

Quick Estimation of Dilute Polymer Solution Rheology and Activation Energy

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Synopsis

A simple method for estimation of dilute polymer solution kinematic viscosity versus shear rate curve at temperature of interest and activation energy for viscous flow through the use of efflux time measurement is demonstrated.

INTRODUCTION

Glass capillary viscometers, which use the hydrostatic head of the fluid to provide driving pressure, are invariably used for low viscosity solutions. The simplest and the most common of them is the U-tube viscometer of Ostwald. The Ostwald viscometer is frequently used for measuring the viscosity of Newtonian fluids and also for detecting the small differences in viscosity between, for instance, a pure solvent and a dilute solution. It is seldom used, however for determining the viscosity behavior of fluids that are non-Newtonian in character. This is mainly because non-Newtonian fluids require a larger pressure range for flow and a number of tubes of varying dimensions in order to cover a useful range of shear rates. Choice of flow tube dimensions and provision of suitable tubes are seldom trivial matters. However, the four-bulb Cannon-Ubbelohde viscometer can be conveniently used for determining the viscosity versus shear rate behavior of non-Newtonian fluids as has been done by McCormick et al.¹

Dilute aqueous solution viscosities of graft copolymer samples were determined by McCormick et al.¹ using a Cannon-Ubbelohde 4-bulb shear dilution viscometer (size 100, S-241). The shear rate and kinematic viscosity were calculated by the following simple equations.

$$\dot{\gamma} = \frac{k}{t} \quad (1)$$

$$\nu = ct \quad (2)$$

where t is the efflux time of the sample, k the shear rate constant, and c the viscometer constant as supplied by the manufacturer and tabulated in Table I.

A typical plot of kinematic viscosity versus shear rate is shown in Figure 1, reproduced from McCormick et al.¹ for graft copolymer sample PC-03 at

TABLE I
Values of Constants for the Four-Bulb Cannon-Ubbelohde Viscometer as given by manufacturer^a

	k	c
1st Bulb	12,000	0.01542
2nd Bulb	26,500	0.01523
3rd Bulb	64,000	0.01389
4th Bulb	125,000	0.0408

^aFrom Ref. 1.

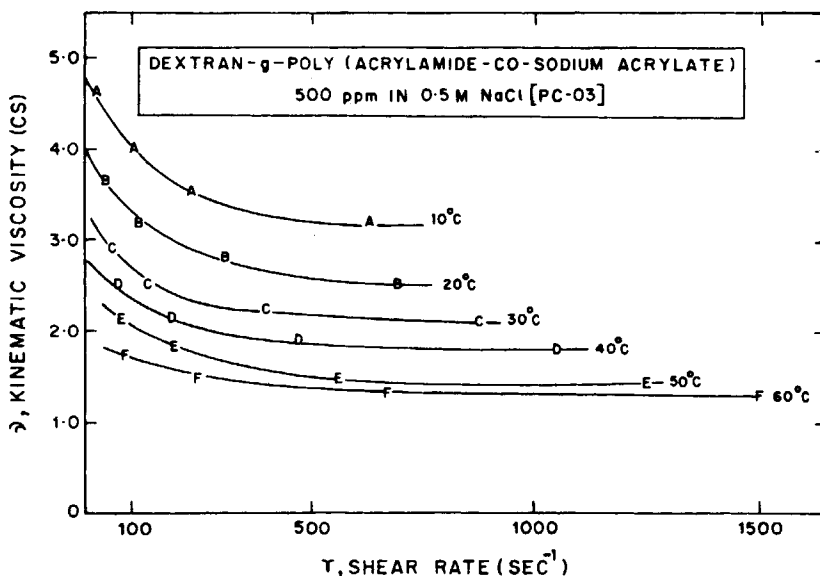


Fig. 1. Variation of kinematic viscosity with shear rate for Dextran-g-poly (Acrylamide-co-Sodium Acrylate) PC-03.

