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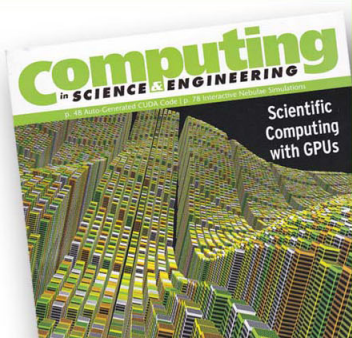
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# The Influence of Velocity Gradient on the Relation Between Viscosity and Concentration in Cuprammonium Solutions of Cellulose\*

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The numerous equations which have hitherto been employed to relate the viscosity of solutions of high polymers to the concentration of the solute have neglected to recognize explicitly the influence which velocity gradient (rate of shear) has upon the observed viscosity of non-Newtonian liquids. Consequently, the theoretically important, intrinsic viscosity, calculated on the basis of these equations, from data obtained on a solution in the anomalous region, is found to have a different value for each velocity gradient prevailing during measurement. A modification of the Baker-Philippoff equation has been developed empirically having the advantage that it yields a uniform value for the intrinsic viscosity of a given solution regardless of changes in velocity gradient. This new equation:

$$\eta_r = \left(1 + \frac{c}{\lambda}\right)^8 + \left(k_i - \frac{8}{\lambda}\right)c,$$

has been found to agree well with data on cuprammonium solutions of cellulose in concentrations below 0.5 g per 100 ml. The parameter  $\lambda$ , interpreted as a function of velocity gradient, is found to increase with gradient, while  $k_i$ , which is shown to be the intrinsic viscosity  $\eta_i$ , is found to have a constant value characteristic of the solute. It appears that the second constant appearing in other recent equations in addition to the intrinsic viscosity, may be interpreted as a velocity gradient adjustment term. The algebraic series into which the various recent equations can be expanded to express  $\eta_r$  are strikingly similar to each other and to a proposed equation based on the Eyring reaction-rate theory.

## INTRODUCTION

THE employment of viscometry for the reliable determination of molecular weights depends upon the determination of a quantity which characterizes the viscous nature of the substance under study irrespective of experimental conditions. Among the important conditioning factors affecting the viscosity of solutions of high-polymeric substances are concentration and velocity gradient (rate of shear). Most attention during the past decade has been focused on the relationship between viscosity and concentration, the tendency being to emphasize zero concentration as the definitive condition for the characteristic viscous constant. Both viscosity and concentration appear explicitly in the analytical expression of the Staudinger theory. In

the calculation of the intrinsic viscosity

$$\eta_i \equiv \lim_{c \rightarrow 0} \frac{\eta_{sp}}{c},$$

where  $\eta_{sp} = \eta_r - 1$  = specific viscosity,  $\eta_r$  = relative viscosity, and  $c$  = concentration, it is generally assumed that the solution behaves as a normal, Newtonian liquid. Many solutions of high polymers, such as cellulose in cuprammonium hydroxide, however, exhibit anomalous behavior in that the apparent viscosity, instead of remaining constant at a given concentration, varies with the velocity gradient prevailing during measurement. In analogy with the treatment of the concentration effect, attempts have been made to evaluate the viscosity at zero velocity gradient, in order to nullify the velocity gradient effect, but these attempts have not been successful.

The neglect of the velocity gradient effect is somewhat justifiable if, as is frequently the case in molecular-weight studies, very low concentrations are employed. Under this circumstance, as

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\*\* This is one of the laboratories of the Bureau of Agricultural and Industrial Chemistry, Agricultural Research Administration, U. S. Department of Agriculture.

was recognized some years ago by Staudinger,<sup>1</sup> the anomalous behavior becomes quite obscure, if not negligible, in many high-polymer solutions. An illustration of the diminishing importance of velocity gradient as the concentration decreases is afforded by Fig. 1, in which are plotted values of the relative viscosity for various values of  $D_P$ , the velocity gradient which appears in the development of the Poiseuille equation.\* While the differences between relative viscosities at the various gradients apparently vanish at the lowest concentrations, the graph clearly suggests that in this sample, Co-159, the small differences are merely masked by experimental error, and that the anomalous effect prevails down to zero concentration. Similar data for the other cellulose sample, Co-1374, are plotted in Fig. 2, for the limited region of low concentrations. Here the consistency of the relative positions of the experimental points for the different  $D_P$ 's at each chosen concentration indicates a real, even though a small, anomalous effect. Table I brings out more clearly the character of the small differences in  $\eta_r$  which are involved in the interpretation of the data for low concentrations.

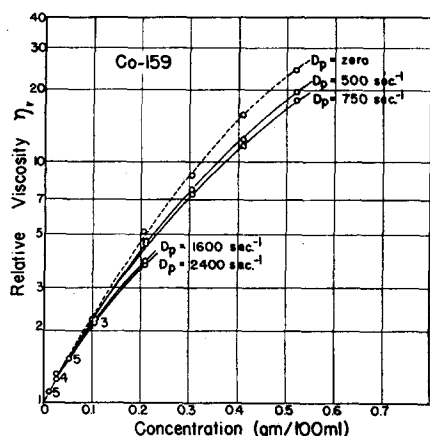


FIG. 1. Relative viscosity vs. concentration for a purified cotton cellulose, Co-159, dispersed in cuprammonium hydroxide, showing different values of  $\eta_r$  found at particular concentrations, depending on the velocity gradient  $D_P$  employed. The numerals beside certain plotted circles indicate the number of experimental values represented by each circle.

