1)^{M-1}}{N_0^{M-2}}e^{-(^3/_2)[\alpha^2-1]} \qquad (16)$$

where we have taken p_i to be $(N_0 - i - 1)/N_0$. In this calculation the polymer molecule is restricted in the polymer region.

Next, in order to get the interaction energy, we must know the numbers of pairs in the system. Adopting a random approximation in the coating and the sea we have the following numbers of pairs

$$\text{segment–segment} = \phi_p'N_0'/2$$

$$\text{segment–solvent 1} = [1 + (z - 1)\phi_p']N_1'$$

$$\text{segment–solvent 2} = [1 + (z - 1)\phi_p']N_2'$$

$$\text{solvent 1–solvent 1} = \frac{1}{2}z'(1 - \phi_p')\frac{(N_1')^2}{N_s'} + z''(1 - \phi_p') \times \frac{N_1'N_1''}{N_s''} + \frac{1}{2}[zN_s'' - z''(1 - \phi_p')N_s']\frac{(N_1'')^2}{(N_s'')^2}$$

$$\text{solvent 2–solvent 2} = \frac{1}{2}z'(1 - \phi_p')\frac{(N_2')^2}{N_s'} + z''(1 - \phi_p') \times \frac{N_2'N_2''}{N_s''} + \frac{1}{2}[zN_s'' - z''(1 - \phi_p')N_s']\frac{(N_2'')^2}{(N_s'')^2}$$

$$\text{solvent 1–solvent 2} = z'(1 - \phi_p')\frac{N_1'N_2'}{N_s'} + z''(1 - \phi_p') \times \frac{N_1'N_2'' + N_2'N_1''}{N_s''} + [zN_s'' - z''(1 - \phi_p')N_s']\frac{N_1''N_2''}{(N_s'')^2} \qquad (17)$$

where z is the coordination number of the lattice, z' is that between lattice sites in the coating, and

$$z'' = z - z' - 1 \qquad (18)$$

is that between lattice sites in the coating and in the sea. Making use of these numbers of pairs leads to an energy of mixing of the form

$$E = [1 + (z - 1)\phi_p'][N_1'\Delta\epsilon_{1p} + N_2'\Delta\epsilon_{2p}] + \left[z\frac{N_1''N_2''}{N_s''} + z'(1 - \phi_p')\frac{N_1'N_2'}{N_s'} + z''(1 - \phi_p')\frac{N_1'(N_2'')^2 + N_2'(N_1'')^2}{(N_s'')^2}\right]\Delta\epsilon_{12} \qquad (19)$$

with eq 8 and

$$\Delta\epsilon_{12} = \epsilon_{12} - (1/2)(\epsilon_{11} + \epsilon_{22}) \qquad (20)$$

We are now in a position to evaluate the partition function and the Helmholtz free energy. This is

$$A = E_{sol} + kT\left[N_1'\ln\frac{N_1'}{N_s'} + N_2'\ln\frac{N_2'}{N_s'} + N_1''\ln\frac{N_1''}{N_s''} + N_2''\ln\frac{N_2''}{N_s''} + N_0\ln(1 - \phi_p) + M - (M - 1) \times \ln(z_p - 1)\right] + (3/2)kT(\alpha^2 - 1) - kT\ln[q_pq_1^{N_1}q_2^{N_2}] \qquad (21)$$

Equilibrium Distribution of Solvent Molecules and Radius of Gyration. Under conditions of constant α and constant N_1 and N_2, the equilibrium distribution of the two solvents in the polymer region and the sea is obtained by the condition that the free energy should take on a minimum value, *i.e.*, the variation A with respect to changes in N_1' and N_2' at constant N_1 and N_2 should be zero. This condition results in the equation

$$[1 + (z - 1)\phi_p'](\Delta\epsilon_{1p} - \Delta\epsilon_{2p}) - \{z'(1 - \phi_p')(\chi_i' - \chi_2' - \chi_1 + \chi_2) - [1 + (z - 1)\phi_p'](\chi_1 - \chi_2)\}\Delta\epsilon_{12} + kT\ln\left(\frac{\chi_1'\chi_2}{\chi_1\chi_2'}\right) = 0 \qquad (22)$$

where χ_1' and χ_1 are the concentrations of solvent 1 in the coating and in the sea (see eq 9) and $\chi_i = \chi_i'' = N_i''/N_s''$.

