

A Generalized Correlation for the Viscosity of Dextrans in Aqueous Solutions as a Function of Temperature, Concentration, and Molecular Weight at Low Shear Rates

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Synopsis

An expression relating the viscosity of dextran solutions to polymer concentration (c), molecular weight (M), and temperature (T) has been derived from experimental data in the following ranges: $5 < c < 25\%$ (wt/wt), $298.2 < T < 363.2$ K, and $71,500 < M < 531,000$ g/mol. The experimental work was based on capillary viscosimeters. Thermodynamic data (entropy and energy of activation for the viscous flow of a Newtonian fluid) are also presented as a function of polymer concentration for the three molecular weights studied. This thermodynamic analysis suggests that dextrans in aqueous solutions behave as flexible polymers. Application of our expression to existing viscosity data for ethylene/vinylacetate copolymers in paraffin has resulted in improved goodness of fit with respect to established correlations.

INTRODUCTION

The objective of this article is to develop a correlation, at low shear rates, between viscosity and three key variables: temperature, concentration, and degree of polymerization. The system dextran/water was chosen as the basis for the experimental study from which the correlation is to be derived.

There have been theoretical approaches to develop viscosity-concentration relationships. In particular, Kelley and Bueche,¹ followed Bueche's approach,² which considers a liquid as a structure having moving holes. Their equation, which holds only for polymeric solutions with marked chain entanglements, is the following:

$$\ell n \eta = \beta^* + 4 \cdot \ell n c_2 + (f_1 \cdot \phi_1 + f_2 \cdot \phi_2)^{-1} \quad (1)$$

where:

- η : viscosity of the solution, Pa · s
- β^* : constant
- c : concentration, %wt of solution
- f : free volume fraction
- ϕ : volume fraction
- 1, 2 refer to solvent and polymer, respectively

with:

$$f_1 = f_{1G} + \alpha_{1L} \cdot (T - T_{1G}) \quad (2)$$

$$f_2 = f_{2G} + (\alpha_{2L} - \alpha_{2G}) \cdot (T - T_{2G}) \quad (3)$$

where:

- f_G : free volume fraction at temperature T_G
- T_G : glass transition temperature, K
- T : temperature, K
- α : coefficient of thermal expansion, K^{-1}
- L, G refer to liquid and glassy states, respectively

Francesconi et al.³ have slightly modified the original Kelley and Bueche equation in order to obtain a general expression for both flexible and stiff chain polymers:

$$\ell n \eta = \beta' + \gamma' \cdot \ell n M_2 + \delta' \cdot \ell n c_2 + (f_1 \cdot \phi_1 + f_2 \cdot \phi_2)^{-1} \quad (4)$$

where β' , γ' , and δ' are constants and M is the molecular weight (g/mol).

An equation which was first derived for describing the Newtonian viscosity of suspensions of rigid spheres and also applicable to the description of the Newtonian viscosity of polymers solutions is⁴:

$$\frac{\eta_{sp}}{c \cdot [\eta]} = \frac{1}{(1 - c/c_m)} + \frac{(c_m \cdot [\eta]/4) \cdot (c/c_m)}{(1 - c/c_m)^2} \quad (5)$$

where:

- c_m : polymer concentration parameter, which corresponds to ϕ_m (maximum volume fraction at which the polymers can aggregate)
- η_{sp} : specific viscosity, $(\eta - \eta_s)/\eta_s$
- η_s : viscosity of solvent, Pa · s
- $[\eta]$: intrinsic viscosity

For concentrated polymer solutions, it has been empirically shown that the dependence of η upon T , c , and M can be adequately described by a power-law function^{5,6}:

$$\eta = K'' \cdot c^{\alpha''} \cdot M^{\beta''} \cdot \exp\left(\frac{q}{R \cdot T}\right) \quad \text{for } c > c_o \quad (6)$$

where K'' , α'' , β'' , and q are constants for a given polymer-solvent system, c_o is a critical concentration, and R is the universal gas constant.

The parameter α'' increases gradually with increasing c and approaches a characteristic value > 5 when the concentration is at and beyond a critical value c_o , which is analogous to the critical molecular weight and which can be determined by the intersection of the two slopes⁷ in a representation of $\ell n(\eta_{sp}/([\eta] \cdot c - 1))$ versus $\ell n(\eta_{sp})$.