<sup>1</sup> H. Staudinger, *Papier-Fabr.* **36**, 473 (1938), especially pp. 478-9.

\* In the Poiseuille equation the velocity gradient  $D_P$  is  $(4V/\pi r^3 t)$ . This quantity is to be distinguished from the mean velocity gradient which is given by the expression  $(8V/3\pi r^3 t)$ , and is frequently used.

That dilution evidently does not remove the anomalous behavior in high-polymeric solutions has also been shown by Conrad,<sup>2</sup> using data of Staudinger for very low concentrations of nitrocellulose in Butyl acetate.

Undoubtedly the families of curves of the type in Fig. 2 converge exactly to a common value of  $\eta_{sp}$  at infinite dilution. Thus we may arrive at the same value for a measure of the viscous character of the solution as we would have attained had we been able to evaluate accurately the viscosities at zero velocity gradient for various concentrations, and to extrapolate these values to infinite dilution. From the above considerations it is evident, however, that while at infinite dilution the velocity gradient ceases to be a pertinent variable, the functional relationship between viscosity and concentration differs with each velocity gradient used in experiment.

The numerous equations which have been proposed relating the viscosity to the concentration of a solution have been assembled and compared by Mark<sup>3</sup> and by Pfeiffer and Osborn.<sup>4</sup> Of special interest in the present discussion is Philippoff's<sup>5</sup> development of Baker's formula:

$$\eta_r = (1 + c/c_0)^8, \quad (1)$$

where  $c_0$  = a characteristic constant. Also of interest is the equation advanced by Schulz and Blaschke<sup>6</sup> and Huggins,<sup>7</sup> viz.:

$$\frac{\eta_{sp}}{c} = \eta_i (1 + k' \eta_{sp}), \quad (2)$$

and the equation proposed by Martin:<sup>8</sup>

$$\log \frac{\eta_{sp}}{c} = \log \eta_i + K \eta_i c. \quad (3)$$

<sup>2</sup> C. M. Conrad, *Ind. Eng. Chem. Anal. Ed.* **13**, 526 (1941).

<sup>3</sup> H. Mark, *Physical Chemistry of High Polymeric Systems* (Interscience Publishers, Inc., New York, 1940), p. 293.

<sup>4</sup> G. H. Pfeiffer and R. H. Osborn, in *Cellulose and Cellulose Derivatives*, ed. by Emil Ott (Interscience Publishers, Inc., New York, 1943), p. 962 ff.

<sup>5</sup> W. Philippoff and K. Hess, *Zeits. f. physik. Chemie* **B31**, 237 (1936). K. Hess and W. Philippoff, *Berichte* **70**, 639 (1937).

<sup>6</sup> G. V. Schulz and F. Blaschke, *J. prakt. Chemie* **158**, 130 (1941).

<sup>7</sup> M. L. Huggins, *J. Am. Chem. Soc.* **64**, 2716 (1942).

<sup>8</sup> A. F. Martin, Abstract of Papers, Memphis Meeting of the American Chemical Society, April, 1942; cf. also reference 4.

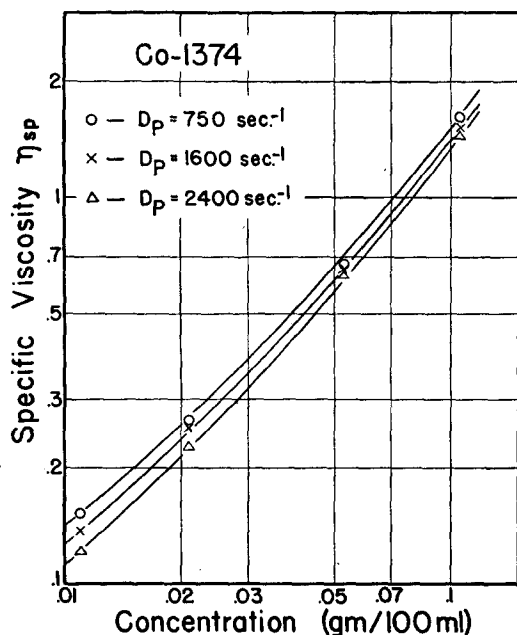


FIG. 2. Specific viscosity vs. concentration for cellulose Co-1374, in the range of low concentrations, showing the influence of velocity gradient.

$k'$  and  $K$  are constants characteristic of solutes from a given homologous series in a given solvent.