It remains to evaluate α. This gives rise to a fundamental problem in the theory of dilute polymer solutions. Flory[5] proceeds by utilizing an additional α^3 term in eq 15 and 16, which we find difficult to justify, and then evaluates α by

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(19) M. V. Volkenstein, "Configurational Statistics of Polymeric Chains," Interscience, New York, N. Y., 1959, Chapter 8.

(20) P. J. Flory, ref 1b, pp 464–469.

minimizing the free energy. We take an alternate route here, one suggested by the work of Hermans and Overbeek[21] and Kurata, Stockmayer, and Roig.[7] The average mean-square radius of polymer molecule, $\overline{s^2}$, is given by

$$\overline{s^2} = \frac{\int_0^\infty s^4 \, e^{-\Delta A/kT} \, ds}{\int_0^\infty s^2 \, e^{-\Delta A/kT} \, ds} \tag{23}$$

This integration is, however, very hard to carry out exactly, and we can get an approximate value of $\overline{s^2}$ by computing the value of $\overline{s^2}$ which makes $s^3 e^{-A/kT}$ a maximum. Carrying out the differentiation of this expression or its logarithm with respect to α with attention to the fact that s is αs_0 and that the Helmholtz free energy A depends upon α gives

$$\frac{z(z-2)}{[1+(z-1)\phi_p']^2} B\phi_p^2([1+(z-1)\phi_p'](\Delta\epsilon_{1p}+\Delta\epsilon_{2p}) + \{2z'(1-\phi_p')(\chi_1\chi_2 - \chi_1'\chi_2') - [1+(z-1)\phi_p'] \times (1-2\chi_1\chi_2)\}\Delta\epsilon_{12}) - \frac{2(z-2)(1-\phi_p')}{1+(z-1)\phi_p'} B\phi_p^2[(z-1)(\chi_1'\Delta\epsilon_{1p} + \chi_2'\Delta\epsilon_{2p}) + \{z''(\chi_1-\chi_1')(\chi_2-\chi_2') - (z-1)\chi_1'\chi_2'\}\Delta\epsilon_{12}] + \frac{z(z-2)}{[1+(z-1)\phi_p']^2} BkT\phi_p' \ln\left(\frac{\chi_1'\chi_2'}{\chi_1\chi_2}\right) + 2kT\left[\ln(1-\phi_p) + \phi_p + \frac{1}{N_0}(\alpha^2-1)\right] = 0 \tag{24}$$

where

$$B = \frac{2}{\beta+1}\left[1 + 2\frac{(1-\phi_p)(1-2\phi_p)}{\beta(\beta+1)}(\eta^2-1)\right] \tag{25}$$

is a factor due to the gathering effect of segments into coating. For the special case of a single solvent, we have $\Delta\epsilon_{12} = 0$, $\chi_2 = 0$, and $\chi_1 = 1$, and also clearly $\chi_1' = 1$ and $x_2' = 0$. When $\phi_p \ll 1$, eq 24 results in

$$\alpha^5 - \alpha^3 = c_M'\left(1 - \frac{\Theta_1}{T}\right)\sqrt{M} \tag{26a}$$

where

$$\Theta_1 = \frac{2(z-2)\Delta\epsilon_{1p}}{k}[1 + (2/kT)\Delta\epsilon_{1p}] \tag{26b}$$

with the correction term $2\Delta\epsilon_{ip}/kT$ being due to the gathering of segments.

If we can assume $\Delta\epsilon_{12} = 0$, we have the exact solution of eq 22

$$\begin{aligned} \chi_1' &= K'\chi_1 \exp\left[-\{1+(z-1)\phi_p'\}\frac{\Delta\epsilon_{1p}}{kT}\right] \\ \chi_2' &= K'\chi_2 \exp\left[-\{1+(z-1)\phi_p'\}\frac{\Delta\epsilon_{2p}}{kT}\right] \end{aligned} \tag{27}$$

with the normalization constant

$$K' = \left[\chi_1 (\exp\left\{-[1+(z-1)\phi_p']\frac{\Delta\epsilon_{1p}}{kT}\right\} + \chi_2 \exp\left\{-[1+(z-1)\phi_p']\frac{\Delta\epsilon_{2p}}{kT}\right\}\right]^{-1} \tag{28}$$