EXPERIMENTAL

The dextrans were obtained from Sigma Co. (St. Louis, MO) (produced by *Leuconostoc Mesenteroides*, Strain no. B-512). Structural studies by Sloan et al.⁸ have shown the dextran produced by B-512 to contain 95% of (1 → 6)-linked units of α -D-anhydroglucopyranose, and 5% of (1 → 3)-linked units. The molecular weight of the dextrans used ranged from 71500 to 531,000 g/mol.

Dilute and concentrated solutions were prepared by shaking a weighed amount of the polymer together with the solvent in volumetric flasks.

Capillary viscosimeters of the Canon-Fenske type were employed in the viscosity measurements. In our experimental conditions, no corrections were necessary for loss of kinetic energy. Viscosimeters were submerged in a stirred thermostatic bath ($\pm 0.02^\circ\text{C}$).

A cone-and-plate rheometer in steady-state fluid mode (Rheometric-System Four) was used only in order to establish the Newtonian behavior of dextran solutions, within the shear rates desired in the present study as will be shown later.

A metallic pycnometer from Fisher Scientific Co., was used to evaluate solution densities. The nominal volume, $V = 11.79 \pm 0.02 \text{ cm}^3$, was determined with glycerol which has a density equal to 1.25 g/cm^3 . The density of solutions depends only on polymer concentration:

$$d = a_0 + a_1 \cdot c + a_2 \cdot c^2 + a_3 \cdot c^3 \quad (7)$$

where d is the density of the solution, kg/m^3 .

The empirically determined constants are: $a_0 = 990$, $a_1 = 1.83$, $a_2 = 0.177$, $a_3 = -3.36 \times 10^{-3}$, with $r = 0.998$ (r : regression coefficient).

This equation is valid for aqueous solutions of glucose and dextrans up to a molecular weight of 531,000 g/mol.

RESULTS AND DISCUSSION

The dextran solutions behave as Newtonian fluids. As observed in Figure 1, the experimental viscosity values show no shear rate dependence for the highest molecular weight at different concentrations. The shear rate scanned with the rheometer covers adequately the range of Canon-Fenske viscosimeters used. This Newtonian behavior can be explained by considering the high compactness of the dextran molecular chains, due to their extensive molecular branching. Wales et al.⁹ found that the exponent of the Mark-Houwink equation should be $a' = 0.675$ for hypothetical linear dextrans. By means of intrinsic viscosity measurements, we obtained $a' = 0.47$. This suggests that the dextrans used are branched.

The measured viscosities are shown in Table I. From these data, the temperature dependence of the viscosity can be evaluated by means of the Guzman-Andrade equation. The parameters A and E can be obtained (our investigation covered three molecular weights at concentrations from 1% to 30%, in the temperature range comprised between 298.2 and 363.2 K) by plotting $\ln \eta$ versus $1/T$. The regression coefficients have been found to be better than 0.999.