While most, if not all of the various equations have at one time or another been considered in connection with the viscosity of solutions of high polymers, none of them explicitly recognizes the influence which velocity gradient has upon the viscous behavior of this class of solutions. Consequently, ambiguous results in the evaluation of  $\eta_i$  are obtained when data for the ranges of concentrations where the anomalous behavior has become appreciable, are substituted in the equations. Corresponding to each velocity gradient at which measurements are made there is (at any single concentration in the anomalous region) a different  $\eta_r$  or  $\eta_{sp}$ . Hence, as is evident from their form, equations of the type of (1), (2), and (3) will yield a different  $\eta_i$  for each velocity gradient. Conrad<sup>2</sup> has shown by numerical example that Eq. (1), written:

$$\eta_i = \frac{8}{c_0} = \frac{8}{c} (\sqrt[8]{\eta_r} - 1), \quad (4)$$

and applied to data on 0.5 percent solutions of cellulose in cuprammonium, and on a 1 percent solution of nitrocellulose in Butyl acetate, yields

intrinsic viscosities ranging from 8.67 to 16.67 in the first case, and from 6.70 to 28.24 in the latter, the particular value of the intrinsic viscosity depending on the mean gradient prevailing during measurement. Where equations which ignore the velocity gradient effect have been successfully applied to solutions in the higher range of concentration, it would appear that the constants are actually parameters associated with particular velocity gradients, or with certain sequences of velocity gradients during discharge, imposed by experimental conditions.

#### PROPOSED EQUATION FOR CONCENTRATION EFFECT

Because in ascertaining the exact concentration of a solution the error generally increases with dilution, it is often preferable to use concentrations sufficiently high that the anomalous behavior is still pronounced. It then becomes necessary, if one is to obtain reliable calculations of intrinsic viscosities, to have an equation for the concentration effect which recognizes the anomalous effect also. The remarkable success with

TABLE I. Relative viscosity  $\eta_r$  of cellulose in cuprammonium hydroxide at various concentrations  $c$  and velocity gradient  $D_P$ .

Sample	$D_P$ (sec. <sup>-1</sup> ) $c$ (g/100 ml)	Zero				
		Relative viscosities $\eta_r$				
Co-159	0.010	1.10*	1.11	1.11	1.10	1.10
	0.026	1.32*	1.25	1.25	1.25	1.23
	0.052	1.54*	1.52	1.52	1.52	1.51
	0.102	2.23*	2.23	2.22	2.15	2.23
	0.210	5.13*	4.69	4.57	3.89	3.78
	0.305	8.80*	7.69	7.33	6.40	—
	0.410	15.7*	12.5	11.6	—	—
	0.520	24.2*	19.6	18.0	—	—
Co-1374	0.011	—	1.14	1.15	1.14	1.12
	0.021	—	1.34	1.26	1.24	1.23
	0.053	—	1.72	1.67	1.66	1.63
	0.106	—	2.65	2.63	2.54	2.45
	0.215	—	5.54	5.40	4.93	4.59
	0.525	—	27.5	24.4	—	—

\* Based on slopes at the origin of extrapolated  $D_P$  vs.  $\eta_r$  curves.

which the Baker-Philippoff formula, Eq. (1), has been applied<sup>5</sup> to a large variety of high-polymeric solutions, over a wide range of concentrations, suggested that it could be profitably used as a basis for the required equation. Equation (1) is adjustable to different velocity gradients by virtue of the fact that  $c_0$  takes a different value for each gradient. However, as appears from the foregoing remarks, and especially from Eq. (4), this implies

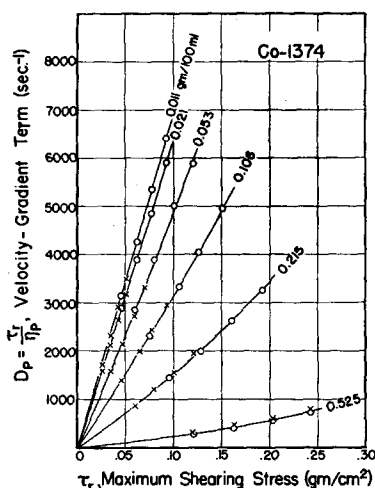


FIG. 3. Typical  $D_P$  vs.  $\tau_r$  curves for cellulose in cuprammonium hydroxide.

that  $\eta_i$  is a function of velocity gradient. Evidently, if  $\eta_i$  as calculated is to be a material constant, the modified equation must contain a term whose evaluation is independent of velocity gradient, and must be of such form that the influence of the gradient disappears as  $c \rightarrow \text{zero}$ .

If the right-hand side of Eq. (1) is expanded in a series we have:

$$\eta_r = \left(1 + \frac{c}{c_0}\right)^8 = 1 + 8\frac{c}{c_0} + \frac{8 \cdot 7}{2!} \left(\frac{c}{c_0}\right)^2 + \frac{8 \cdot 7 \cdot 6}{3!} \left(\frac{c}{c_0}\right)^3 + \dots, \quad (5)$$

$$\frac{\eta_r - 1}{c} = 8\frac{1}{c_0} + \frac{8 \cdot 7}{2!} \frac{c}{c_0^2} + \frac{8 \cdot 7 \cdot 6}{3!} \frac{c^2}{c_0^3} + \dots \quad (6)$$

Evidently, it is only the coefficient  $8/c_0$  which remains when the lim is taken in Eq. (6). The fact that by definition this limit is the intrinsic viscosity  $\eta_i$  leads to the relation in Eq. (4). If we remove from the expression for  $\eta_r$ , Eq. (5), the term  $8(c/c_0)$ , and replace it with one involving a constant independent of velocity gradient, we shall obtain an analytical expression for the condition represented by Fig. 1, wherein the relative viscosity-concentration relation is independent of the velocity gradient as  $c \rightarrow \text{zero}$ . This modifica-

tion is achieved by writing

$$\eta_r = \left(1 + \frac{c}{\lambda}\right)^8 + \left(k_i - \frac{8}{\lambda}\right)c, \quad (7)$$

where  $k_i$  is the new constant, and  $\lambda$  represents the parameter  $c_0$  now interpreted as a function of velocity gradient. Here now,

$$\lim_{c \rightarrow 0} \frac{\eta_r - 1}{c} = \eta_i = k_i \quad (8)$$

regardless of velocity gradient.

