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A Kinetic Calculation Method for Two-Step Polymerizations in Solution. Phenols- and Tannins-HCHO Reactions

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ABSTRACT

A kinetic calculation method for the calculation of the rate constants of phenolic and natural-polyphenolic compounds reactions with formaldehyde is presented. It is based on obtaining the intrinsic viscosity curve as a function of reaction time for the intended reaction mixtures. The method is capable of giving acceptable results only in cases where the experimental error is truly negligible.

INTRODUCTION AND APPROACH

Phenols and natural polyphenolic materials such as flavonoid-type tannins react with formaldehyde to give resins which are extensively used for the preparation of adhesives [1]. The series of reactions involved can be schematically illustrated as follows:

$$\begin{tikzcd}
\text{Phenols + HCHO} \arrow[r, "k_1"] \arrow[rr, bend left, "k_3"] & \text{phenol–}CH_2OH \arrow[r, "k_2"] & \text{phenols–}CH_2\text{–phenols} \\
\text{I} & \text{II} & \text{III}
\end{tikzcd}$$

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The rate constants of these reactions have been calculated for various phenols [2] and natural polyphenolic materials [3, 4] by several authors using several methods. In the case of natural polyphenolic materials where the calculation of the rate constants is complicated by the complexity and relative impurity of the polyphenolic materials used, only the total rate constant k_3 has been calculated. This has been due to

1. The overriding interest in the value of k_3, and relative lack of interest in k_1 and k_2, in adhesive resins chemistry and consequently
2. The nature of the method of analysis used (hydroxylamine hydrochloride method) [3-6]

Different methods of analysis are available to obtain the k_1 and k_2 values [5]; however, it was decided to evaluate a new method for their calculation. The value of the k_1 constant can be calculated easily by the same method used to calculate the total rate constant k_3. The hydroxylamine hydrochloride method [5] will give the concentration of free unreacted formaldehyde in the reaction mixture at any given time while the reaction is proceeding. Thus a curve of formaldehyde concentration as a function of time can be constructed (or a curve of formaldehyde consumption versus time if that is preferred). All the formaldehyde consumed during the reaction goes to form hydroxymethyl alcohols (II) and only part (or all, given enough reaction time) of these do condense to form condensates of Type III. Thus, in the hydroxymethylation step, one molecule of formaldehyde reacts with one natural flavonoid unit (only one reaction site per unit is available [3]) and consequently it is also possible to construct a curve (or table) of the total tannin amount which has been hydroxymethylated as a function of reaction time. Thus the rate constant k_1 can easily be calculated. This assumption is very reasonable indeed, and particularly near to reality during the early part of the total reaction where the condensation reaction II→III is negligible or absent.

The calculation of the rate constant k_2, however, is not as easy. It can, however, be calculated if a curve of total tannin amount that has reacted to form condensates of Type III as a function of time can be obtained experimentally. The formation of condensates of Type III leads to noticeable increases in the molecular weight of the mixture in solution. Thus a curve defining the increase in molecular weight will be useful for the calculation of k_2 if the increase in molecular weight can be both calculated and equated to the variation of tannin concentration in solution. The determination of molecular weight as a function of reaction time for tannin-formaldehyde (TF) condensates is difficult. Various techniques are available but all suffer from many disadvantages as applied to this particular case. Techniques such as gel permeation chromatography and vapor-phase osmometry require the TF to be dissolved in suitable solvents. However, it is not possible to isolate the TF condensate from the aqueous reaction mixture without causing further condensation. Therefore, the viscosity of the reaction mixture was measured by using a capillary viscometer, hence determining the intrinsic viscosity of the dissolved material. Determination of the intrinsic viscosity of aqueous solutions of tannin-formaldehyde reaction mixtures has already been shown possible by Pastore [6]. Relationships between molecular weight build-up and intrinsic viscosity already exist [7].