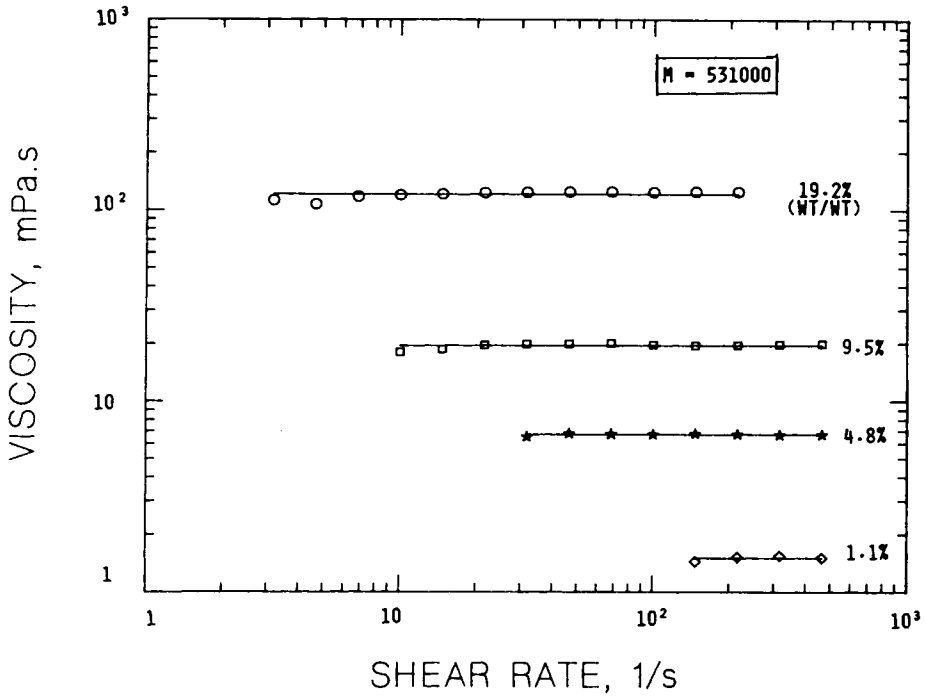


Fig. 1. Profiles of viscosities as a function of shear rate at different concentrations for the dextran having a molecular weight of 531,000.

Figure 2 shows that the pre-exponential factor increases with concentration and reaches a plateau at high concentrations ($c > 25\%$). The same behavior has been observed for the other molecular weights. This behavior can be explained as follows: when the solution has a high solute content, intermolecular attractions and repulsions of solvated macromolecules become competitive, forcing the entropy of activation to reach an asymptotic value. In dilute solutions ($c < 5\%$), solute molecules are less perturbed by the presence of other molecules, the net result being less hindrance of the transport process. This may explain the deviations observed at low solute concentrations with respect to the linear behavior at intermediate concentrations.

From Figure 2 and analogous plots for the two other molecular weights, we have shown that for the dextran solutions at concentrations comprised between 5 and 25% the pre-exponential factor is a linear function of the concentration for each molecular weight:

$$A = \eta_o + \alpha_v \cdot c \quad (8)$$

where:

A: pre-exponential factor of the viscosity, Pa · s (Guzman-Andrade equation)

η_o : pre-exponential factor at infinite dilution, Pa · s

α_v : constant for a given molecular weight, Pa · s · %⁻¹

TABLE I
 Values of the Experimental Viscosity for Aqueous Solutions of Dextrans as a Function
 of Molecular Weight, Temperature, and Concentration

c (%)	M = 71,500			M = 249,000			M = 531,000		
	η (mPa · s)			η (mPa · s)			η (mPa · s)		
	T = 25.0°C	T = 50.0°C	T = 90.0°C	T = 25.0°C	T = 50.0°C	T = 87.7°C	T = 25.0°C	T = 50.0°C	T = 87.2°C
1.0	1.15	0.70	0.36	1.33	0.80	0.43	1.52	0.92	0.49
4.7	2.34	1.35	0.74	2.38	1.38	0.77	3.20	1.83	1.02
9.6	5.56	3.11	1.56	4.26	2.42	1.30	6.18	3.45	1.87
14.0	10.97	5.74	2.79	12.98	6.92	3.47	22.70	11.98	5.98
19.3	25.43	12.56	5.59	31.69	16.20	7.59	56.03	28.29	13.36
23.3	44.29	20.88	8.92	76.70	37.04	16.60	170.89	79.66	35.20
28.4	96.52	41.87	16.62	167.26	74.74	31.88	559.82	238.78	96.51
				448.61	184.81	71.68			

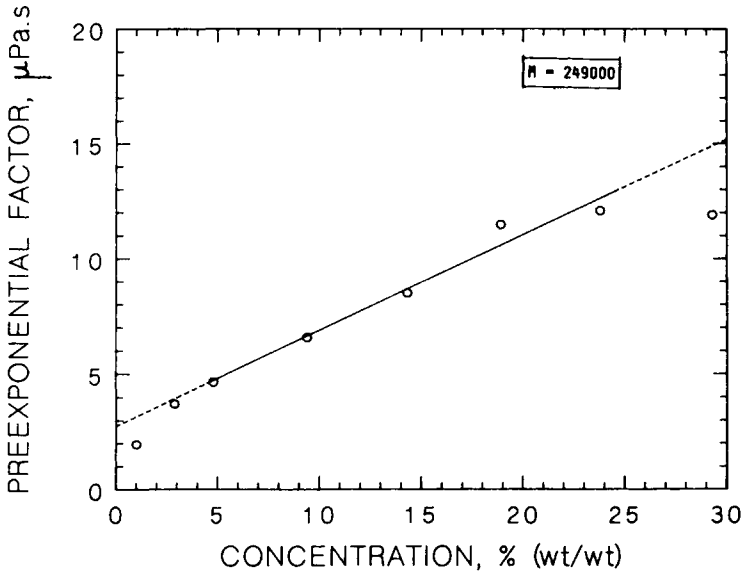


Fig. 2. Profile of the pre-exponential factor as a function of the concentration for the dextran having a molecular weight of 249,000. (The straight line was fitted by linear regression for 5–25% concentration range.)