### EXPERIMENTAL PROCEDURE

Viscosity determinations were made in accordance with the method already fully described by Conrad.<sup>2</sup> The capillaries used with the buret viscometers have a uniform length of 5.00 cm, and seven different bore radii ranging from 0.017 to 0.079 cm. Weighed samples of cotton cellulose were introduced into the burets in amounts calculated on the basis of moisture content to give concentrations near certain selected values. Exact concentrations, in g/100 ml of solution, were finally computed on the basis of cellulose content. The composition of the cuprammonium-hydroxide solvent was in accordance with the specifications of the Committee on the Viscosity of Cellulose of the American Chemical Society. Measurements of discharge times were made in a constant-temperature bath held at  $25 \pm 0.05^\circ\text{C}$  (extreme variation).

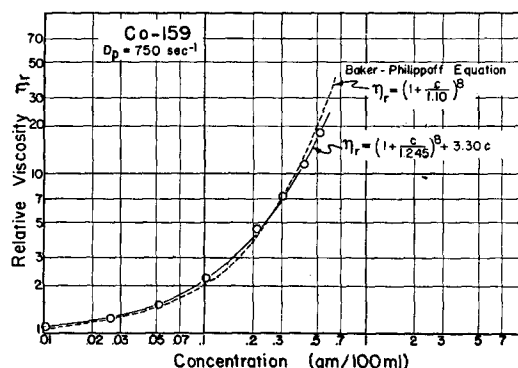


FIG. 4. Relative viscosity vs. concentration with  $D_P = 750 \text{ sec}^{-1}$ , showing curve of Eq. (7) with best-fitting Baker-Philippoff curve for comparison.

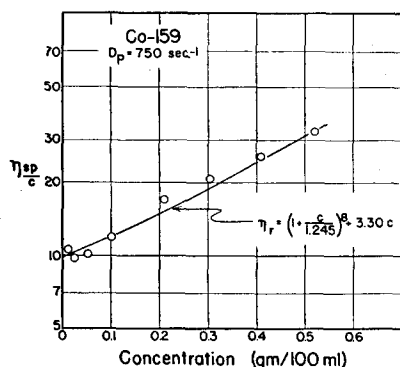


FIG. 5. Specific viscosity-concentration ratio vs. concentration; data of Fig. 4, with curve of Eq. (7).

### MATERIALS

Two samples of cellulose were used. One of the samples, Co-159, obtained from Dr. R. E. Reeves of the staff of this Laboratory, had been prepared from a supply of Coker's Super-Seven cotton. It was extracted 8 hr. each with ethanol-benzene (in the ratio 1:1) and water. The extractions were followed by a treatment for 8 hr. at 75°C with a 1 percent solution of NaOH in an atmosphere of hydrogen. The second cellulose sample, Co-1374, was prepared from a carefully cleaned cotton by first thoroughly extracting the sample at a temperature held above 60°C, with 95 percent ethanol. After two washings with water, and drying in air, the sample was extracted for 8 hr. at the boiling point with a 1 percent NaOH solution. During this treatment purified nitrogen was bubbled through the cotton to keep any atmospheric oxygen swept out, and to provide agitation. The cotton was then washed free of alkali, immersed in 1 percent acetic acid, again thoroughly washed with distilled water, and finally dried. The cellulose content of the treated sample was found to be 94.7 percent of the air-dry weight.

For the purpose of calculating the relative viscosities, measurements of viscosity were obtained on the pure cuprammonium-hydroxide solvents. That used with sample Co-159 was found to have a viscosity of 0.01273 poise, while the solvent used with Co-1374 had a viscosity of 0.01293 poise, both values having standard errors within 0.36 percent.

### TREATMENT OF DATA

From the flow-times and previously tabulated buret and capillary constants the fluidities of the cellulose solutions were calculated in accordance with the Poiseuille equation for each 5-ml section of the burets. Corrections for kinetic-energy losses were applied to the observed values, and the resulting apparent coefficients of viscosity  $\eta_P$

finally expressed in g-sec./cm<sup>2</sup>. Using the mean hydrostatic head in each 5-ml section, as given by Meissner's formula, the shearing stress at the capillary wall  $\tau_r$  was calculated by means of the equation

$$\tau_r = \frac{rP}{2l}, \quad (9)$$

where  $r$  = capillary radius (cm),  $P$  = mean pressure (g/cm<sup>2</sup>) converted from hydrostatic head, and  $l$  = length of capillary (cm). For the present study it was necessary to have a measure of the velocity gradient corresponding to each value of  $\tau_r$ . For use with  $\tau_r$ , the most reasonable choice is the velocity gradient  $D_P$ , which is given by the simple relation :\*

$$D_P = \frac{\tau_r}{\eta_P}. \quad (10)$$

The choice of this velocity gradient term as the representative velocity gradient is dictated solely by its relation to  $\tau_r$ , for, as Eq. (10) shows, the ratio of the two gives the apparent, Poiseuille viscosity. For a Newtonian liquid  $D_P$  in Eq. (10) would be exactly the maximum velocity gradient, for here  $\eta_P$  is the "true" rather than "apparent" viscosity. The  $\eta_P$  has a uniform value throughout the cross section of the capillary, including the lamina adjacent to the wall. Thus, for a Newtonian liquid,  $D_P$  as given by