When a polymer sample is dissolved in a solvent, the frictional characteristics of this is changed due to the considerable difference between the mass of the solvent and solute molecules. The extent of viscosity increase can be empirically related to the molecular weight of the polymer sample. For this reason viscometry is widely used in determining the molecular mass for macromolecules.

U-tube viscometers are employed in constant temperature, atmospheric pressure, capillary viscometry which is one of the simpler methods of viscosity measurement. The efflux times of solvent and solution are measured.

The ratio of the flow time of a polymer solution (t) to that of the solvent (t_0) is equal to the ratio of their viscosities (η/η_0) if a solution and solvent have the same density. This is assumed to be true for dilute solutions [6, 7]. Thus the relative viscosity is given by

$$\eta_r = \eta/\eta_0 = t/t_0$$

As η_r has a lower limit of 1, the specific viscosity η_{sp} is used more

$$\eta_{sp} = \frac{\eta - \eta_0}{\eta_0} = \frac{t - t_0}{t_0} = \eta_r - 1$$

Molecular interference which affects the increase in viscosity cannot be totally prevented even at dilute concentrations [6, 7]. In order to overcome this effect, η_{sp} is extrapolated to zero concentration. The specific viscosity at that point theoretically reflects the influence of an isolated polymer molecule on the viscosity of the solvent. The extrapolation can be carried out in two ways. In one of them η_{sp} is expressed as a reduced quantity η_{sp}/c and a plot of this quantity against the concentration c gives a straight line which is defined by

$$\eta_{sp}/c = [\eta] + k'[\eta]^2 c$$

where k' is a shape-dependent factor and $[\eta]$ is the limiting viscosity number, usually called intrinsic viscosity. This parameter is characteristic for the polymer in a specific solvent.

The second method of extrapolation uses the inherent viscosity defined as ln η_r/c. This is plotted against concentration to give a straight line defined by

$$\frac{\ln \eta_2}{c} = [\eta] - k''[\eta]^2 c$$

Again the intercept is the intrinsic viscosity and k" is another shape-dependent factor. The Mark-Houwink equation, which follows, relates the intrinsic viscosity to weight-average molecular weight (M) of a polymer in a specific solvent and at a specific temperature [6, 8]:

$$[\eta] = KM^{\alpha}$$

In this equation K and α are constants for the polymer/solvent system at a specific temperature. They are obtained through calibration with polymer samples which have had their weight-average molecular weight (M) determined by absolute methods such as vapor-pressure osmometry, light scattering, or gel-permeation chromatography. The Mark-Houwink equation is known to apply for dilute solutions of only one polymer, where $[\eta]$ will reflect the average of the molecular weight distribution of this polymer. If the solution contains a mixture of chemically similar compounds, it is reasonable to expect that the intrinsic viscosity will reflect the average of the molecular weight distribution of all compounds in the mixture. Tannin can be considered a mixture of chemically similar compounds (natural flavonoid-type polyphenols) and so can its reaction medium when tannin is condensed with formaldehyde. After the condensation reactions have taken place, the mixture will be composed of polyphenolic polymers of different molecular weight, and $[\eta]$ will reflect the average of the molecular weight distribution of all the polyphenolic condensates. If this assumption is valid [6], tannin and formaldehyde can be reacted under different conditions and the increase in molecular weight during the reactions can be compared with each other just by comparison of the increase in $[\eta]$ for each reaction. If, as a further assumption [6], the Mark-Houwink equation holds for tannin systems, it is possible to take K and α as assuming constant values for all the polyphenolic polymers, as K and α vary only slightly for similar polymers. In this manner it is then possible to derive a useful expression for the relative increase in molecular weight from the Mark-Houwink equation. At times t = 0 and t = t min, this equation can be respectively written as

$$[\eta_0] = KM_0^{\alpha} \qquad [\eta_t] = KM_t^{\alpha}$$

where M_0 and M_t are the initial average molecular weight and the average molecular weight of the mixture after t minutes of reaction, respectively. Thus

$$K = [\eta_0]/M_0^{\alpha} \qquad \text{and} \qquad K = [\eta_0]/M_t^{\alpha}$$

$$[\eta_0]/M_0^{\alpha} = [\eta_t]/M_t^{\alpha}$$

$$(M_t/M_0)^{\alpha} = [\eta_t]/[\eta_0]$$

$$M_t/M_0 = ([\eta_t]/[\eta_0])^{1/\alpha}$$

The last expression represents the number of times that the average molecular weight has increased at time t.