The volume expansion coefficient α is obtained by the substitution of these expressions into eq 24. The general expression for $\alpha^5 - \alpha^3$ is, however, very complicated, and in order to get the effective Θ value, we must expand the formula with respect to $\Delta\epsilon_{ip}/kT$ and put $\phi_p \rightarrow 0$, except the front factor ϕ_p^2 of eq 24. If there is no gathering effect of the segments and $B = 1$

$$\Theta = x_1\Theta_1 + x_2\Theta_2 + \frac{1}{4}x_1x_2\frac{(\Theta_1-\Theta_2)^2}{T} \tag{29}$$

If this is not the case, we have approximately

$$B = \eta^2 = 1 + 2(\chi_1\Delta\epsilon_{1p} + \chi_2\Delta\epsilon_{2p})/kT \tag{30}$$

and eq 24 results in

$$\Theta = \chi_1\Theta_1 + \chi_2\Theta_2 + \frac{1}{4}\frac{z-6}{z-2}\chi_1\chi_2\frac{(\Theta_1-\Theta_2)^2}{T} \tag{31}$$

These results predict an increase in Θ or a decrease in solvent quality, provided that z is larger than 6. This is an undesirable result. Comparing eq 31 with eq 29, however, we can see that the effect of gathering of segments results in a tendency to improve solvent power.

Therefore, we must proceed to a general case with $\Delta\epsilon_{12} \neq 0$. Now, it may be very difficult to solve eq 22 exactly. Because of the front factor ϕ_p^2 of eq 24, it is possible to assume $\phi_p \rightarrow 0$ in the other places and to expand the results as power series of $\Delta\epsilon_{ij}/kT$ and neglect the higher than second-order terms in order to get the effective Θ value up to the second-order approximation. Keeping this fact in mind we have the solution of eq 22 in the following form

$$\begin{aligned} \chi_1' &= \chi_1^* + g\chi_1^*\chi_2^*\frac{\Delta\epsilon_{12}}{kT}\left[1 + h\left(\frac{\Delta\epsilon_{12}}{kT}\right)\right] \\ \chi_2' &= \chi_2^* - g\chi_1^*\chi_2^*\frac{\Delta\epsilon_{12}}{kT}\left[1 + h\left(\frac{\Delta\epsilon_{12}}{kT}\right)\right] \end{aligned} \tag{32}$$

where x_1^* and x_2^* are the zero-order concentrations given by (27) and

$$g = z'(\chi_1^* - \chi_2^*) - (z'+1)(\chi_1 - \chi_2) \tag{33}$$

$$h = 2z'\chi_1\chi_2 - \frac{1}{2}g(\chi_1^* - \chi_2^*) \tag{34}$$

Substituting these expressions into eq 24 gives, after some tedious calculations, the effective Θ value for two cases, (i) no segmental gathering effect, $B = 1$

$$\Theta = \chi_1^*\Theta_1 + \chi_2^*\Theta_2 - 2\chi_1^*\chi_2^*\frac{z-2}{z}\Theta_{12} + \frac{1}{4}\chi_1^*\chi_2^*\frac{1}{T} \times \left[(\Theta_1-\Theta_2) + \frac{z-2}{z}(\chi_1^* - \chi_2^*)\theta_{12}\right]^2 \tag{35}$$

where Θ_{12} is given by $2z\Delta\epsilon_{12}/k$, and (ii) with segmental gathering effect

$$\Theta = \chi_1\Theta_2^* + \chi_2^*\Theta_2 - 2\chi_1^*\chi_2^*\frac{z-2}{z}\Theta_{12} + \frac{1}{4}\chi_1^*\chi_2^*\frac{1}{T} \times \left[(\Theta_1-\Theta_2) + \frac{z-2}{z}(\chi_1^* - \chi_2^*)\Theta_{12}\right]^2 - \chi_1^*\chi_2^*\frac{1}{T} \times \left[\frac{1}{z-2}(\Theta_1-\Theta_2)^2 + \frac{1}{z}(\chi_1^*\Theta_1 + \chi_2^*\Theta_2)\Theta_{12}\right] \tag{36}$$

If Θ_{12} is positive, that is, the solvent mixture is an endothermic solution of two solvents, the mixture acts as a better solvent than the simple average in the first-order approximation, although the second-order term may act against this tendency.

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[21] J. J. Hermans and J. Th. G. Overbeek, *Recl. Trav. Chim. Pays Bas*, 67, 761 (1948).

