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A THEORY OF VISCOSITY OF DILUTE AND MODERATELY CONCENTRATED POLYMER SOLUTIONS

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Abstract—A model theory of viscosity η for moderately concentrated polymer solutions is based on the assumption of a "local viscosity" effect and intermolecular hydrodynamic and thermodynamic interactions. It is shown that η is given by

$$\eta = \eta_0\{1 + \gamma c[\eta]\}^{1/\gamma}\cdot\exp\left\{\frac{\mathrm{H}_0}{\mathrm{RT}}\frac{a\phi}{1 - a\phi}\right\}$$

where γ is 0–0.4 and depends on the quality of the solvent, a varies between 0,4 and 0.8 and depends on the fraction of the "free volume" of the systems, H_0 is the activation energy of the solvent and ϕ is the polymer volume concentration. The dependence of η and "activation energy" of ϕ and T for various molecular weights and qualities of solvents is described quantitatively. Anomalous dependences of $[\eta]$ and of η on M for low polymer are obtained. An expression for η is proposed:

$$\left(\frac{\eta}{\eta_0}\right)^{1-2K} = \{1 + (1 - 2K)c[\eta]\}\,F(\phi)$$

where K is the Huggins–Martin coefficient and $F(\phi) = 1$ for most solutions when T is $> T_g$. For poor solvents the H vs c curve (where H is the activation energy of η of solution) has a minimum value at moderate concentrations. For good solvents, H depends slightly on the molecular weight according to an empirical equation:

$$\mathrm{H} = \mathrm{H}_0 + \frac{660}{\alpha^3}\ln\frac{\eta}{\eta_0}.$$

Expressions are given from the viscosities of solutions of miscible and also solutions of immiscible polymers.

The dependence of the viscosity η of polymer solutions on concentration c, temperature T and molecular weight M is of importance for the commercial production and processing of polymers. This paper presents a theory of polymer solution viscosity. The theory enables a quantitative description of all experimental data available for dilute and moderately concentrated solutions and for solutions of mixtures of polymers. In part 1 of the paper, a short account of the theoretical calculations is given; in part 2 it is shown that the theoretical results satisfactorily fit experimental data; in part 3 an example of a calculation of the viscosity of solution of polymer is given; in part 4 theory of viscosity of mixtures of compatible polymers is given; finally in part 5, the approximate theory of viscosity of dilute solutions of a mixture of two incompatible polymers is given.

1. BASIC CONCEPTS

The theory is based on three assumptions [1–3], the first being that the viscosity of macromolecules depends on the mobility of their segments and that of the solvent molecules. This micro-Brownian motion is described by introducing a "local viscosity" parameter η_{loc}. The second assumption is that the rotation of a long chain macromolecule is resisted by other macromolecules. This resistance is similar to that experienced by a macroscopic spherical particle moving in a suspension of similar particles. It can be described in terms of an "effective viscosity" of the medium. It can be shown that the "effective viscosity" is roughly equal to the macroscopic viscosity of the solution. The third assumption is that the contribution of each macromolecule to the viscosity of the solution is dependent on its hydrodynamic volume. In dilute solutions the hydrodynamic volume of a flexible chain macromolecule is equal to its geometric volume V and is proportional to the intrinsic viscosity $[\eta]$. When the concentration is increased, the geometric volume V decreases as a result of intermolecular thermodynamic interactions.

By further calculation [3] the viscosity may be represented thus

$$\eta = \eta_0\left(\frac{\eta_{\mathrm{loc}}}{\eta}\right)(1 + \gamma c[\eta])^{1/\gamma} \tag{1}$$

where γ is a parameter representing intermolecular thermodynamic interaction and η_0 is the solvent vis-

