

VISCOMETRIC PROPERTIES OF CONCENTRATED POLYMER SOLUTIONS. III.*

DEPENDENCE OF VISCOSITY ON TEMPERATURE AND DETERMINATION OF THE PARAMETERS OF VOGEL'S EQUATION

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It has been found, in the course of determination of the parameters of Vogel's equation in order to express the temperature dependence of the viscosity of concentrated polymer solutions and melts, that the graphic method so far in use stresses the experimental errors. This can lead to unreliable results. A more accurate determination of the parameters was carried out with a computer by solving the linearized Vogel's equation directly by using the least squares method. The values thus calculated were used to determine their concentration dependences and the activation energy of the flow of polystyrene solutions in cyclohexanone and poly(vinyl acetate) in diethyl phthalate.

The viscosity of polymer melts and concentrated solutions can be expressed by a product of two functions, namely, the structural factor $F(X)$ and the frictional factor ζ . According to Fox and Allen^{1,2}, the structural factor is given by

$$F(X) = (N/6) X_c (X/X_c)^a \quad (1)$$

while it holds that

$$X = Z(s_0^2/M)\varphi_2/v_2 \quad (2)$$

Z denotes the number of atoms in the backbone of the polymer chain, $(\bar{s}_0^2)^{1/2}$ is the radius of gyration of an unperturbed polymer coil, φ_2 is the volume fraction of the polymer in solution, \bar{v}_2 is the partial specific volume of the polymer in solution, and N is Avogadro's number. The exponent a should depend on the magnitude of X with respect to the critical value of X_c or Z_c ; if $X \geq X_c$, then $a = 3.4$, for $X < X_c$ $a = 1.0$. From the dependence of the frictional factor on the density of the medium, its dependence on temperature and polymer concentration can be deduced in the first place; in the case of short polymer chains, the frictional factor also depends to a small extent on the molecular weight. Vogel's empirical equation^{3,4}

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$$\ln \zeta = \ln \zeta_0 + 1/\alpha(T - T_0), \quad (3)$$

with the parameter α and T_0 and the characteristic frictional factor ζ_0 has been found to express adequately the temperature dependence of the frictional factor. The equation has been formerly successfully applied to the viscosity of oils and inorganic glasses. The characteristic frictional factor ζ_0 is assumed to be constant for a given polymer and depending very little on its structure. Since both the structural factor and the quantity ζ_0 are temperature-independent, they can be included into a single constant $A = F(X) \zeta_0$ in the expression of the temperature dependence of viscosity, thus giving

$$\ln \eta = \ln A + 1/\alpha(T - T_0). \quad (4)$$

The dependence of the frictional factor on the polymer concentration or on its molecular weight is defined by the parameters α and T_0 . The effect of the molecular weight on α and T_0 appears⁵ for polymers having $M < 5 \cdot 10^3 - 10 \cdot 10^3$. The parameters α and T_0 vary in a much more pronounced manner with concentration of the polymer in solution.

The importance of the parameters of Vogel's equation consists in that they will allow recalculation of viscosities measured at a constant temperature η_T to values at a constant frictional factor η_ζ . Such correction of viscosities is necessary^{3,6} if the slopes of the dependences $\ln \eta$ vs $\ln X$ drawn through the experimental points should have the theoretical values 1.0 and 3.4. It has been the aim of this work to check the existing method of determination of α and T_0 or to suggest a more suitable procedure.

EXPERIMENTAL

Two polystyrene samples having molecular weight $\bar{M}_n = 270 \cdot 10^3$ and $57.1 \cdot 10^3$ were prepared by block polymerization initiated with di-tert-butyl hyponitrite. The sample having the lower molecular weight was divided into three fractions by gradual precipitation of the polymer from 1% benzene solutions with methanol; one of these fractions, that with the lowest molecular weight, $\bar{M}_n = 30.1 \cdot 10^3$, was used in the measurements (after reprecipitation and drying *in vacuo* over phosphorus pentoxide at 60°C).