various temperatures. The polymer concentration was 500 ppm in a 0.5M aqueous NaCl solution. The flow curves generated for other samples were analyzed by multiple linear regression and fitted with the following equation.

$$\ln \nu = \ln(A\dot{\gamma}^{n-1}) + (E/R)(1/T) \quad (3)$$

The values of A and activation energy E , as well as the power-law index n determined by them for three graft copolymer samples, are given in Table II. Using these values, two typical curves at 35°C and 55°C have been drawn in Figure 2. Each curve is for a different grade of graft copolymer, namely, PC-73 and PC-53, respectively. Again, the polymer concentration was 500 ppm in a 0.5M aqueous NaCl solution. Generation of the six curves in Figure 1 and the two curves in Figure 2 required 32 data points. However, it can be shown that all the curves could be coalesced into a single master curve and then regeneration of the original curves can be done merely from one data point per curve.

TABLE II
Values of A , E , and n for Three Hydrolyzed Copolymers^a

Sample number	Pre-exp term $A \times 10^2$	E (kcal/mole)	Power-law index n
PC-03	0.03	3.18	0.854
PC-53	0.03	3.13	0.864
PC-73	0.02	3.13	0.871

^aAs determined by McCormick et al., Ref. 1.

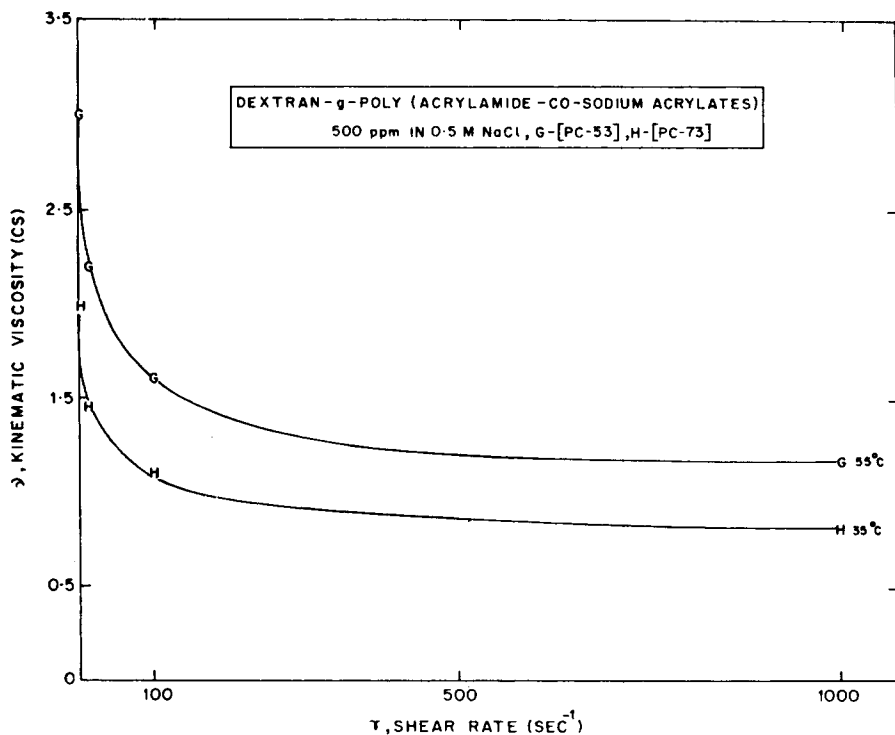


Fig. 2. Variation of kinematic viscosity with shear rate for Dextran-g-poly (Acrylamide-co-Sodium Acrylate) PC-53 and PC-73.