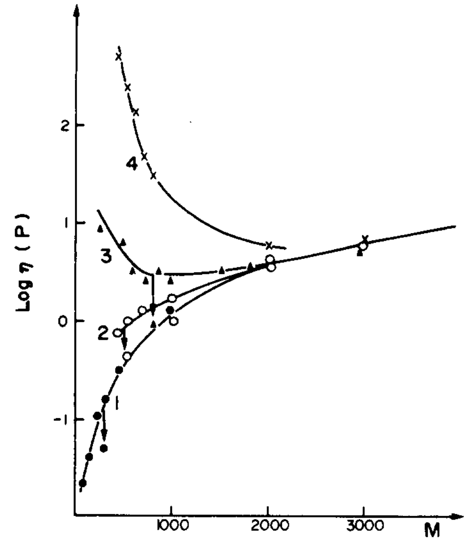

Fig. 1. Viscosity vs M for polyoxypropylene polyols. 1–4 mono-, di-, tri- and pentaols. Arrows denote changes in viscosity after acetylation.

cosity. The value of η_{loc}/η_0 describes the change in the "local mobility" in the polymer solution with changing concentration. The third term $(1 + \gamma c[\eta])^{1/\gamma}$ accounts for the intermolecular hydrodynamic and thermodynamic interaction. A detailed derivation of Eqn (1) has been given [3].

(a) The dependence of the "local viscosity" on concentration and T can be obtained by using the theory of "free volume" [4–6]. After rearrangement, it can be written:

$$\eta_{loc} = \eta \exp\left\{\frac{H_0}{RT}\frac{a\phi}{1 - a\phi}\right\} \tag{2}$$

where ϕ is the volume concentration of the polymer, H_0 is the activation energy for the solvent flow and the value of a is given by

$$a = 1 - \frac{\alpha_2}{\alpha_1}\left(1 - \frac{T^*}{T}\right). \tag{3}$$

In Eqn 3 α_1 and α_2 are volume expansion coefficients of solvent and polymer, respectively. T^* is the characteristic temperature of the polymer: $T^* = T_g - 50$. The value of a is usually between 0.4 and 0.8. As ϕ tends to unity, $\log \eta_{loc}$ is proportional to $(T - T^*)^{-1}$ in accordance with well known empirical relationships [7]. More precise relationships accounting for the difference between the kinetic units of the polymer chains and of the solvent molecules have been given [6].

(b) At low concentrations, the value of $\tilde{\eta} = \eta/\eta_{loc}$ can written as

$$\tilde{\eta} = 1 + c[\eta] + \frac{1-\gamma}{2}c^2[\eta]^2 + \frac{1-2\gamma}{2}\cdot\frac{1-3\gamma}{2}c^3[\eta]^3 + \dots \tag{3}$$

Hence, the Huggins coefficient K for high molecular polymer will be

$$K = \frac{1-\gamma}{2}. \tag{4}$$

For a θ-solvent, γ is zero ($K = 0.5$), and for "good" solvents, γ is virtually independent of the molecular weight and quality of the solvent and is 0.3–0.4. Therefore for calculation of the viscosity of a solution, it is possible to use an approximate equation for

$$\begin{aligned} \gamma &= 0.4(\alpha^3 - 1) \quad &\text{when} \quad \alpha^3 \leqslant 2 \\ \gamma &= 0.4 \quad &\text{when} \quad \alpha^3 \geqslant 2 \end{aligned} \tag{5}$$

where α is the expansion factor for macromolecules.

2. THE COMPARISON OF THEORETICAL RESULTS WITH EXPERIMENTAL DATA

(a) A considerable change in η_{loc} with M is observed for low molecular polymers containing one or several specific groups e.g. OH [8,9]. Figure 1 shows the relationship between η and M for molten polyoxypropylene polyols with the number of hydroxyl groups, v, ranging from 0 to 5. Similar effects were observed for solutions of these substances in tetrachloromethane. Measurement [10] of "local rearrangement" rates (measurement of the spin-lattice relaxation time) showed that these effects are closely related to the influence of the molar fraction of OH groups on the "local mobility". The given theory explains this effect. Indeed, the viscosity of the melt (as a solution) of these polymers is given by the equation

$$\ln\frac{\eta}{\eta_b} = A + \frac{B}{N} + \frac{v}{N}(\rho d - b) \tag{6}$$

where η_b is the viscosity of polymer without any specific groups, ρ is a probability of formation of a hydrogen bond, A, B, d, b are characteristic constants for this polymer, N is the number of kinetic elements in the chain. The relationship (6) between η and N fits the experimental data.