The solutions were prepared in conic flasks by stirring with steel balls, 15 mm in diameter, by rotating the flasks on an inclined plane at 60°C (the dissolution, especially at rather high concentrations of the polymer, took as much as several weeks); the solutions were then filtered by squeezing through glass frits. The viscosity measurements were made in calibrated capillary viscometers of Ubbelohde's type (shear stress approx. 10 dyn cm^{-2}); the correction for the loss of kinetic energy and the end effect, as well as the adhering of the solution to the walls of the viscometer cell (drainage effect) were negligible owing to long flow times. The molecular weight of the samples was determined on the basis of the intrinsic viscosity of benzene solutions at $25^\circ \pm 0.05^\circ\text{C}$ according to Meyerhoff⁷, $[\eta] = 1.23 \cdot 10^{-4} M^{0.72}$.

RESULTS AND DISCUSSION

Berry and Fox^{3,6} give a very simple procedure for determination of the parameters α and T_0 based on Eq. (5), which can be obtained by transformation of Eq. (4):

$$-(T - T_r) / \ln(\eta/\eta_r) = i + m(T - T_r); \quad (5)$$

here, T_r denotes a deliberately chosen reference temperature within the temperature interval under investigation and η_r is the viscosity at a temperature T_r . The constants i and m can be determined graphically from the presumably linear dependence $-(T - T_r) \ln(\eta/\eta_r)$ vs $(T - T_r)$; they are related unambiguously to the parameters α and T_0 :

$$T_0 = T_r - i/m; \quad \alpha = m^2/i. \quad (6a,b)$$

This method was used for the treatment of the results obtained by the measurements of the temperature dependence of solutions of both polystyrene samples in cyclohexanone (polydisperse and fraction) within the concentration range 10–40 g/100 cm³ at five temperatures ranging from 25 to 80°C. However, it has been found that this graphical procedure has certain serious drawbacks. The shape of the curves of the relationship $-(T - T_r) / \ln(\eta/\eta_r)$ vs $(T - T_r)$ depended on the place of the reference temperature within the region of temperatures under investigation. If T_r is chosen on the margin of this interval, the dependences are satisfactorily straight or only slightly curved. However, the straight lines plotted through the calculated points correspond to different values of the constants α and T_0 . If T_r chosen by us lies in the middle of the interval of the temperatures used, the scatter of points becomes more pronounced (Fig. 1a). To verify this behaviour also for another system, we treated Kishimoto's⁸ results for poly(vinyl acetate) in ethyl phthalate which were at disposal in the literature within the broadest concentration

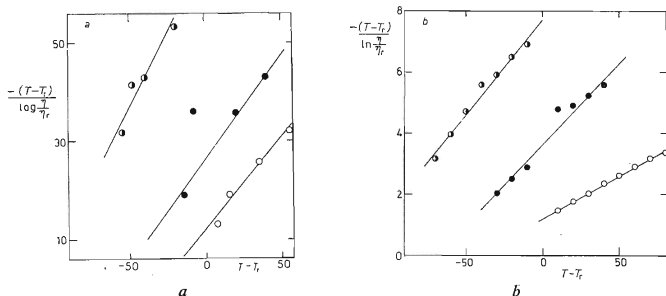


FIG. 1

A Graphical Method for Determination of the Parameters α and T_0 by Using (5) and (6)
 a Solution of a polydisperse polystyrene sample in cyclohexanone; concentration 30 g/100 cm³; T_r , K: ○ 298, ● 313, ◐ 353; b poly(vinyl acetate) solution in diethyl phthalate according to Kishimoto⁸; Concentration $\varphi_2 = 1$; T_r , K: ○ 283, ● 333, ◐ 373.

and temperature interval ($\varphi_2 = 0.05-1$ and $10-100^\circ\text{C}$). The shape of the dependences was similar to polystyrene solutions (Fig. 1b).