For most polymers, α varies between 0.5 and 1.0. Taking these limits, the last expression can be expressed as

For $\alpha = 0.5$:

$$M_t/M_0 = ([\eta_t]/[\eta_0])^2$$

For $\alpha = 1.0$:

$$M_t/M_0 = [\eta_t]/[\eta_0]$$

Therefore

$$[\eta_t]/[\eta_0] \leq M_t/M_0 \leq ([\eta_t]/[\eta_0)]^2$$

The relative increase in the average molecular weight can then be well represented by the relative increase in intrinsic viscosity. Without knowing an accurate value of α, it is not possible to obtain absolute values of M_t/M_0. However, the $[\eta_t]/[\eta_0]$ ratio allows comparisons to be made between different reactions. This has been obtained by Pastore [6], notwithstanding the fact that determination of α by an absolute method was not done [6].

It is possible, however, and this is the theme of this article, to calculate the values of the rate constants k_2 without recurring to the exact determination of average molecular weight and α by absolute methods by just employing the $[\eta]$ curve as a function of time expressed as concentration of total dimerized tannin (flavonoid units) (III). The approach employed consists of

1. Obtaining by logarithmic regression analysis a mathematical function describing the increase versus reaction time of the total hydroxymethylated tannin concentration (T-CH_2OH), which is already known from the [HCHO] consumption curves obtained by the hydroxylamine hydrochloride method. Then
2. To mathematically extrapolate from the logarithmic regression function a prevision of the time = x at which all the tannin has passed through the hydroxymethylation stage (tannin all reacted with HCHO).
3. To express the $[\eta]$ versus time curve as a logarithmic function, by regression analysis and to make mathematical prevision on the value of $[\eta]$ at the time = x determined for the hydroxymethylated tannin curve.
4. To force on the intrinsic viscosity $[\eta]$ versus time curve that the concentrations of tannin at the beginning and at the end of the reaction at times $t_0 = 0$ and t = x be equal for both the $[\eta]$ and the total hydroxymethylated tannin curves and that the points at times 0 and x be coincident for the two curves.

We can then express, without varying its shape, the $[\eta]$ versus time curve in tannin concentration units. When the values of $[\eta]$ obtained experimentally are correct and significant, we will have the relationship of the two curves versus time, namely the curve of total tannin which has passed through hydroxymethylation and the curve of the total tannin dimerized ($[\eta]$ curve) as shown in Fig. 1.

If the $[\eta]$ curve is higher than the other curve, then the $[\eta]$ values were not correct or significant enough.

The forced extrapolation of the two curves to coincide (or intersect) at a common time = x is reasonably correct as at the completion of the reaction it can be assumed that all the hydroxymethylated tannin flavonoid units have dimerized with themselves or by reaction with other tannin flavonoid units.

Thus, by subtracting from the values of the curve of total tannin consumed (which represent the total cumulative amount of tannin which has been hydroxymethylated and <u>not</u> the amount of tannin present at any time = n which is present as hydroxymethylated tannin), obtained by HCHO methods, the values of the curve of the amount of tannin that has dimerized (obtained from the adapted $[\eta]$ curve), the values of decreasing hydroxymethylated tannin (II) versus reaction time can be obtained and from these the k_2 calculated.