The gathering effect of segments may partly cancel this second-order effect.

Effect of Solvent Molecular Size. In the above treatment it is assumed that a segment of polymer chain and a solvent molecule have the same volume, which is equal to the cell volume of the lattice model. Some research has emphasized the effect of the size of the solvent molecules and pointed out that it has some effect on the apparent solvent power. It is therefore desirable to treat the above problem with the inclusion of size of the solvent molecules.

It is convenient to consider the notation of the previous calculation. N represents the number of cells in the lattice model whose volume is just that of the segment of a polymer chain. We assume that a molecule of i solvent has X_1 segments of the same volume as that of the polymer segment. The number of molecules of i solvent in the system is, therefore, $n_i = N_i/X_i$.

If there is no gathering effect of solvent molecules into the coating, we can calculate the ratio of the numbers of configurations in an arrangement of solvent molecules with no size effect, that is, $X_i = 1$, and with the size effect. Using the usual lattice model with a zero-order approximation, we have ($N_s = N_1 + N_2$)

$$\frac{\Omega(x_i)}{\Omega(x_i = 1)} = \left(\frac{z}{z-1}\right)(N_1/x_1 + N_2/x_2) \times \frac{(z-1)^{[1-(1/x_1)]N_1+[1-(1/x_2)]N_2}}{N_s^{[1-(1/x_1)]N_1+[1-(1/x_2)]N_2}} \frac{N_1;N_2!}{(N_1/x_1)!(N_2/x_2)!} \tag{37}$$

The front factor is due to the number of arrangements of second segments of the solvent molecules in the lattice model, and eq 37 does not tend to unity even in the case of $x_i = 1$. This has, however, no effect on the following calculations: this factor cancels out in the free energy of mixing, and we could omit it from eq 37 for self-consistency. If there is a gathering effect of solvent molecules, this may not be the case. However, it may prove to be not too bad an approximation to use as a correction to the earlier theory. This is due to the fact that the coating is a two-dimensional lattice around the polymer molecules, and a solvent molecule may lie in the sea of the boundary between the sea and coating. If this is not the case, and the coating is essentially a three-dimensional region in the system and a solvent molecule lies either in the coating or in the sea, we must apply eq 37 to both the coating and the sea separately.

On the other hand, in treating the energetic terms, the effective coordination number between solvent molecules is no longer given by z, because some nearest-neighbor sites of a solvent segment are occupied by segments of the same molecule. The effective coordination number for a segment will be given by

$$z_s = \frac{[(z-2) + 2/x_1]N_1 + [(z-2) + 2/x_2]N_2}{N_s} \tag{38}$$

It is noted that for the polymer–segment pairs we must use z because the molecular size effect of the polymer is already considered in eq 10.

After procedures similar to those of the previous section, the concentrations of solvent segments in the coating and the value of the Θ temperature can be determined.

(a) If there is no excess interaction between solvents, $\Delta\epsilon_{12} = 0$. In this case the size of solvent molecule has no effect on either the concentrations of solvent segments in the coating or the value of the Θ temperature.

(b) For the general case with a nonzero $\Delta\epsilon_{12}$ value, we have for modified expressions of g and h in eq 32

$$g = z_s'(1 - \phi_p')(\chi_1^* - \chi_2^*) - [(1 + z_s') - z_s''\phi_p'](\chi_1 - \chi_2) \tag{39}$$

$$h = 2z_s'(1 - \phi_p)\chi_1^*\chi_2^* - (1/2)g'(\chi_1^* - \chi_2^*) \tag{40}$$

We then obtain for Θ, for (i) $B = 1$

$$\Theta = \chi_1\Theta_1 + \chi_2\Theta_2 - 2\frac{[1 + (z - z_s)](z-2)}{z_s}\chi_1\chi_2\Theta_{12} + \frac{1}{4}\chi_1\chi_2\frac{1}{T} \times \left[(\Theta_1 - \Theta_2) + \frac{z-2}{z_s}(\chi_1 - \chi_2)\Theta_{12}\right]^2 - \frac{1}{2}\frac{z - z_s}{z_s}\chi_1\chi_2 \times (\chi_1 - \chi_2)\frac{\Theta_{12}}{T}\left[(\Theta_1 - \Theta_2) + \frac{z-2}{z_s}(\chi_1 - \chi_2)\Theta_{12}\right] \tag{41a}$$