If there is interaction between the last group and the basic chain of macromolecules, the dimension of the kinetic element will be changed. Then the viscosity of such a polymer is given by

$$\ln\frac{\eta}{\eta_b} = A + \frac{B}{N} + \frac{v}{N}(\rho d - b) - \frac{m}{N^2}(D + vg) \tag{7}$$

where m is the value of the change of kinetic elements of the chain, D and g are constants for this polymer.

The change in "local mobility" with increasing polymer concentration explains the anomalous dependence [11,12] of the intrinsic viscosity of oligomers on M.

(b) Equations (1), (2) and (5) quantitatively explain the fact that the use of the normalization of the parameters $c[\eta]$ [13,14] and $Kc[\eta]$ [15] will reduce all experimental results for each polymer solution to one master curve. Equations (1) and (4) will give an expression for $\eta(c)$:

$$\left(\frac{\eta}{\eta_0}\right)^{1-2K} = \{1 + (1 - 2K)c[\eta]\}F(\phi) \tag{8}$$

where $F(\phi)$ is based on "local viscosity". This relation is invariable for different polymers at moderate concentrations. Figure 2 shows data for solutions of polyisobutylene [16] ($K = 0.45$–0.40), poly(dimethyl-

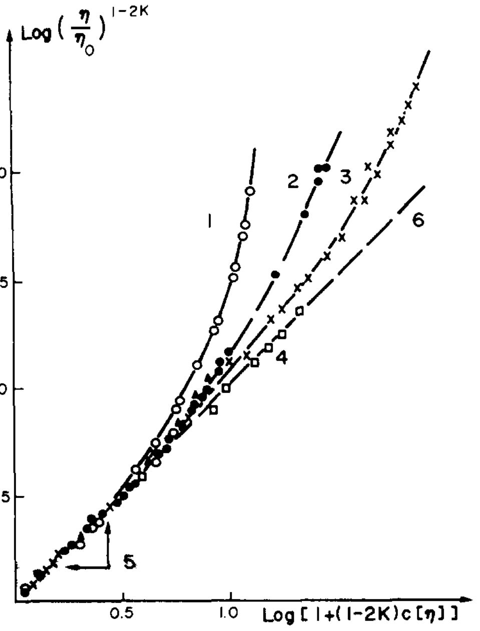

Fig. 2. Plot of $(\eta/\eta_0)^{1-2K}$ vs $(1-2k)c\,[\eta]$ for solutions of polystyrene (1); polydimethyl siloxane (2); polyisobutylene (3); cellulose tributyrate (4); polyvinyl alcohol (5); (6) is the theoretical dependence.

siloxane) [17] ($K = 0.4$–0.35), polystyrene [13] ($K = 0.34$) cellulose tributyrate [18] ($K = 0.4$) and polyvinyl alcohol [19] ($K = 0.46$). It is possible to obtain a master curve for η vs c for these polymers up to $\eta/\eta_0 \simeq 10^4$–10^5. At higher concentrations, $F(\phi)$ exceeds unity and the experimental curves will differ from the theoretical curve (Fig. 2). Depending on the value of $(T - T^*)$ these differences may be observed for polystyrene ($\phi \simeq 0.2$; $[\eta] = 0.8$ dl/g) much earlier than for poly(dimethylsiloxane) ($\phi \simeq 0.4$; $[\eta] = 1$ dl/g) and for polyisobutylene ($\phi \simeq 0.4$; $[\eta] = 4$ dl/g).

(c) Temperature dependence of η/η_{loc}. Equations (1), (2) and (5) also describe the relationship between $\text{H} = R\text{d}\ln\eta/\text{d}(1/T)$ (apparent activation energy) and the molecular parameters. We shall consider the value of $\Delta\text{H} = \text{H} - \text{H}_{\text{loc}}$ where H_{loc} is the apparent "local viscosity" activation energy: $\text{H}_{\text{loc}} = R\text{d}\ln\eta_{\text{loc}}/\text{d}(1/\ )$. The value of Δ H is given by

$$\Delta\text{H} = R\,\frac{\text{d}\ln(1 + \gamma c[\eta])^{1/\gamma}}{\text{d}\left(\dfrac{1}{T}\right)}. \tag{9}$$

At low concentrations and poor solvents, the dependence of ΔH on concentration is anomalous [20]. It satisfactorily fits experimental curves for polystyrene in decalin [21].