An analysis of relationship (5) shows that for T approaching T_r the left-hand side of the equation becomes an uncertain expression of the type $0/0$. In this case a very small experimental error in the viscosity value causes a large deviation in the expression $-(T - T_r)/\ln(\eta/\eta_r)$. Sensitivity of this graphical method will therefore be reflected in deviations from linearity mainly for temperatures near T_r . The deviations are most striking if T_r is chosen in the middle of the interval of the temperatures used. The treatment of data for various polymer concentrations has revealed that the method discussed here for the determination of the parameters α and T_0 is relatively more accurate for higher φ_2 values, where the dependence of viscosity on temperature is more pronounced than at lower concentrations. However, even for φ_2 values close to one of quite accurate data by Kishimoto we obtained for different reference temperatures T_r Vogel's parameters differing by as much as 50%. If the scope of the data was smaller and the concentrations were lower (as in the case of our systems), the plotting of the straight lines was less unambiguous and the differences were even larger.

It follows from the analysis given above of the graphical method for obtaining parameters of Vogel's equation that this method stresses the experimental errors and leads to unreliable results, which in its turn can be reflected in incorrectly determined dependences of the parameters on the concentration and molecular weight of the polymer. To determine these dependences with more accuracy, we used a different procedure of determination of α and T_0 . We regarded as most advantageous a direct calculation of the constants A , α and T_0 by applying the least squares method

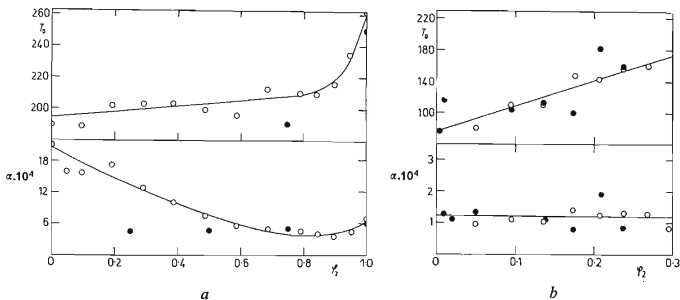


FIG. 2

Dependence of Vogel's Parameters α (K^{-1}) and T_0 (K) on the Concentration of Polymer Solutions

a Poly(vinyl acetate) solution in diethyl phthalate; \circ values calculated according to Kishimoto⁸, \bullet values taken from the paper by Berry and Fox³; *b* polystyrene solutions in cyclohexanone: \circ fraction, \bullet polydisperse sample.

to modified Vogel's equation (4) which by multiplying with the difference $(T - T_0)$ is transformed into the linear form

$$Y = T \ln \eta = Q_1 T + Q_2 \ln \eta + Q_3 \quad (7)$$

The product $T \ln \eta$ was introduced as a new variable Y which is a function of T and $\ln \eta$. The optimum values of constants Q_1 , Q_2 , Q_3 obtained by calculation are unambiguously related to the parameters α and T_0 :

$$\ln A = Q_1 \quad T_0 = Q_2 \quad \alpha = 1/(Q_3 + Q_1 Q_2) \quad (8a,b,c)$$

The calculation was carried out with a Tesla 200 computer. The numerical method used here gives mathematically correct and unambiguous results. It is only necessary, before treating the data, to exclude evidently wrong points; with respect to the three constants of Vogel's equation, sufficiently numerous sets of measured data must be used. We have found by reverse calculation that the deviations between the experimental and calculated $\ln \eta$ values amount to 1% at the utmost. However, even such a small difference between the experimental values and Vogel's function will cause difficulties in the determination of reliable values of the constants α and T_0 and T_0 by the Berry-Fox method^{3,6}. Generally, the results described above permit

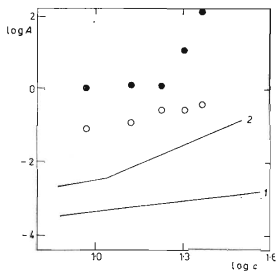


FIG. 3

Relationship between the Parameter A and Concentration of Polystyrene Solutions in Cyclohexanone

○ Fraction, ● polydisperse sample; dependences calculated according to theory: 1 for fraction, 2 for polydisperse sample.

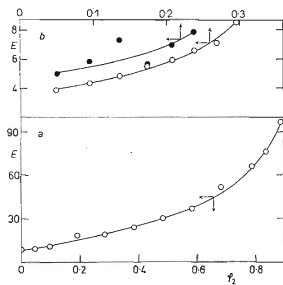


FIG. 4

Dependence of the Activation Energy of the Flow E (kcal) on Polymer Concentration φ_2
 a Poly(vinyl acetate) solution in diethyl phthalate, b polystyrene solution in cyclohexanone: ○ fraction, ● polydisperse sample.

to state that Vogel's empirical equation is suited for the description of the temperature dependences of systems under investigation for a concentration region having approximately $\varphi_2 > 0.1$.