GENERATION OF THE MASTER CURVE

From Eqs. (1) and (2), it is evident that once the bulb of the viscometer is fixed, the shear rate and kinematic viscosity can be calculated from the efflux time. This forms a single point on the viscosity versus shear rate line. Rearrangement of Eqs. (1) and (2) gives the following

$$\dot{\gamma}t = k \quad (4)$$

$$\frac{\nu}{t} = c \quad (5)$$

Equations (4) and (5) indicate that $\dot{\gamma}t$ as well as ν/t are constant, independent

TABLE III

Values of Efflux Time of Flow through 2nd Bulb of Cannon-Ubbelohde Viscometer for Each of the Curves in Figures 1 and 2

Sample number	Temperature of measurement, °C	Efflux time, t sec
PC-03	10	261
	20	220
	30	182
	40	139
	50	126
	60	101
PC-53	55	90
PC-73	35	57

of the polymer grade and the temperature of measurement, as they are only dependent on the geometric factors of the viscometer tubes. Thus, a plot of ν/t versus $\dot{\gamma}t$ should result in a master curve if appropriate values of t are used. From Figures 1 and 2, the second data point in each case corresponding to the second bulb of the four-bulb Cannon-Ubbelohde viscometer, is used. The ν and $\dot{\gamma}$ values corresponding to the data point are read from the curves. Using Eqs. (1) and (2) and the values of $k = 26500$ and $c = 0.01523$, the values of t are estimated, as tabulated in Table III. A plot is now made of ν/t versus $\dot{\gamma}t$ using the appropriate values of t , resulting in the coalescence of all the curves as shown in Figure 3.

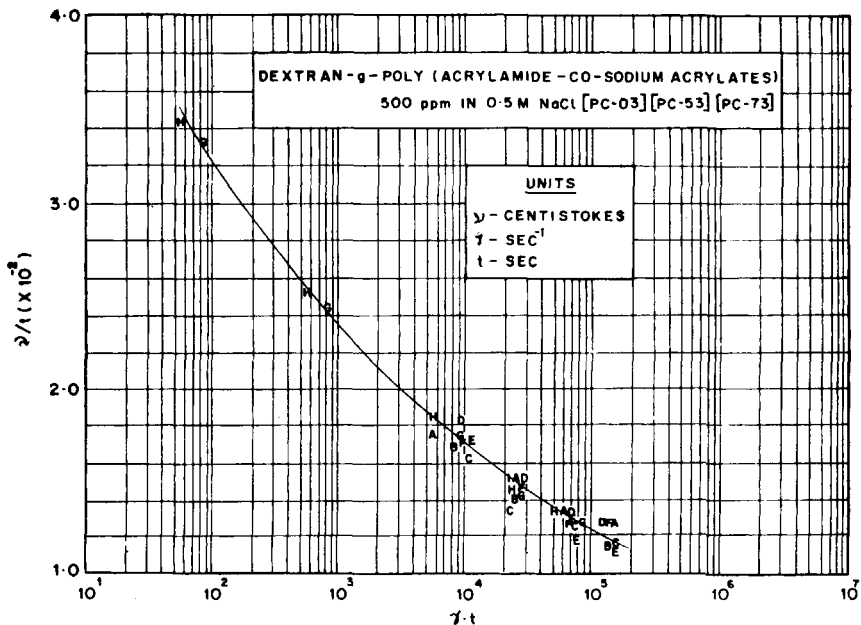


Fig. 3. Coalesced curve for Dextran-g-poly (Acrylamide-co-Sodium Acrylate) PC-03, PC-53, PC-73.

A note of caution is that the master curve in Figure 3 is system specific; hence it is valid only for systems of the same kind. It would thus be applicable for each of the graft copolymers of the PC series of McCormick et al.¹ However, for the HP series which are comparatively more linear, there would have to be a separate master curve. As a check of this hypothesis, the data for HP-3 were tried for coalescence on Figure 3. It was found that the coalescence was good in the higher shear rate region but not at all good in the lower shear rate region. This is, of course, understandable because the effects of the differences in the molecular structure like branching and MWD is known to show up more predominantly in the low shear viscosity data.