The parameter η_o could not be correlated with M within the range of molecular weights considered and an average value is taken ($\eta_o = 3.30 \times 10^{-6}$ Pa · s). The parameter α_v , which represents the variation of A with c for a given molecular weight, can be correlated as follows:

$$\alpha_v = \Phi_v + \theta_v \cdot M \quad (9)$$

with:

$$\Phi_v = 3.19 \times 10^{-8} \text{ Pa} \cdot \text{s} \cdot \%^{-1}$$

$$\theta_v = 1.33 \times 10^{-12} \text{ Pa} \cdot \text{s} \cdot \text{mol} \cdot \text{g}^{-1} \cdot \%^{-1}$$

$$r = 0.998$$

With the assumption $(a/\delta) \rightarrow 1$ in Eyring's theory, which means that the molecular jump from cage to hole has the same length as the distance between viscous layers, we can relate the pre-exponential factor to the activation entropy of viscous flow:

$$A = \frac{N_A \cdot h}{V_m} \cdot \exp\left(-\frac{\Delta S}{R}\right) \quad (10)$$

where:

N_A : Avogadro number, 6.023×10^{23} molecule/mol

h : Plank constant, 6.625×10^{-34} J · s

V_m : molar volume of the solution, m^3/mol

ΔS : activation entropy of viscous flow, J/mol · K

By considering Eqs. (8) to (10), the entropy of activation is therefore calculated as follows:

$$\Delta S = -R \cdot \ell n \left(\frac{F(c, M)}{N_A \cdot h} \right) \quad (11)$$

where:

$$F(c, M) = A \cdot V_M = (\eta_o + (\Phi_v + \theta_v \cdot M) \cdot c) \cdot V_m \quad (12)$$

The molar volume for a two-component solution can be calculated as follows:

$$\frac{1}{V_m} = 10^3 \cdot d \cdot \left(\frac{1 - c/100}{M_1} + \frac{c/100}{M_2} \right) \quad (13)$$

According to Moore,¹⁰ the variations of A with M and c are quite different for the two types of polymer chains:

$$\text{Flexible chains: } A = A_o^* + K_a \cdot M^\beta \cdot c \quad (14)$$

$$\text{Stiff chains: } A = A_o^* \cdot \exp(-K_a \cdot M^\beta \cdot c) \quad (15)$$

where:

A_o^* refers to the pure solvent

K_a, β depend on the polymer and the solvent

An interpretation of these differences has been made in terms of the Eyring rate theory.^{11,12} For flexible chain polymers, A increases (i.e., ΔS decreases) with both concentration and molecular weight [Eq. (14)]. However, for stiff chain polymers, ΔS increases with both concentration and molecular weight. In Figure 3 we have plotted the values of ΔS derived from the experimental and calculated data versus polymer concentration. A decrease of ΔS with increase of both c and M is observed. Thus, the dextrans behave as flexible polymers in aqueous solutions. This finding agrees with our own studies on the flexibility index of dextrans in water.¹³

The activation energy of viscous flow is also a linear function of the concentration for each molecular weight:

$$E = E_o + \delta_v \cdot c \quad (16)$$

where:

E : activation energy of viscous flow, J/mol (Guzman-Andrade equation)

E_o : activation energy of viscous flow at infinite dilution, J/mol

δ_v : constant for a given M , J · mol⁻¹ · %⁻¹

E_o cannot be correlated with M and we assume it to be constant within the molecular weight range considered, by taking an average value ($E_o = 15.0$

