A simple Equation for the Viscosity and the Rate Constant of High-polymer Substances under Depolymerization

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Several attempts have been made to evaluate simple formulas for the calculation of reaction constants from viscosity measurements on solutions of high-polymer substances subjected to depolymerization. Sillén[1, 2] has reviewed shortly the literature on this subject and has established a very inspiring mathematical treatment of this problem.

The present author, who has been interested in this subject in connection with his studies on viscosimetrical methods for the assay of enzymic activity[3, 4, 5] has made some attempts to attain further simplification for the calculation of rate constants from viscosity measurements, and the results will be given in this article.

THEORETICAL

Staudinger and Heuer[6] have established the following formula for the specific viscosity of diluted solutions of polymeric homologous substances:

$$\eta_{sp} = K_m c_{gm} M \tag{1}$$

where:

η_{sp} = the specific viscosity,
K_m = the viscosity-molecular weight constant,
c_{gm} = the concentration in basic moles per litre, and
M = the molecular weight.

This equation, however, is only valid for polymeric homologous substances whose viscosity is not influenced by the pH of the solution nor by the ionic strength of the various salts present. For other polymeric homologous sub-

stances, Kern[7] has introduced an ionic factor J. Hence a more correct expression for the specific viscosity of the solutions of these substances is:

$$\lim_{c_{gm} \to 0} \eta_{sp} = JK_m c_{gm} M \qquad (2)$$

For the further mathematical treatment, the following notation is employed.

α = the degree of depolymerization (the number of broken linkages devided by the number of linkages at complete polymerization),

k = the rate constant for the break down of the linkages,

M_0 = the basic molecular weight,

N = the number of molecules per mole (Loschmidt's number),

N = the total number of basic molecules,

n = the number of basic molecules per molecule,

P_v = the degree of polymerization, determined viscosimetrically = $\dfrac{\Sigma n^2 z_n}{\Sigma n z_n}$,

R = the original number of basic molecules in the molecules,

t = the time,

V = the volume in liters,

z_n = the number of molecules with n basic molecules.

The rate constant

On observing that $M = nM_0$, and that for each degree of polymerization $c_{gm} = nz_n/NV$, we can write equation (2) in the following form:

$$\eta_{sp} = \frac{JK_m M_0}{NV} \sum_{n=1}^{R} n^2 z_n \qquad (3)$$

The sum $\displaystyle\sum_{1}^{R} n^2 z_n$ has been calculated by Sillén[1] under the assumption that the molecules with different chain lengths have all originated by decomposition of one kind of molecule with the original number R of basic molecules. The break down is postulated to take place under such conditions that all linkages are broken with equal ease and that the rate constant is k. If $x = e^{-kt}$,

$$\sum_{1}^{R} n^2 z_n = N \left(\frac{1 + x}{1 - x} \right) - \frac{2 \, Nx(1 - x^R)}{R(1 - x)^2} \tag{4}$$

and

$$\lim_{R \to \infty} \frac{\sum_{1}^{R} n^2 z_n}{N} = \frac{1 + x}{1 - x} \tag{5}$$

The following equation is obtained for the derivative $\dfrac{\mathrm{d} \frac{1}{\eta_{sp}}}{\mathrm{d}t}$:

$$\frac{\mathrm{d} \frac{1}{\eta_{sp}}}{\mathrm{d}t} = - \, k \, \frac{x \mathrm{d} \frac{1}{\eta_{sp}}}{\mathrm{d}x} = \frac{2 \, k \, NV}{JK_m M_0 N} \cdot \frac{x}{(1 + x)^2} \tag{6}$$

$$k = 2 \, JK_m c_{gm} M_0 \, \frac{\mathrm{d} \frac{1}{\eta_{sp}}}{\mathrm{d}t} \cdot \frac{(1 + x)^2}{4 \, x} \tag{7}$$

The function $\dfrac{(1 + x)^2}{4 \, x}$ will in all cases — except where the depolymerization is followed extremely far — assume the value 1, which can be demonstrated as follows.