At moderate concentrations ($c[\eta] > 1$, $\phi < 0.2$) the equation for ΔH may be simplified to

$$\Delta\text{H} = K' - R\cdot\ln\tilde{\eta}\cdot\frac{\text{d}\ln\gamma}{\text{d}\left(\dfrac{1}{T}\right)} \tag{10}$$

where K' is small and independent of concentration. The value of $-\text{d}\ln\gamma/\text{d}(1/\text{T})$ decreases with increasing α, i.e. it decreases both when the quality of the solvent is improved and when the molecular weight increases. On the other hand, the value of $\ln\eta$ increases when these two parameters vary as indicated. The net results of these two opposing trends is that the dependence of ΔH on molecular weight and on solvent quality is insignificant. Figure 3 shows the dependence of $\text{dH}/\text{d}\ln\eta$ on α^3 obtained from experimental data [16,19,22] and theoretical calculations. The data presented in Fig. 3 show that the theoretical and experimental data agree well although the theoretical curve is slightly lower. Experimental data can be described by an empirical equation:

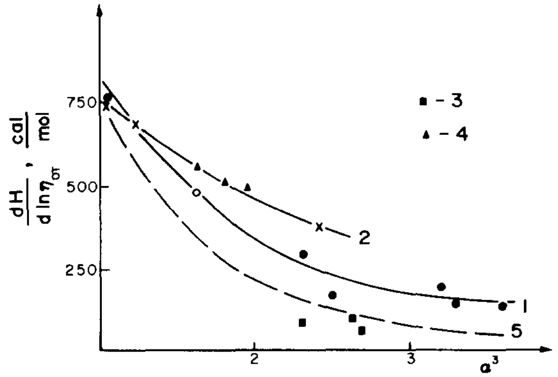

Fig. 3. Plot of dH/d log η vs α^3 for solutions of polyisobutylene (3); polyacrylamide (2); polyvinylalcohol (4) in water; (5) is the theoretical dependence.

$$\Delta\text{H} = \frac{660}{\alpha^3}\ln\frac{\eta}{\eta_0}\left(\frac{\text{cal}}{\text{mol}}\right). \tag{11}$$

Hence, ΔH may be taken as 2–6 kcal/mol. This component of ΔH depends on intermolecular hydrodynamic and thermodynamic interactions. An increase in H beyond the above range will be associated with a change in "local viscosity".

3. CALCULATIONS OF THE DEPENDENCE OF VISCOSITY AND TEMPERATURE COEFFICIENT OF VISCOSITY ON CONCENTRATION

In Section 2 we showed that the theoretical and experimental results agree. Now we give a calculated relationship between $\eta(\phi)$ and $\text{H}(\phi)$ for some arbitrarily chosen polymer samples. The calculations indicate that the basic parameters may have an effect upon η and H (Fig. 4).

For each case, we also take a to be 0.5 ($T = 2T_g - 100$) and 0.8 ($T = 1.4T_g - 70$). At $T_g = 0°$, in the first case $T - T_g = 200°$ and in the second case $T - T_g = 40°$. The activation energy of viscosity for moderate concentrations was calculated from Eqn (11): H_0 was taken as 2.4 kcal/mol and α was $0.5\,\alpha$. Figure 4 relates log η and H to ϕ, taking into account "local viscosity" variation for low molecular ($[\eta] = 10\,\text{cm}^3/\text{g}$) and high molecular ($[\eta] = 200\,\text{cm}^3/\text{g}$) polymers.