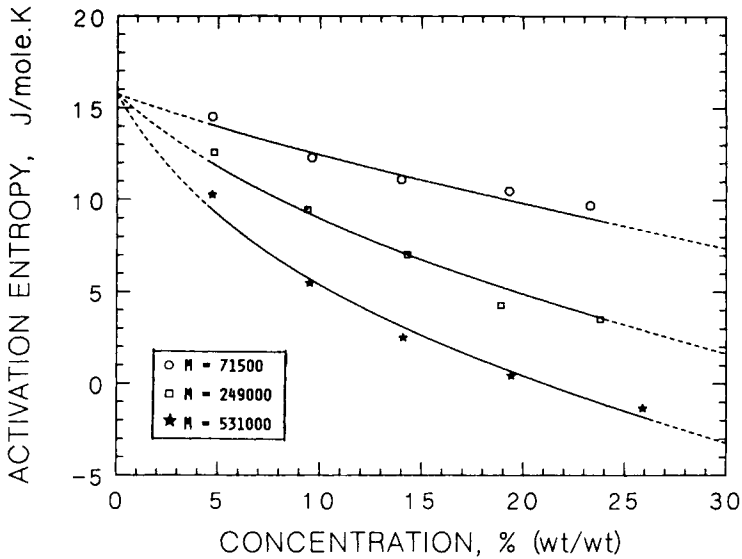


Fig. 3. Variation of the activation entropy of viscous flow with concentration for three different molecular weights.

kJ/mol). The parameter δ_v , which takes into account the variation of E with c for each molecular weight, can be correlated as follows:

$$\delta_v = \epsilon_v \cdot M^{\sigma_v} \quad (17)$$

with:

$$\epsilon_v = 64.8 \text{ J} \cdot \text{mol}^{-0.862} \cdot \%^{-1} \cdot \text{g}^{-0.138}$$

$$\sigma_v = 0.138$$

$$r = 0.993$$

Therefore, the activation energy of viscous flow can be evaluated as follows:

$$E = E_o + \epsilon_v \cdot M^{\sigma_v} \cdot c \quad (18)$$

Figure 4 shows the variation of E with c for three different molecular weights, where a small variation of E with M is noticeable, especially for the highest molecular weights. However, the concentration is the overriding parameter affecting the activation energy. Therefore, the activation barrier increases with concentration.

Katime and Ochoa¹⁴ found that the methyl isobutyl ketone is an athermal solvent for the poly(cyclohexyl methacrylate) because E did not vary with either c and M . This is only true in the concentration range they worked ($c < 1\%$). For a wide concentration range (specially for $c > c_o$) a variation of E with both c and M might be expected, by taking into consideration the increasing interactions between solvated macromolecules.

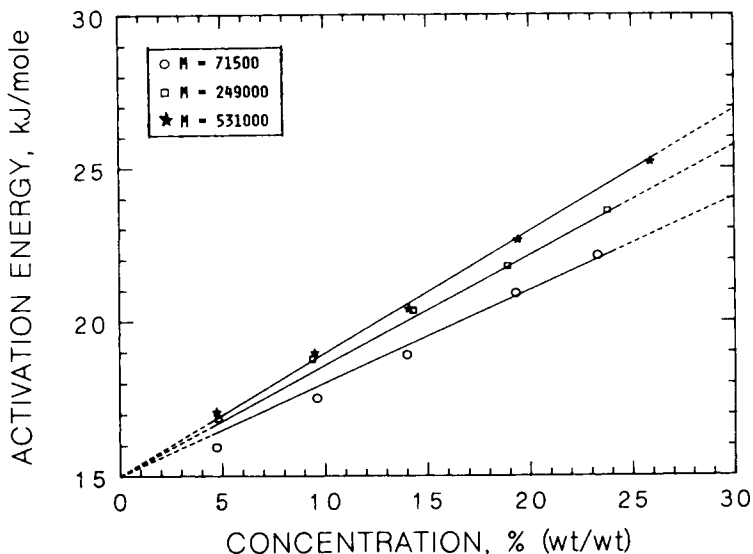


Fig. 4. Variation of the activation energy of viscous flow for three different molecular weights.

The complete expression relating η to c , M , and T is as follows:

$$\eta = (\eta_o + (\Phi_v + \theta_v \cdot M) \cdot c) \cdot \exp\left(\frac{E_o + \epsilon_v \cdot M^{\sigma_v} \cdot c}{R \cdot T}\right) \tag{19}$$

Figure 5 illustrates the viscosity curves obtained by the application of the correlation found. Each diagram (at a given average molecular weight of dextran) shows the variation of the viscosity with the concentration at three different temperatures.

The goodness of fit can be estimated by the following error equation:

$$\Delta\eta = \frac{\sum (\ell n\eta_i^{\text{exp}} - \ell n\eta_i^{\text{calc}})^2}{N} \tag{20}$$

where N is the number of experimental points.

When the experimental viscosity data of dextran solutions are compared to the theoretical ones, the variance $\Delta\eta$ takes values comprised between 0.05 and 0.17.