The parameters obtained were plotted as a function of the polymer concentration (Fig. 2a). According to Kishimoto's viscosity data for poly(vinyl acetate) solutions in ethyl phthalate, the parameter T_0 increases with increasing polymer concentration; starting approximately with $\varphi_2 = 0.7$, its increase is faster. On the contrary, the parameter α decreases with increasing φ_2 , the decrease being much faster for lower concentrations. Vogel's parameters for the same system are also given by Berry and Fox³ in their paper, unfortunately only for four concentration values; the parameters were allegedly obtained from the experimental data by Nakayasu and Fox⁹ by means of the graphical method using Eq. (5). It can be seen from the comparison of the results (Fig. 2a) that the data coincide only in the high concentration region. The Berry-Fox's values for lower concentrations are somewhat smaller.

Fig. 2b gives the concentration dependence of Vogel's parameters obtained from our viscosity data on polystyrene solutions in cyclohexanone. Within the concentration region investigated, the parameter T_0 increases linearly with increasing volume fraction of polystyrene, while the parameter α remains almost constant. Both parameters are virtually independent of the molecular weight within the values of the given samples. This result is in accordance with the statement by Berry and Fox³ that α and T_0 are independent of the molecular weight for $Z > 500$; this condition is fulfilled by both samples used. For polystyrene, only dependences of Vogel's parameters for solutions in dibenzyl ether have been found in the literature³. In this case, the parameter T_0 also exhibits a linear increase with φ_2 within the interval $c \cdot 0 < \varphi_2 < 0.3$, but α falls off much faster than in the cyclohexanone solution.

We have compared the empirically obtained constants A for solutions of both samples of polystyrene in cyclohexanone with the values calculated as a product of the structural factor and characteristic frictional factor. The structural factor was calculated from relationships (1) and (2). Values tabulated in the paper by Berry and Fox³ were substituted for the parameters X , $(\overline{s_0^2}/M)$ and ζ_0 . The exponent a was chosen according to the calculated value of X ; for the fraction with $\overline{M}_\eta = 30.1 \cdot 10^3$ it holds $X < X_c$, and therefore $a = 1$, for the polydisperse sample $\overline{M}_\eta = 270 \cdot 10^3$ it holds, with the exception of the lowest concentration used, that $X > X_c$, and therefore $a = 3.4$. For both samples the experimental $\log A$ values are higher than the calculated ones for the concentrations within the given range (Fig. 3). For a polymer having a lower molecular weight the empirical dependence $\log A$ vs $\log c$ is practically linear with a slope only a little larger than the theoretical value 1, so that both curves coincide if shifted vertically. Their difference, which is approximately 2, is rather large with respect to the tabulated error in the characteristic frictional coefficient, ± 0.6 . It is not likely to consist in a wrongly determined parameter A ; it will rather be due to the insufficient expression of the structural coefficient by relationship (1).

At a higher molecular weight the experimental results exhibit a somewhat larger scatter, and they cannot be connected reliably by a straight line. Even so, however, it can be estimated that their departure from the theoretical values is approximately the same as for a polymer with a lower molecular weight.

The parameters of Vogel's equation can also be applied to the calculation of the activation energy of the flow $E = \partial \ln \eta / \partial (1/RT)$ (R is the universal gas constant). By differentiating Vogel's equation we obtain

$$E = R/[\alpha(1 - T_0/T)^2]. \quad (9)$$

The activation energy values obtained by means of this relationship are plotted against the volume fraction of the polymer in poly(vinyl acetate) and polystyrene solutions (Fig. 4). For polystyrene solutions in cyclohexanone (Fig. 4b) we obtained for a sample having a higher molecular weight insignificantly higher activation energy values, which agrees well with what Ferry and co-workers¹⁰ observed for poly(vinyl acetate) solutions.

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