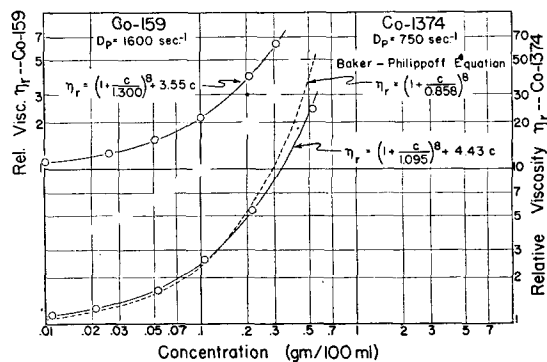


FIG. 6. Relative viscosity vs. concentration for cellulose Co-159 with  $D_P = 1600 \text{ sec}^{-1}$ , and cellulose Co-1374 with  $D_P = 750 \text{ sec}^{-1}$ .

\* Direct substitution of numerical values in the expression  $(4V/\pi r^3) = D_P$  would neglect kinetic-energy losses. The computation of  $D_P$  by Eq. (10) embraces the corrections for these losses.

Eq. (10), can be taken rigorously as the velocity gradient *at the wall*. While such studies as those of Kroepelin<sup>9</sup> permit us to conclude that, for anomalous liquids also, the maximum velocity gradient prevails at the capillary wall, this maximum value is not that given to  $D_P$  by Eq. (10). In anomalous liquids, the value of  $\eta_P$  as obtained by the present method is an average, or representative value for the whole cross section of flowing liquid, and is not exactly the viscosity in the lamina adjacent to the capillary wall, so that  $D_P$  is not the velocity gradient at this boundary. No rigorous analytical expression is yet available for the latter gradient, but its numerical value may be expected to be slightly greater than  $D_P$ .

### RESULTS

From each series of observations at various selected concentrations, graphs of  $D_P$  versus  $\tau_r$ , such as that shown in Fig. 3, were prepared. Each point represents a single observation of flow-time in a 5-ml section of the viscometer. Since the ratio of abscissa to ordinate on these graphs is  $\eta_P$ , the graphs were used for the interpolation of  $\tau_r$  (and thence  $\eta_P$ ) at the different concentrations for various chosen  $D_P$ 's. To obtain rough estimates of  $\eta_P$  at zero velocity gradient ( $D_P=0$ ), tangents to the curves were drawn at the origin, the inverse of the slopes of these tangents being the desired  $\eta_P$ .

In Fig. 4 are plotted the results\* on one of the cellulose samples Co-159, for  $D_P=750 \text{ sec}^{-1}$ . The curve for Eq. (7) is drawn in, with  $\lambda=1.245$  and  $k_i-(8/\lambda)=3.30$ , illustrating satisfactory agreement between Eq. (7) and experiment. The constants here give, in accordance with Eq. (8),

$$\eta_i = k_i = 3.30 + \frac{8}{1.245} = 9.73.$$

On this graph is also drawn the best fitting curve of the Baker-Philippoff equation,  $c_0$  having been evaluated by the method of averages, using the eight experimental points. This equation gives  $\eta_i = (8/c_0) = 7.27$ . In Fig. 5 the same data are plotted as  $\eta_{sp}/c$  (on a logarithmic scale) *versus*

concentration. The curve is for Eq. (7), using the same constants mentioned above. It will be seen to be slightly concave upward, rather than linear.

The relative viscosity of the same cellulose sample with  $D_P=1600 \text{ sec}^{-1}$  is plotted in Fig. 6. The curve, representing Eq. (7), is drawn for  $\lambda=1.300$  and  $k_i-(8/\lambda)=3.55$ . The corresponding value of  $\eta_i$  is 9.70, which is in satisfactory agreement with the value found above for the same cellulose at another gradient,  $D_P=750 \text{ sec}^{-1}$ . This agreement indicates the general applicability of Eq. (7) to various values of  $D_P$ , but cannot be taken as a proof of its validity.

Also plotted in Fig. 6 are the results on the other cellulose sample, Co-1374 for  $D_P=750$

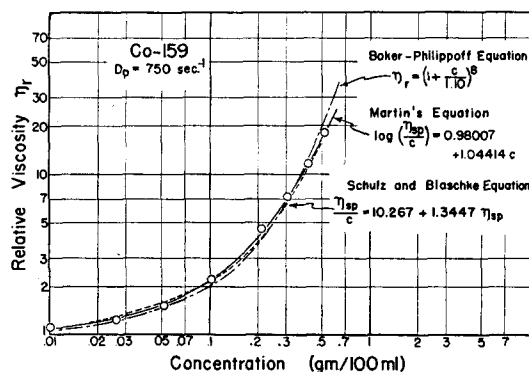


FIG. 7. Relative viscosity *vs.* concentration with  $D_P=750 \text{ sec}^{-1}$ , showing best-fitting curves calculated according to the Baker-Philippoff, the Schulz and Blaschke, and the Martin equations.