Equation (19) has been applied to the viscosity data of Francesconi et al.³ which is based on solutions of ethylene/vinylacetate copolymers in paraffin. By use of successive linear regression of their data the following parameters of Eq. (19) were obtained for this nonaqueous system:

$$\Phi_v = \theta_v = 0$$

$$\eta_o = 1.2 \times 10^{-3} \text{ Pa} \cdot \text{s}$$

$$E_o = 16.7 \text{ kJ} \cdot \text{mol}^{-1}$$

$$\epsilon_v = 1.67 \times 10^{-3} \text{ J} \cdot \text{mol}^{0.07} \cdot \text{\%}^{-1} \cdot \text{g}^{-1.07}$$

$$\sigma_v = 1.07$$

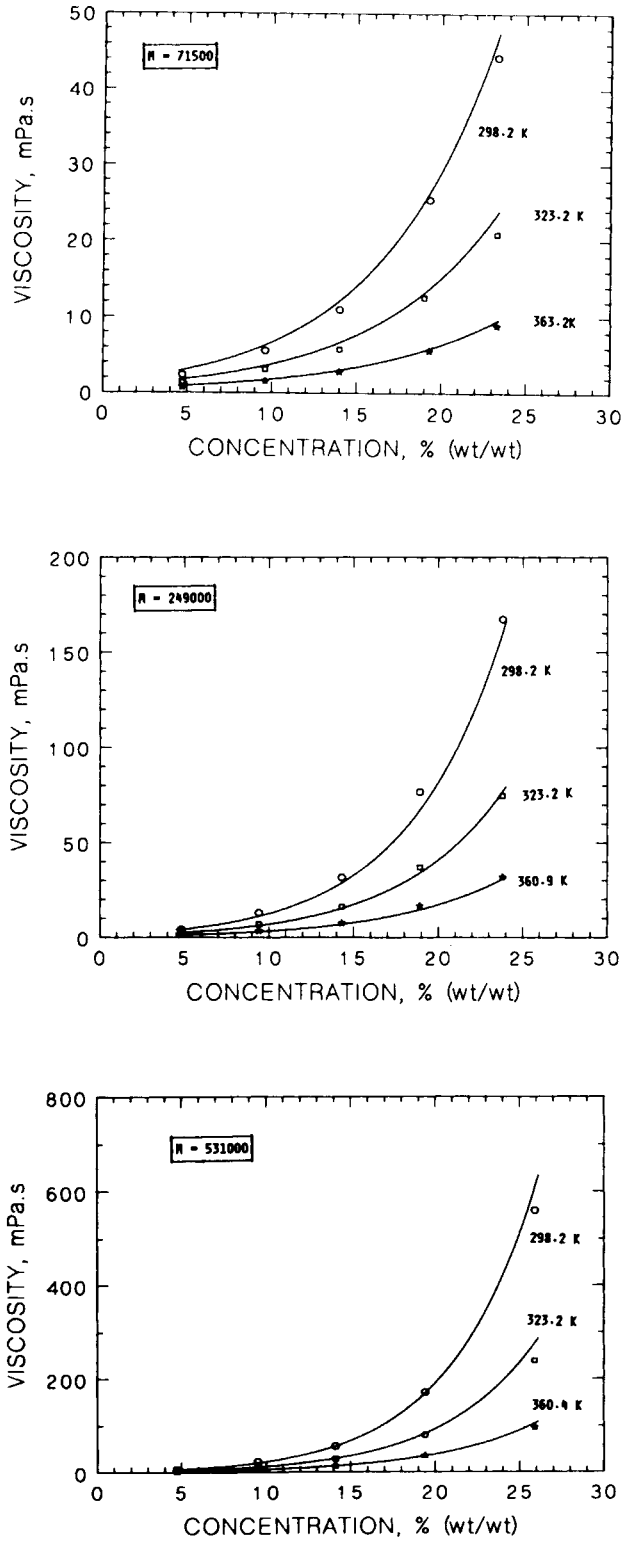


Fig. 5. Viscosity profiles as a function of the concentration at three different temperatures (dextran molecular weights: (5a) $M = 71,500$, (5b) $M = 249,000$, (5c) $M = 531,000$).

It is significant to notice that A , the pre-exponential factor, is independent of concentration and molecular weight for this system and within the range of variables considered. This means that the activation entropy must vary very little with either concentration or molecular weight. This is quite different than in the case of dextrans where both variables influence the value of A .