and for (ii) $B \neq 1$

$$\Theta = \chi_1\Theta_1 + \chi_2\Theta_2 - 2\frac{[1 + (z - z_s)](z-2)}{z_s}\chi_1\chi_2\Theta_{12} + \frac{1}{4}\chi_1\chi_2\frac{1}{T}\left[(\Theta_1 - \Theta_2) + \frac{z-2}{z_s}(\chi_1 - \chi_2)\Theta_{12}\right]^2 - \chi_2\chi_2\frac{1}{T}\left[\frac{1}{z-2}(\Theta_1 - \Theta_2)^2 + \frac{1}{z_s}(\chi_1\Theta_1 + \chi_2\Theta_2)\Theta_{12}\right] - \frac{1}{2}\frac{z - z_s}{z_s}\frac{1}{T}\chi_1\chi_2\left[2(\chi_1\Theta_1 + \chi_2\Theta_2) + (\chi_1 - \chi_2)\left\{(\Theta_1 - \Theta_2) + \frac{z-2}{z_s}(\chi_1 - \chi_2)\Theta_{12}\right\}\right]\Theta_{12} \tag{41b}$$

Here, from eq 38

$$z - z_s = 2\frac{[1 - (1/x_1)]N_1 + [1 - (1/x_2)]N_2}{N_1 + N_2} > 0 \tag{42}$$

From these equations we can see that the gathering effect of polymer segments in the coating as well as the size effect of the solvent molecules will tend to compel the mixed solvent to be a better solvent in almost all cases of mutually endothermic solutions.

Discussion

When we began this analysis, we expected that due to the gathering of the better solvent to the polymer region, the effective solvent power of the mixed solvent would be greater than the simple average of those of two solvents: the effective Θ value would be smaller than $\chi_1\Theta_1 + \chi_2\Theta_2$. Let us contrast the Shultz–Flory theory and that developed in this paper in this respect. To improve the basis for comparison we have redeveloped these authors' model into our formulation. If we take $\Delta\epsilon_{12}$ equal to zero we again obtain eq 29. This equation suggests that due to the gathering effect of the better solvent to the polymer region, the effective solvent power of the mixed solvent is biased toward being *poorer* than the simple average. This is a rather strange thing. Both the Shultz–Flory and our own models predict this puzzling result.

Let us now turn to the case where $\Delta\epsilon_{12}$ is not equal to zero. Again taking $\phi_p \ll 1$, we obtain for the Shultz–Flory model without considering molecular size effects in the solvent that

$$\Theta = (\chi_1\Theta_1 + \chi_2\Theta_2) + \frac{1}{4}\chi_1\chi_2\frac{1}{T}\frac{[(\Theta_1 - \Theta_2) + (\chi_1 - \chi_2)\Theta_{12}]^2}{1 - (\Theta_{12}/T)\chi_1\chi_2} \tag{43}$$

where Θ_{12} is $2z\Delta\epsilon_{12}/k$ and is the characteristic temperature for the mixture of two solvents, and χ_1 and χ_2 are mole fractions of the two solvents within the polymer coil. In eq 43, $\chi_1\chi_2$ is always smaller than $^1/_4$; therefore, if $\Theta_{12}/T < 4$, the last term is always positive and the above-mentioned argument will be applicable even in this case. A simple lattice theory of mixtures[21] shows that if Θ_{12}/T is larger than 4, two substances are not always miscible and phase separation will occur. As we use two miscible solvents as a mixing solvent, Θ_{12}/T is smaller than 4. Again, we find the Shultz–Flory model to predict that the Θ temperature of the solvent mixture is more than the simple average of the individual solvents. This is not the case in our coating–sea model, as may be seen from eq 35. We can attribute this unexpected result for Θ in the Shultz–Flory model to an entropy effect. Actually, the volume of the polymer region is rather strongly affected by the change of conformational expansion of the polymer molecule, and the number of solvent molecules trapped in this volume is approximately proportional to this volume, though the change of interaction energy between polymer segments and solvent molecules is probably small. This means a greater expansion of the polymer molecule causes a greater trapping of solvent molecules and a greater decrease of entropy with a slight decrease of the enthalpy. The enthalpy decrease accordingly increases the free energy of mixing and has a tendency to shrink the polymer molecule. This increases Θ and decreases solvent ability. The apparent failure of the Shultz–Flory model is due to the overpowering influence of the entropy factor.