$\text{sec}^{-1}$ . Equation (7) adapted to these data yields for  $\eta_i$  the value  $4.43 + 8/1.095 = 11.74$ . The Baker-Philippoff curve tends to diverge from experiment toward excessively high values for  $\eta_r$  as concentration increases, a tendency found also in Martin's<sup>4</sup> graphs of this equation for a higher range of concentrations of cellulose in cuprammonium hydroxide.

### DISCUSSION

The results of the present investigation indicate that in addition to being in satisfactory agreement with experimental data, Eq. (7) is of such form as to yield a uniform value for the intrinsic viscosity  $\eta_i$  for various velocity gradients. The latter property evidently has required the introduction of two constants into the em-

<sup>9</sup> H. Kroepelin, *J. Rheology* 2, 385 (1931).

\* In the results reported in this paper,  $\eta_r = \eta_P/\eta_0$ , where  $\eta_0$  is the viscosity of the solvent.

pirical equation, while only one  $c_0$  appears in the original Baker-Philippoff equation. It is significant that two constants also appear in Eqs. (2) and (3), and that these equations, as Fig. 7 indicates, are in good agreement with experiment. Thus, it might be inferred that two constants are required in equations relating viscosity and concentration, especially in view of the failure (when applied to high-polymer solutions) of the older equations involving only one constant. Since solutions of the long-chain polymers generally exhibit anomalous viscous behavior, the necessity for two constants might be rationalized on the theory that one constant represents an enduring property of the solute-solvent system, reflected by the intrinsic viscosity, while the other constant represents the conditions of flow, as reflected by velocity gradient. In Eq. (7) these two factors are recognized;  $k_i$  is identified as the intrinsic viscosity  $\eta_i$ , while  $\lambda$  is introduced as a function of velocity gradient  $D_P$  as well as of  $\eta_i$ . In both Eqs. (2) and (3),  $\eta_i$  appears as one of the two constants. The other two constants  $k'$  and  $K$ , however, have not up to the present been interpreted as terms reflecting flow conditions. As presently interpreted,  $k'$  and  $K$  are constants for a given solute-solvent system, and are not means for compensating for differences in the velocity gradients at which viscosities may be measured. Hence if  $\eta_{sp}$  is computed from readings taken in the anomalous region, the Schulz and Blaschke and the Martin equations, like the Baker-Philippoff equation, will evidently yield different values for  $\eta_i$ , depending on the prevailing velocity gradient. Whether  $k'$  and  $K$  are actually insensitive to differences in velocity gradient would appear to be a suitable subject for further study. In this connection, it may be remarked that Martin's equation, with constants evaluated from the present data, and represented by the curve in Fig. 7, has  $K=0.109$  while Martin<sup>8</sup> himself gives the value of 0.130 for cellulose in cupram-

monium hydroxide. A difference in velocity gradient suggests itself as a possible reason for the difference in the value of  $K$ .

A means of comparing the equations under discussion here is afforded by the values of  $\eta_i$  given by each. The following values of  $\eta_i$  are those corresponding to the data plotted in Figs. 4 and 7:

Baker-Philippoff, Eq. (1)	7.27
Schulz and Blaschke, Eq. (2)	10.27
Martin, Eq. (3)	9.55
Eq. (7)	9.73.

It will be noted that the two latter equations, which give values of  $\eta_i$  in fair agreement with each other, are also the two which yield curves best fitting experimental points in Fig. 7. Such agreement between empirical equations of dissimilar form, as to a value which is essentially an extrapolation, tends to enhance the reliability of either of the two values of  $\eta_i$ .

The above-recorded values of  $\eta_i$  are based on observations at eight different concentrations, this number being employed in the present study to test and compare the various equations. An acceptable formula, however, should yield a reliable value for  $\eta_i$  for a given sample with much fewer observations. From what has been said regarding the character of the parameters  $\lambda$  and  $k_i$  in Eq. (7), it is evident that neither one can be fixed by the *type* of macromolecule in solution. Also the comparison of the values of  $\lambda$  in Figs. 4 and 6, for the two different cellulose samples, *viz.*, 1.245 and 1.095, both for  $D_P=750$  sec.<sup>-1</sup>, indicates quite clearly that  $\lambda$  does not remain constant with  $D_P$ . It thus appears that two unknowns,  $\lambda$  and  $k_i$ , must be evaluated for each sample. Hence viscosity determinations at two concentrations, adjusted to a common  $D_P$  (or a common *mean* velocity gradient), are necessary and sufficient to evaluate  $\eta_i$  according to Eq. (7). In Table II intrinsic viscosities obtained with this equation at two velocity gradients are compared with those obtained with Eq. (1) using the same original data. These data are those plotted in Figs. 4 and 6 for Co-159 at  $c \leq 0.10$  and 0.30 g/100 ml. While the value of  $\eta_i$  given by Eq. (1) varies over a range of 20 percent of the mean, that given by Eq. (7) has a range of 0.4 percent.