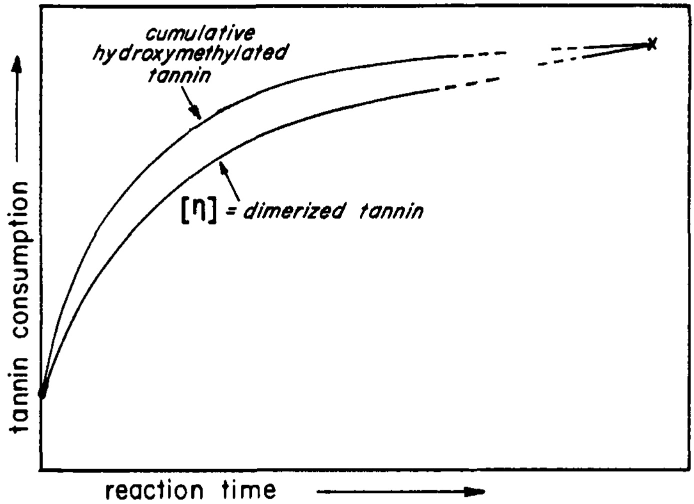

FIG. 1. Fitting of [η] and cumulative hydroxymethylated tannin curves as a function of reaction time.

EXPERIMENTAL

1. Formaldehyde Consumption

The values of formaldehyde consumption versus reaction time already reported [3, 6] for the reaction of pine tannin, wattle tannin, and simple phenols with HCHO at 25 to 40°C [3] and at 90°C [6] were used.

2. Intrinsic Viscosity Curve

The values of intrinsic viscosity of the reaction of wattle tannin with HCHO at 90°C already reported [6] were used. Furthermore, intrinsic viscosity curves were obtained by capillary viscometry at constant temperature bath by Ubbelohde U-tube viscometer.

From the HCHO consumption values and intrinsic viscosity values the k_1 and k_2 rate constants were calculated. The results obtained are shown in Table 1. In Table 1 the rate constants are expressed as k of the unreacted flavonoid polymer (k monomer) and k of the already dimerized or reacted polyflavonoid (k polymer).

TABLE 1. Example of Reaction Rate Constants Obtained with Method Tried

Reaction	Molar ratio	Reaction pH	Reaction temperature (°C)	k_1 monomer 2nd order ($L \times mol^{-1} \times s^{-1}$)	k_1 polymer 2nd order ($L \times mol^{-1} \times s^{-1}$)	k_2 monomer 2nd order ($L \times mol^{-1} \times s^{-1}$)
Pine tannin:formaldehyde	1:1	4.9	25	8.22×10^{-3}	5.40×10^{-5}	2.38×10^{-2}
Pine tannin:formaldehyde	1:1	9.0	25	2.85×10^{-2}	6.48×10^{-4}	2.54×10^{-2}
Wattle tannin:formaldehyde	1:1	9.0	25	6.41×10^{-3}	5.44×10^{-4}	Not calculable
Wattle tannin:formaldehyde	1:1	9.0	40	-	4.06×10^{-3}	1.48×10^{-3}
Phloroglucinol:formaldehyde	1:1	4.9	25	2.34×10^{-1}	6.75×10^{-3}	Not calculable

DISCUSSION

The method is experimentally very simple but the mathematical treatment of the values is fairly complicated. Two problems often beset this method.

1. Regression curves at the 95 to 99% significance (coefficient of correlation) are not always good enough to give good results: this causes the following problem.
2. The $[\eta]$ curve expressed in tannin concentrations does very often present higher values than the cummulative hydroxymethylated curve. This result is obviously absurd. This problem affected all Pastore's [6] experimental values as well as some of Rossouw et al.'s [3]. In the case of Pastore's results where (as for most of Rossouw's results) the regression coefficient of correlation is often very near to the 99% significance level, the explanation which can be offered is that the system of measurement of viscometry is far too slow for the speed of the reaction.

In a few cases, where both the coefficient of correlation is very good and the experimental error is likely to be really negligible, the method presented works well; these are the cases listed in Table 1.

In conclusion, the particular method exposed is too unyielding and necessitates measurement precisions far in excess of other existing experimental methods, at least for phenols- and tannins-HCHO reactions in water solution, and as such its use is not recommended.

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