4. THE VISCOSITY OF A SOLUTION OF A MIXTURE OF COMPATIBLE POLYMERS

Using the approximations given above, we can

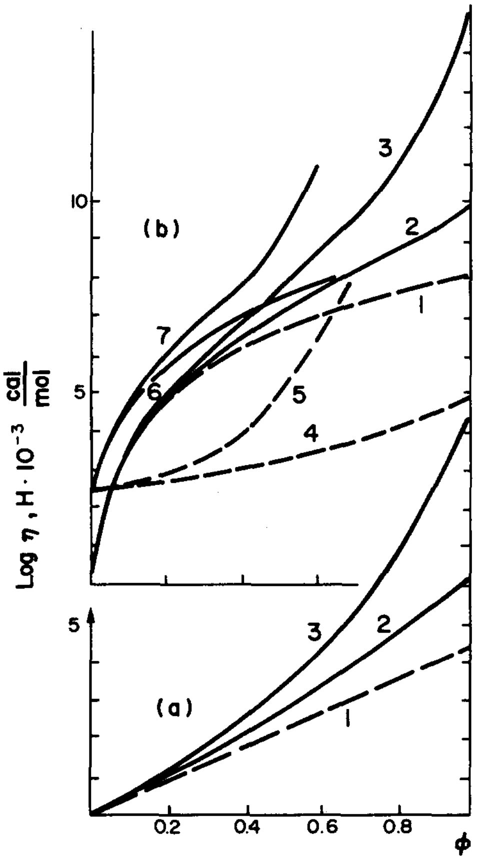

Fig. 4. Plot of l g η and H vs ϕ (a) $[\eta] = 10\,\mathrm{cm^3/g}$, $\gamma = 0$, $a = 0$ (1), $a = 0.5$ (2), $a = 0.8$ (3); (b) $[\eta] = 200\,\mathrm{cm^3/g}$, $\gamma = 0.2$, $a = 0$ (1), $a = 0.5$ (2), $a = 0.8$ (3); 4,5-$H_{loc}(\phi)$ at $a = 0.5$ and $a = 0.8$; 6.7 − $H(\phi)$ at $a = 0.5$ and $a = 0.8$.

obtain for the viscosity η_m of solutions of a mixture of compatible polymers

$$\eta_m = \eta_0 \Pi(1 + \langle\gamma_i\rangle[\eta]_i c)^{x_i/\langle\gamma_i\rangle} \tag{12}$$

where $\langle\gamma_i\rangle$ is calculated by

$$\langle\gamma_i\rangle = \frac{1}{[\eta]_i}\sum_j \gamma_{ij}x_j[\eta]_j \tag{13}$$

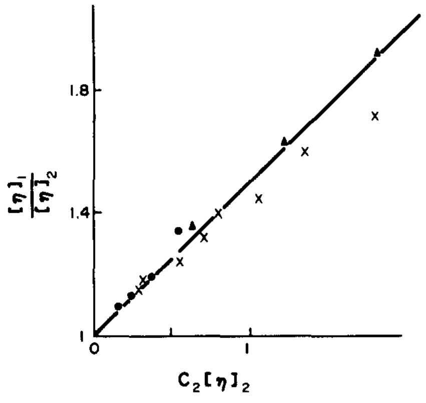

Fig. 5. $[\eta]_1/[\eta]_{12}$ vs c_2 $[\eta]_2$ for solutions of mixtures of polyvinylpyrolidone and polymethylmethacrylate.

and x_i and $[\eta]_i$ are the fraction and intrinsic viscosity of the i-th component, γ_{ij} is an interaction parameter of i-th and j-th components.

If one assumes that $2\gamma_{ij} = \gamma_{ii} + \gamma_{jj}$ for the miscible polymers, then the Huggins constant K_m is given by

$$K_m = \frac{1}{[\eta]^2}\Sigma x_i x_j [\eta]_i [\eta]_j (K_i + K_j). \tag{14}$$

This relation gives a better fit to experimental data than the relation given previously [23].

The intrinsic viscosity of the first polymer in a solvent which is the solution of the second polymer is given by the equation

$$[\eta]_{12} = \frac{[\eta]_1}{1 + \gamma_{12}c_2[\eta]_2} \tag{15}$$

Figure 5 shows data for a mixture of solutions of polyvinylpyrolidone and polymethylmethacrylate [24]. The theoretical result fits the experimental data.