TABLE II. Intrinsic viscosity  $\eta_i$  of cellulose in cupramonium hydroxide, sample Co-159, as calculated according to two equations at two different velocity gradients  $D_P$ .

	$D_P = 750$ sec. <sup>-1</sup>	$D_P = 1600$ sec. <sup>-1</sup>
Baker-Philippoff, Eq. (1)	7.42   Mean 8.23/7.82	6.74   Mean 7.84/7.29
Eq. (7)	9.29	9.33



That the value of  $\eta_i$  given by this equation in Table II is lower than the value 9.73 recorded above evidently arises from the fact that the observations at  $c \cong 0.30$  g/100 ml are slightly out of line. The data at this concentration greatly influence the results in Table II, where only two concentrations are involved. The equations cannot improve on the observations, and must reflect discrepancies in the latter.

### THEORETICAL CONSIDERATIONS

With the present limited knowledge of the intermolecular processes occurring during viscous flow in high-polymer solutions, there is little theoretical basis for attempting a choice between Eqs. (2), (3), and (7). Schulz and Blaschke's equation written

$$\eta_r = 1 + \eta_i c + k'(\eta_i c)^2 + k'^2(\eta_i c)^3 + \dots, \quad (11)$$

Martin's equation written

$$\eta_r = 1 + \eta_i c + 2.30K(\eta_i c)^2 + \frac{(2.30K)^2}{2!}(\eta_i c)^3 + \dots, \quad (12)$$

and Eq. (7) written

$$\eta_r = 1 + \eta_i c + \frac{8.7}{2!} \left( \frac{c}{\lambda} \right)^2 + \frac{8.7 \cdot 6}{3!} \left( \frac{c}{\lambda} \right)^3 + \dots, \quad (13)$$

show remarkable similarity. Each of these equations, evidently, is effectively an empirical revision of the Einstein equation  $\eta_r = 1 + \eta_i c$ , the differences being in the coefficients of the higher powers of  $c$  which are introduced to account for the experimental consequences of complicated intermolecular forces and conditions peculiar to solutions of long-chain polymers. Each of the expansions involve  $\eta_i$  as well as another parameter; the absence of  $\eta_i$  from the higher power terms of Eq. (13) is only apparent, for  $\lambda$  is evidently a function of  $\eta_i$ .

The Eyring<sup>10</sup> reaction-rate theory of viscosity provides a possible theoretical basis for Eqs. (11)–(13), though it does not lend support to any particular one. The fundamental equation in this

theory is:

$$\eta = \frac{f s_1}{s \left[ \exp \left( \frac{f s_2 s_3 s}{2kT} \right) - \exp \left( \frac{-f s_2 s_3 s}{2kT} \right) \right]} \frac{h}{kT} \cdot \frac{F_n}{F_a^*} \exp \left( \frac{\Delta E_a}{kT} \right), \quad (14)$$

where  $\eta$  = coefficient of viscosity;  $f$  = force per cm<sup>2</sup> tending to displace one molecular layer with respect to another;  $s$  = distance between equilibrium positions in the direction of flow;  $s_1$  = perpendicular distance between adjacent layers of molecules;  $s_2$  = distance between adjacent molecules in direction of flow;  $s_3$  = distance between molecules in the plane of flow and normal to the direction of flow;  $F_n$ ,  $F_a^*$  = partition functions;  $\Delta E_a$  = energy of activation;  $h$  = Planck's constant; and  $k$  = Boltzmann's constant. Now,

$$\exp \left( \frac{f s_2 s_3 s}{2kT} \right) - \exp \left( \frac{-f s_2 s_3 s}{2kT} \right) = 2 \sinh \frac{f s_2 s_3 s}{2kT}.$$

For the present experiments on cotton cellulose in cuprammonium hydroxide, let us assume

$$1A < s_2 \cong s_3 < 5A, \text{ and } s < 10A,$$

so that  $s_2 s_3 s < 250A^3$ . The maximum shearing stress  $\tau_r \leq 0.25$  g/cm<sup>2</sup>. Hence  $f < 245$  dynes/cm<sup>2</sup>, and

$$f s_2 s_3 s < 6.1 \cdot 10^{-22} \text{ erg.}$$

At 25°C,

$$2kT = 8.2 \cdot 10^{-14} \text{ erg.}$$

Hence, we may say:  $f s_2 s_3 s \ll 2kT$ , and under this condition,

$$2 \sinh \frac{f s_2 s_3 s}{2kT} \cong 2 \left( \frac{f s_2 s_3 s}{2kT} \right).$$

Equation (14) becomes then,

$$\begin{aligned} \eta &= \frac{f s_1}{\frac{f s_2 s_3 s}{s} \frac{h}{kT}} \cdot \frac{F_n}{F_a^*} \exp \left( \frac{\Delta E_a}{kT} \right) \\ &= \frac{s_1 h}{s_2 s_3 s^2} \cdot \frac{F_n}{F_a^*} \exp \left( \frac{\Delta E_a}{kT} \right). \end{aligned} \quad (15)$$

<sup>10</sup> H. Eyring, J. Chem. Phys. 4, 283 (1936). R. H. Ewell, J. App. Phys. 9, 252 (1938), especially p. 254.