The goodness of fit of different viscosity correlations using Francesconi et al.³ data are the following:

Correlation	Mathematical expression	$\Delta\eta$ range
Kelley and Bueche ¹	Eqs. (1), (2), (3)	1.5–2.2
Francesconi et al. ³	Eqs. (4), (1), (2)	0.14–0.29
Onogi et al. ⁵	Eq. (6)	0.52–0.62
This work	Eq. (19)	0.06–0.15

When the parameters f_1 and f_2 are adjusted mathematically via linear regression rather than calculated from theoretical principles, the goodness of fit is improved, and $\Delta\eta$ compares well with our own correlation.

A final point of our discussion concerns the flexibility of the polymer chains in solution. According to Moore,¹⁰ the dependence of the activation energy with concentration can be expressed as:

$$E = E_o^* + K_e \cdot M \cdot c \quad (21)$$

where E_o^* is the activation energy of the solvent and K_e is a parameter related to polymer flexibility and independent of concentration.

By comparing Eqs. (18) and (21), the constant related to the chain flexibility is therefore evaluated as follows:

$$K_e = \epsilon_v \cdot M^{\sigma_v - 1} \quad (22)$$

Our findings suggest that K_e is not an important function of molecular weight for the ethylene/vinylacetate copolymers since $\sigma_v = 1.07$ whereas K_e is a strong function of M for the dextrans since $\delta_v = 0.138$. The experimental values obtained indicate that ethylene/vinylacetate copolymer is not clearly identified as a flexible molecule since $K_e = 5 \times 10^{-3} \text{ J} \cdot \text{dL}/\text{g}^2$ lies between Moore's criteria¹⁰ of $K_e > 10^{-2}$ for stiff molecules and that of $K_e < 10^{-3}$ for fully flexible molecules.

CONCLUSIONS

From the experimental data and using basic viscosity relationships, we have shown that the viscosity of dextrans solutions can be explicitly expressed as a single function of polymer concentration, average molecular weight and temperature. This correlation is shear rate independent within the range 10 to 1000 s^{-1} because of the Newtonian behavior of dextran solutions. Thus, capillary viscosimeters which are characteristic of these shear rates can be easily used for viscosity measurements.

Using Eyring's theory of liquids, we have derived thermodynamic data which shows that for viscous flow, the entropy and the energy of activation are functions of dextran concentration and to a lesser extent, of the average molecular weight. The entropy of activation decreases with increasing concentrations and molecular weights, thus giving support to a flexible chain model for dextran molecules in aqueous solutions.

When applying our correlation to existing data on ethylene/vinylacetate copolymers we have found a superior fit when compared to previously established correlations. These copolymers are not clearly flexible and their entropy of activation for viscous flow is independent of concentration and molecular weight.

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References

1. F. N. Kelley and F. Bueche, *J. Polym. Sci.*, **50**, 549 (1961).
2. F. Bueche, *J. Chem. Phys.*, **25**, 599 (1956).
3. R. C. Francesconi, C. Castellari, and F. Comelli, *Rheol. Acta*, **18**, 280 (1979).
4. R. F. Fedors, *Polymer*, **20**(2), 225 (1979).
5. S. Onogi, S. Kimura, T. Kato, T. Masuda, and N. Miyanaya, *J. Polym. Sci., C*, **15**, 381 (1966).
6. R. F. Landel, J. W. Berge, and J. D. Ferry, *J. Colloid. Sci.*, **12**, 400 (1957).
7. K. K. Chee, *J. Macromol. Sci.-Phys.*, **B19**(2), 257 (1981).
8. J. W. Sloan, B. H. Alexander, R. L. Lohmar, I. A. Wolff, and C. E. Rist, *J. Am. Chem. Soc.*, **76**, 4429 (1954).
9. M. Wales, P. A. Marshall, and S. G. Weissberg, *J. Polym. Sci.*, **10**, 229 (1953).
10. W. R. Moore, *Prog. Polym. Sci.*, **1**, 3 (1967).
11. W. R. Moore, *Nature*, **191**, 1292 (1961).
12. W. R. Moore, *Nature*, **206**, 184 (1965).
13. F. Carrasco, R. P. Overend, and E. Chornet, *J. Appl. Polym. Sci.*, **34**, 153 (1987).
14. I. Katime and J. R. Ochoa, *J. Appl. Polym. Sci.*, **29**(12, Part 2), 4427 (1984).

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