Equation (5) gives for the degree of polymerization

$$P_v = \frac{1 + x}{1 - x} \tag{Sillén 12'}$$

For $P_v = 19$ we get $x = 0.9$, and the function has the value 1.0028. For $P_v = 9$ we get $x = 0.8$, and the function has the value 1.0125. For $P_v = 4$, we get $x = 0.6$, and the function has the value 1.0667. Hence the function $(1 + x)^2/4 \, x$ may be omitted. If we assume the ionic factor to have the value 1, which also means that this factor is included in K_m, we have

$$k = 2 \, K_m c_{gm} M_0 \, \frac{\mathrm{d} \frac{1}{\eta_{sp}}}{\mathrm{d}t} \tag{8}$$

From the form of this differential equation we gather that we get a straight line when plotting the inverse of the specific viscosity against time. We may also write equation (8) in the following form

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$$k = 2 \, K_m c_{gm} M_0 \, \frac{\Delta \dfrac{1}{\eta_{sp}}}{\Delta t} \tag{9}$$

and counting the time from the moment corresponding to the point where the straight line cuts the time axis, we may write

$$k = 2 \, K_m c_{gm} M_0 \, \frac{\dfrac{1}{\eta_{sp}}}{t} \tag{10}$$

Equation (8) may also be directly calculated from Silléns equation (12'), for

$$\frac{\eta_{sp}}{K_m c_{gm} M_0} = P_v = \frac{1 + x}{1 - x} \tag{11}$$

and from this we get a derivative, identical with equation (6).

Sillén has the equation

$$k = \frac{1}{t} \ln \frac{P_v + 1}{P_v - 1} \tag{Sillén 55}$$

which was calculated from Silléns equation (12'), and which seems to be a little more laborious, for the function $\dfrac{P_v + 1}{P_v - 1}$, where $P_v = \eta_{sp}/K_m c_{gm} M_0$ must be calculated for each measurement with great accuracy, and the logarithm must be looked up. The time must be corrected to be counted from the moment corresponding to the point where the function $\ln \dfrac{P_v + 1}{P_v - 1}$ cuts the time axis (Sillén 55 a). Instead of this time correction it is of course possible to count with the differences in the values of the function and the difference in the corresponding times. — The function $1/\eta_{sp}$, however, can easily be calculated on a slide rule with sufficient accuracy.

The degree of depolymerization

It follows from the definition of the degree of depolymerization and from the law of decomposition that

$$1 - \alpha = x \tag{Sillén 13}$$

Combined with (11) this equation gives the following expression for the degree of depolymerization:

$$\frac{\alpha}{1 - \frac{\alpha}{2}} = 2 \, K_m c_{gm} M_0 \, \frac{1}{\eta_{sp}} \tag{12}$$

For low degrees of depolymerization it simplifies to

$$\alpha = 2 \, K_m c_{gm} M_0 \, \frac{1}{\eta_{sp}} \tag{13}$$

The inverse of the specific viscosity (or preferably the function c_{gm}/η_{sp}) is concequently directly proportional to the degree of depolymerization, and as it is a linear function of the time in depolymerization processes, calculations may be made very rapidly graphically by the break down procedure.

EXPERIMENTAL

Comparison between the formulas for the rate constant

The calculation of rate constants from formula (10) will be compared with the calculation using the more accurate formula (Sillén 55 a) in the following example.

Ekenstam[8, Table 65] investigated the break down of cotton in 65.1 % sulphuric acid at 20° C ($c_{gm} = 0.01267$; $K_m = 13.9 \cdot 10^{-4}$). From his viscosity measurements, Sillén[2] calculated the reaction constant. To Ekenstam's time notations Sillén added a constant, $t_0 = 20$ minutes, obtained by drawing the straight line of the function $\ln \frac{P_v + 1}{P_v - 1}$ plotted against the time until it cut the time axis. Sillén's values and the values obtainable with equation (10) from the corrected zero time, where $1/\eta_{sp}$ is assumed to have the value 0, to each of Ekenstam's measurements are given in Table 1.

To faciliate an accurate comparison of the mathematical differences obtained when the equations (Sillén 55 a) and (10) are employed for the calculation of the rate constant, the last 5 values, where the difference should be greatest, were computed to an accuracy far beyond any chemical significance. The differences, however, may be omitted even for the lowest degrees of polymerization in this experiment.

Table 1. Rate constants for the depolymerization of cotton in sulphuric acid, calculated by Sillén from his equation (55 a) and by the present author from equation (10).

$t + t_0$	η_{sp}	P_v	$k \cdot 10^6$	
			(55 a)	(10)
20	0.5009	175.6	570	570
26.6	0.3915	137.2	549	548
32.95	0.3191	111.9	544	543
39.3	0.2671	93.6	544	544
45.15	0.2356	82.6	536	536
62.85	0.1651	57.9	551	550
79.2	0.1308	45.85	550	551
143.3	0.0677	23.73	588.4	588.2
167.7	0.0557	19.53	611.2	610.8
224.0	0.0408	14.32	624.6	624.3
288.0	0.0315	11.04	630.8	628.9
366.0	0.0241	8.447	649.8	646.8

In Table 1 the rate constant was calculated for every viscosity measurement, and the time was thereby counted from the corrected zero time, which was obtained from a graph. For most practical purposes this way of calculation is unnecessarily time-consuming. It is simpler to plot the inverse of the specific viscosity against the uncorrected time, for which it is valid and draw a straight line through the points. The derivative of this line is easily read off. It should perhaps be mentioned that one can obtain the time, for which a viscosity measurement is valid, by adding half the flow time to the time when the measurement was commenced [9].