This situation is contrary to the case of a polyelectrolyte molecule in an electrolyte solution. In such a system, the strong gathering of the counterions into the polymer region occurs because of the Coulombic attraction between them, and this effect always results in greater expansion of the polyelectrolyte molecule. This tendency is partly due to the neutralization of the repulsive force between ionic groups of the polymer molecule, but it has been pointed out that the entropy effect plays an important role.[4] That is, owing to the electroneutral condition, the number of gathering counterions is nearly constant and independent of the degree of expansion of the polymer molecule; we can then consider the boundary of the polymer molecule as a semipermeable membrane, and the *osomotic* pressure of the counterions gives rise to the expansion of the polymer region. In our case, however, the number of gathered solvent molecules is not kept constant, and the entropy effect acts in the opposite direction.

On the other hand, in the coating–sea model, the volume of the coating available to the solvent molecules is not as strongly affected by the degree of expansion of the polymer molecule, and the enthalpy effect exceeds the opposite entropy effect and tends to increase the expansion of the molecule. Furthermore, even for cases where Θ_1 and Θ_2 are positive, that is, two solvents which are both poor for the polymer, if these solvents also have a poor compatibility with each other and Θ_{12} is a large (but $\Theta_{12}/T < 4$) positive value, the apparent value may become negative, and the mixed solvent behaves as a good solvent. In such a case, the molecules of the better (but still poor) solvent have a tendency to gather around the polymer molecule, cutting off the less compatible solvent 1–solvent 2 pairs, and this resembles the gathering effect of a good solvent.

Generally speaking, the Shultz–Flory model emphasized the effect of a mean potential in the polymer region, although this is not considered explicitly in the theory. On the other hand, the coating–sea model is based completely on the short-range force acting between nearest-neighbor lattice sites. In an actual system, there may be both of these effects, the results of these effects may cancel out, and the simple average of the solvent power of individual solvents may indeed give a good approximation of the solvent power of a mixed solvent.

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Photochemistry of Ketone Polymers. V. Photochemistry of the Linear 2-Alkanones in Solution

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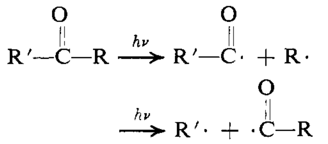
ABSTRACT: Studies have been made of the liquid phase photolysis (at 313 nm) of the linear 2-alkanones ranging from C_6 (2-hexanone) to C_{19} (2-nonadecanone) to determine the effect of chain length on the quantum yields of photolysis products. The major photolytic products are those expected from the Norrish types I and II primary reactions, but for all ketones studied the yields of type I products were less than 10% of the type II products at all temperatures up to 120°. The type II quantum yields are independent of both temperature and solvent viscosity, but the type I yields increase with temperature and decrease with solvent viscosity below 68°. The type I yields decrease with increasing chain length, but type II are only slightly dependent on chain length. Quenching studies indicate that the partition of chemical reaction (type II) between singlet and triplet is independent of chain length. These results confirm that there is a chain-length dependence of total photochemical product yields for linear alkanones in solution.

The photochemistry of aliphatic ketones has been the object of extensive study over the years, and considerable progress has been made in the elucidation of the various photophysical and photochemical pathways by which these compounds dissipate their excitation energy.[1]

The three main photochemical reactions of aliphatic ketones which possess a hydrogen on the carbon γ to the carbonyl are as follows.

(1) The Norrish type I reaction results in the formation of two free radicals through cleavage of the bond between the carbonyl and the α carbon (eq 1); at elevated temperatures the acyl radical can decarbonylate with the forma-



$$\begin{aligned} R'-\overset{\overset{O}{\|}}{C}-R &\xrightarrow{h\nu} R'-\overset{\overset{O}{\|}}{C}\cdot + R\cdot \\ &\xrightarrow{h\nu} R'\cdot + \cdot\overset{\overset{O}{\|}}{C}-R \end{aligned} \qquad (1)$$

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(1) See, for example, J. G. Calvert and J. N. Pitts, Jr., "Photochemistry," Wiley, New York, N. Y., 1966; N. J. Turro, "Molecular Photochemistry," W. A. Benjamin, New York, N. Y., 1965.