Kauzmann and Eyring<sup>11</sup> have shown that the energy of activation  $\Delta E_a$  for viscosity in normal paraffins increases with the chain length. This would seem to be in accord with the interpretation of activation energy given by Ewell,<sup>10</sup> as the work required to provide space into which a molecule can flow. Evidently, more energy will be required to dislodge a single macromolecule with many points of attraction than would be required to produce shifts in the positions of an equal volume of smaller uncombined molecules. The introduction of chain molecules into a solvent liquid, then, will tend to increase the average activation energy, and for dilute solutions this increment may be supposed to be directly proportional to the number of high-polymer solute molecules in unit volume, i.e., the concentration  $c$ . Thus, the activation energy for viscous flow in a dilute, high-polymer solution is  $\Delta E_{a,0} + Bc$ ,  $\Delta E_{a,0}$  being the activation energy for the pure solvent. The proportionality factor  $B$  may be supposed to be a function of the velocity gradients prevailing between the various shearing layers, if, as seems likely, the orientation of the chain molecules influences their activation energies. The effect of the long-chain structure is offset by a high degree of orientation, which in turn, is associated with a high velocity gradient. We may, therefore, expect  $B$  to decrease with increasing velocity gradient, though not necessarily in a linear relationship.

For a high-polymer solution, then,

$$\eta = \frac{s_1 h}{s_2 s_3 s^2} \cdot \frac{F_n}{F_a^*} \exp \left( \frac{\Delta E_a + Bc}{kT} \right),$$

$$= \eta_0 \exp \frac{Bc}{kT}. \quad (16)$$

For constant temperature and velocity gradient, this equation becomes

$$\ln \frac{\eta}{\eta_0} = \ln \eta_r = \text{constant} \cdot c, \quad (17)$$

which is Arrhenius' formula for the concentration effect.

Expanding Eq. (16), we have

$$\eta_r = \frac{\eta}{\eta_0} = 1 + \left( \frac{B}{kT} \right) c + \frac{1}{2!} \left( \frac{B}{kT} \right)^2 c^2 + \frac{1}{3!} \left( \frac{B}{kT} \right)^3 c^3 + \dots \quad (18)$$

In this equation the reaction-rate theory of viscosity evidently supplies a better theoretical basis than does the Einstein formula, for the many serially-expandable, empirical equations, such as Eqs. (11)–(13), expressing the concentration effect. While the Einstein treatment provides no interpretation of the higher powers of  $c$  which appear in the empirical equations, these powers seem to be a natural consequence of the Eyring theory.

Equation (18) is not completely in accord with the empirical equations, excepting, of course, the Arrhenius equation. There are evidently second-order effects which the derivation of Eq. (18) has neglected. However, the comparison of this equation with Eqs. (11)–(13) reveals a close relationship, if not identification, between  $B/kT$  and  $\eta_i$ . The implied dependence of  $\eta_i$  on  $B$ , and hence on velocity gradient, is unsatisfactory, and inconsistent with the current interpretation of  $\eta_i$  as an absolute, material constant. On the other hand, the appearance of  $B$  in the expression  $B/kT$  in Eq. (18) indicates that the coefficients of the higher powers of  $c$  should be functions of not only temperature, but also velocity gradient. The dependence on the latter factor was found in the present experiments (for all of which  $T = \text{constant}$ ), and is reflected in the appearance of  $\lambda$  in the coefficients of Eq. (13). As indicated previously,  $B$ , and therefore the coefficients, should be expected to decrease with increasing gradient. The present results confirm this theory; thus, for  $D_P = 750 \text{ sec.}^{-1}$ ,  $\lambda = 1.245$ , while for  $D_P = 1600 \text{ sec.}^{-1}$ ,  $\lambda = 1.300$ , in sample Co-159. Equations (11) and (12) make no explicit provision in the coefficients for the influence of velocity gradient, though Huggins, in his theoretical deduction of Eq. (2), interprets  $k'$  as a kind of shape factor. Since the shape of the chain molecules may conceivably depend on velocity gradient, there is the suggestion that gradient may influence the value of the coefficients in Eq. (11).

<sup>11</sup> W. Kauzmann and H. Eyring, J. Am. Chem. Soc. **62**, 3113 (1940).

### SUMMARY

The present study calls attention to the fact that the viscosity-concentration relationship for a high-polymer solution such as that of cellulose in cuprammonium hydroxide depends on the velocity gradient at which the viscosity is measured. This dependence is reflected by changes in the values of the parameters in the expression for the viscosity-concentration effect given by Eq. (7). In such formulas as the Baker-Philippoff equation the alteration of the values of the so-called constants alters the computed  $\eta_i$ , while with Eq. (7), and probably other equations employing more than one parameter, the substitution of data for different velocity gradients yields a substantially uniform value of  $\eta_i$ . Equation (7) is of most interest as an example of the type of equation required for the viscosity-

concentration effect; the evaluation of  $\lambda$  and  $k_i$  being quite tedious, the equation does not recommend itself for easy application. The partial conformity which has been pointed out between the expanded expression for  $\eta_r$  in Eq. (13) and Eq. (18), based on the reaction-rate theory of viscosity, would appear to lend support to a relation of the type of Eq. (7).

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