Experiments at different concentrations

From equation (8) we gather that the product of the concentration and the derivative $d\frac{1}{\eta_{sp}}/dt$ is constant. Equation (8) includes some postulations and approximations, and its applicability will be illustrated by the following experiment. This experiment is not selected from a larger series.

A solution of cellulose in sulphuric acid was prepared according to Smith's [10] directions (an application of Ekenstam's methods): 1 g of filter paper was treated with 10 ml of 61 % sulphuric acid (equal parts of water and concentrated sulphuric acid). After 5
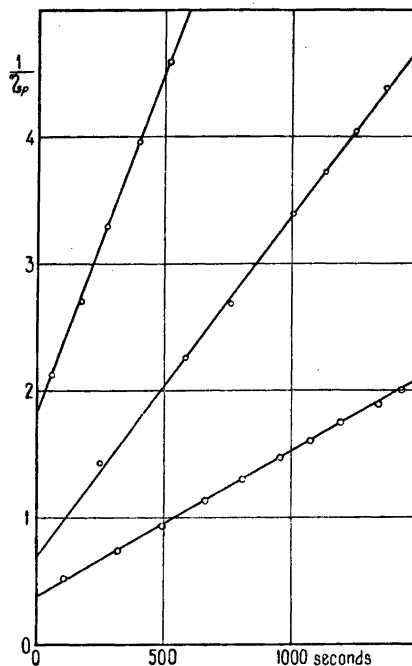
Fig. 1. Depolymerization of cellulose at 30° C in 67 % sulphuric acid.

minutes, the cellulose was dissolved on addition of 20 ml of 70 % sulphuric acid (1 part of concentrated sulphuric acid and 3 parts of 61 % sulphuric acid). From this original cellulose solution, two other solutions were prepared by dilution of 1 part of the original solution with 1 part and 3 parts respectively of sulphuric acid of the same concentration. The solutions were preserved in a refrigerator before the viscosity measurements. In this way the reaction velocities were retarded so much that the solutions could afterwards be easily measured, one after the other.

Table 2. Depolymerization of cellulose at 30° C in 67 %
sulphuric acid. Time in seconds.

c_{gm}	$\dfrac{d\,\dfrac{1}{\eta_{sp}}}{dt} \cdot 10^3$	$\dfrac{d\,\dfrac{1}{\eta_{sp}}}{dt} \cdot c_{gm}$
0.206	1.15	0.237
0.103	2.66	0.274
0.0515	5.40	0.278

The viscosity measurements and the calculations were performed mainly in the same way as described previously by the present author [11]. The results are given in Figure 1 and summarized in Table 2.

In the original solution, the concentration seems to have been too high with regard to the degree of polymerization, for the value of the derivative is here too low. It is frequently observed in depolymerization experiments that Staudinger's formula, upon which the theoretical treatment is founded, is not valid for high concentrations and high degrees of polymerization. With continued depolymerization the agreement usually increases.

SUMMARY

1. For depolymerization processes the following differential equation is established: $k = 2\,K_m c_{gm} M_0 \cdot \mathrm{d}\dfrac{1}{\eta_{sp}}/\mathrm{d}t$, where $k =$ the rate constant, $K_m =$ the viscosity-molecular weight constant, $c_{gm} =$ the concentration of basic moles per litre, $M_0 =$ the basic molecular weight, $n_{sp} =$ the specific viscosity and $t =$ the time, for which the viscosity measurement is valid. When the inverse of the specific viscosity is plotted on square paper against the time, the points will lie on a straight line, the slope of which gives the derivative.

2. If the time is counted from the moment corresponding to the point, where this straight line cuts the time axis, the equation simplifies to

$$k = 2\,K_m c_{gm} M_0 \cdot \frac{1}{\eta_{sp}}/t.$$

3. The degree of depolymerization (the number of broken linkages divided by the number of linkages at complete polymerization) is approximately $\alpha =$

$$2\,K_m c_{gm} M_0 \cdot \frac{1}{\eta_{sp}}.$$

4. The theory is exemplified by some experiments on the depolymerization of cellulose in sulphuric acid. When the cellulose concentration and its degree of polymerization are high, the experimental values differ somewhat from those calculated from the formulas.

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