RESULTS AND DISCUSSION

Since the generated coalesced curve contains data for three different grades of graft copolymers of the PC series and at eight different temperatures, the master curve given in Figure 3 can be considered to be grade and temperature independent for this particular system. The curve in Figure 3 can now be used for generating the kinematic viscosity versus shear rate curve for any grade of the graft copolymer of the PC series, at any temperature of interest, by using the appropriate value of t determined from the second bulb of the 4-bulb viscometer.

It is essential to use this particular bulb as the master curve was obtained using the value of efflux time generated by the constants ($k = 26500$ and $c = 0.01523$) pertaining to the second bulb. A situation may arise when the second bulb is found inappropriate for a particular grade of the graft copolymer at a particular temperature. Then the data would have to be generated on a different bulb, and the efflux time for the second bulb would have to be estimated. This can be done as follows. Since the polymer solutions are shear thinning and their viscosity versus shear rate behavior can be represented by a power law model as given by McCormick et al.¹ we have

$$\nu \propto \dot{\gamma}^{n-1} \quad (6)$$

Using Eqs. (1) and (2) we can then write

$$t \propto \left(\frac{k}{c} \right)^{1/n} \quad (7)$$

$$\frac{t_2}{t_1} = \left[\left(\frac{k_2}{k_1} \right)^{n-1} \frac{c_1}{c_2} \right]^{1/n} \quad (8)$$

From Eq. (8) the efflux time t_2 for the second bulb can be generated by taking the data in any other bulb and using the appropriate bulb constants. In the present case, the value of $n = 0.863$ is recommended based on the average values for the three grades PC-03, PC-53, and PC-73.

The utility of determining the entire flow curve of kinematic viscosity versus shear rate merely from the single efflux time measurement has been demonstrated above. It will be shown in the following that the efflux time

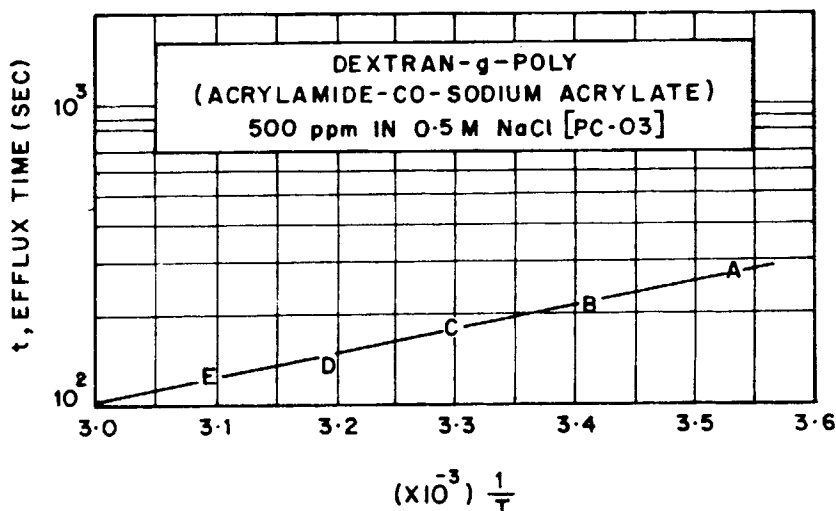


Fig. 4. Temperature dependence of efflux time for Dextran-g-poly (Acrylamide-Co-Sodium Acrylate).

determined at two different temperatures gives a convenient measure of activation energy for viscous flow. The values of efflux time t measured at different temperatures for graft copolymer PC-03 as given in Table III were plotted on a semilogarithmic scale against $1/T$. It is seen from Figure 4 that this resulted in a straight line, indicating that an Arrhenius type relationship holds as follows.