Equations (12) and (13) make it possible to obtain the relationship between the viscosity of a solution of a mixture of polymers and the viscosities (η_1, η_2) of primary solutions $(\gamma_{11} \simeq \gamma_{22} \simeq \gamma_{12})$:

$$\eta_m \simeq \eta_1^{x_1}\cdot\eta_2^{x_2}\cdot\left(\frac{\eta_1}{\eta_2}\right)^{x_1x_2([\eta]_1 - [\eta]_2)/[\eta]} \tag{16}$$

Equation (16) is important for practical use.

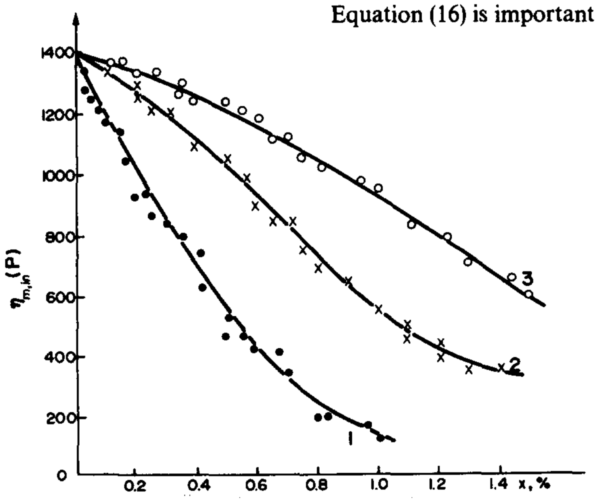

Fig. 6. $\eta_{m,in}$ vs χ_1 for solutions ($c = 0.13\,\mathrm{g^2/cm^3}$) of mixtures of polystyrene [10^4 M = 136 (1), 31 (2), 5 (3)] and polysioprene.

5. THE VISCOSITIES OF SOLUTIONS OF A MIXTURE OF INCOMPATIBLE POLYMERS

For very low concentrations, the solution of a mixture of incompatible polymers may be considered as a solution of a mixture of compatible polymers. If the concentration increases, phase separation occurs and part of the polymer will generate a new phase. This new phase has a concentration c_3 and is in the liquid as a colloid emulsion. Then the system can be considered as a liquid formed by a solution of a mixture of polymers with concentrations x_1 and $x_2 - x_3$ and by many droplets of emulsion with concentration x_3. The presence of these droplets does not significantly change the viscosity of the liquid. Therefore as a first approximation, the viscosity $\eta_{m,in}$ of a solution of a mixture of incompatible polymers may be given by

$$\frac{\eta_{m,in}}{\eta_2} \cong \left(\frac{\eta_1}{\eta_2}\right)^{x_i\{([\eta]_1)/[\eta]\}} \cdot \left(\frac{\eta_2}{\eta_0}\right)^{-x_3\{([\eta]_2)/[\eta]\}} \tag{17}$$

and the value $\eta_{m,in}$ will decrease with increase of x_3. the fraction of new phase. Using this equation, a fraction x_3 may be determined. Figure 6 shows data for solutions of mixtures of polystyrene ($10^4\,M = 5$; 31; 136) and polyisopropene ($M = 10^6$) (these data were obtained by N. N. Sigaeva). The value of x_3 is given by

$$X_3 \cong X_1 (c - c_0) \cdot 1.1 \cdot 10^{-3} M^{0.51} \tag{18}$$

where c_0 is a critical concentration below which the solution of the mixture is uniphase. This relationship is similar to one obtained by turbidimetry [25].

CONCLUSION

A model theory of viscosity for moderately concentrated polymer solutions is presented, assuming a "local viscosity" effect and intermolecular hydrodynamic and thermodynamic interactions. The theoretical results are shown to describe adequately the experimental data. The theory is based on clear physical assumptions for the low concentration range; for high concentrations, it becomes semi-empirical. However it permits a description of a variety of relationships for the viscosity of concentrated polymer solutions and viscosity of solutions of mixtures of compatible and incompatible polymers.

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