$$t = A \ln \frac{E}{RT} \quad (9)$$

where R is the gas constant, E is taken to be the energy of activation for viscous flow, and A is the frequency term, depending on the entropy of activation for flow. E and A in Eq. (9) vary from system to system. Within a narrow temperature range E is expected to be nearly constant. Normally, the activation energy is determined from the viscosities at two different temperatures. For non-Newtonian materials, viscosity is dependent on shear stress or shear rate. Bestul and Belcher (1953)² have shown mathematically that, in the shear-thinning region of flow, a clear demarcation should be made between E at constant shear stress ($E\tau$) and E at constant shear rate ($E\dot{\gamma}$). It can be easily shown graphically or analytically that $E\tau > E\dot{\gamma}$. A number of authors Bestul and Belcher,² Philippoff and Gaskins,³ Mendelson,⁴ Meissner,⁵ Porter and Johnson,⁶ have shown that $E\tau$ remains constant over a broad range of temperatures while $E\dot{\gamma}$ does not. From a fundamental point of view, constant-shear rate "activation energies" are truly incorrect because the Arrhenius equation is a rate equation and holding the rate process constant would make data treatment meaningless. In any case, the Arrhenius equation is freely used to determine $E\tau$ and $E\dot{\gamma}$ though, strictly speaking, its validity is

restricted to constant shear stress. For non-Newtonian shear-thinning fluids, $E\tau$ and $E\dot{\gamma}$ are related by the following relationship.

$$E\dot{\gamma} = nE\tau \quad (10)$$

Equation (9) basically gives E because the shear stress in the capillary of the Cannon-Ubbelohde viscometer is constant as can be shown below.

$$\tau = \partial\nu\dot{\gamma} = \partial ct \frac{k}{t} = \partial ck \quad (11)$$

The activation energy as determined from Figure 4 gives a value of 3.72 kcal/mole. Since the value given in Table II is at constant shear rate of 100 sec^{-1} , it is essential to find a comparable value by taking $nE\tau = 0.854 \times 3.72 = 3.177$ kcal/mole. As can be seen, this compares excellently with the value of 3.18 kcal/mole given in Table II. Equation (9) can thus be effectively used for determining the activation energy of a system. Alternatively, if the activation energy is known, the efflux time at the temperature of interest can be determined knowing the efflux time at some other temperature through the following equation.

$$\ln \frac{t_2}{t_1} = \frac{E}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right) \quad (12)$$

CONCLUSION

An effective method is proposed to estimate the kinematic viscosity versus shear rate curves of a graft copolymer of the type studied by McCormick et al¹ at any temperature of interest merely from the value of the efflux time for flow through the second tube of a Cannon-Ubbelohde 4-bulb viscometer. In situations where the efflux time cannot be accurately determined through the second tube, the same may be conveniently determined through any other tube and then an estimated value determined from Eq. (8). In situations where the efflux time cannot be determined at the temperature of interest, Eq. (12) may be used to get an estimated value based on the measurement at some other temperature. The more important use of Eq. (12) is for determination of the activation energy for viscous flow of any system. All prior literature uses zero-shear viscosity to evaluate the activation energy. However, the use of efflux time of flow through a Cannon viscometer is probably the simplest and the easiest method for determination of E . This method has been effectively demonstrated for the first time in the present work.

NOMENCLATURE

- A Pre-exponential term depending on the entropy of activation of flow.
- c Viscometer constant supplied by Cannon-Ubbelohde manufacturer.
- c_1, c_2 Viscometer constants for two different bulbs.
- E Activation energy for viscous flow, kcal/mole.
- $E_{\dot{\gamma}}$ Activation energy at constant shear rate, kcal/mole.

E_{τ}	Activation energy at constant shear stress, kcal/mole.
k	Shear rate constant supplied by Cannon-Ubbelohde manufacturer.
k_1, k_2	Shear rate constants for two different bulbs.
n	Power-law index.
R	Gas constant = 1.987 cal/mole °K
t	Efflux time, sec
t_1, t_2	Efflux time for two different bulbs, sec.
T	Temperature, °K

Greek letters

$\dot{\gamma}$	Shear rate, sec^{-1} .
ν	Kinematic viscosity, cm^2/sec .
ϑ	Density, g/cm^3 .

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