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Description and Analysis of (Hydroxyethyl)cellulose

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ABSTRACT: (Hydroxyethyl)cellulose (HEC) is described by a statistical kinetic model. Closed-form mathematical expressions relate quantities of interest (e.g., molar substitution, average length of oxyethylene side chains, and number of enzymatically effected polymer chain breaks) and the relative rate constants of oxyethylation of the three hydroxyls on the glucosyl unit of cellulose and the one on the pendent hydroxyethyl group. Materials made under variable alkali conditions are also described. Literature data are analyzed according to this model. It is shown that, for a complete description, the characterization of HEC must include the measurement of at least four suitably chosen analytical quantities. However, three suitable measurements may provide information sufficient to predict accurately such quantities of interest as the average length of the oxyethylene side chains and the number of enzymatically effected polymer chain breaks.

Introduction

The reactivity of the three hydroxyl groups at positions 2, 3, and 6 on the glucosyl unit of cellulose offers a variety of possibilities for making useful derivatives. Cellulose-based polymers with predetermined properties are made by appropriate derivatization. In most cases the desired properties are achieved by making a partially substituted derivative, i.e., by substituting on the average only one or two of the three hydroxyl hydrogens. Thus, the original homopolymer is transformed into a copolymer of eight or more monomers randomly distributed along the polymer chain. The description and characterization of polymers of such complexity have been challenging problems of longstanding interest. The theoretical framework for studying the distribution of substituents in partially substituted cellulose esters and ethers was presented by Spurlin in 1939.[1] It was only recently, however, that the validity and utility of his statistical models were clearly demonstrated.[2,3] As expected,[1] cellulose nitrate esters are consistent with the equilibrium model,[2] while (carboxymethyl)cellulose ethers conform to the kinetic model.[3]

(Hydroxyethyl)cellulose (HEC) is an important water-soluble polymer with a variety of industrial applications. It is made by the reaction of alkali cellulose with ethylene oxide.[4] The resulting product can be regarded as a copolymer of many monomers: glucosyl units of different degrees of substitution with oxyethylene side chains of different length. The manner in which the substituents are distributed along the polymer chain and among the three positions on the glucosyl unit is important in determining the properties of HEC, e.g., solution quality and resistance to enzymatic degradation.[5,6] These distributions are governed by the rate constants of reaction of the hydroxyls and by the extent of reaction. The relative rate constants of the three hydroxyls and of the pendent hydroxyethyl depend on the reaction conditions in general and on the alkali concentration in particular.[6,7] Information on the kinetic parameters can be extracted from suitable quantities determined by analytical methods. Croon and Lindberg[8] hydrolyzed HEC to monosaccharides and fractionated these on a carbon column. Then they used a statistical model in order to determine the relative rate constants from the analytical data. However, it can be shown that one of the assumptions made in the derivations does not hold in most cases of interest. In order to avoid such assumptions, Glass et al. used a stochastic model and computer simulations.[6] While this approach is accurate, its application to a set of analytical data on a given product is rather impractical.

This article presents a comprehensive mathematical framework for the description of HEC and for the treatment and interpretation of analytical data. Models for the enzymatic hydrolysis of HEC and for the description of materials made under variable alkali conditions are also provided. The resulting expressions are applied in the analysis of data taken from the literature. Analytical strategies for the characterization of HEC can be formulated on the basis of this framework and on the results of the ensuing computer simulations.

Theory

Mathematical Description. The model used in this work is similar to previous ones.[5,6,8] It involves the following assumptions: (a) All glucosyl units in the cellulose chain are equally accessible for reaction. (b) The *relative* rate constants (k_i and k_x) of reaction of the hydroxyls remain unchanged throughout the process. (c) Substitution within a given unit does not affect the reactivity of the remaining hydroxyls. (d) The effects of end groups are negligible.

Thus, for any given position i on the glucosyl unit one can write the following sequence of reactions with ethylene oxide (EO):

$$-\mathrm{C}_i\underset{p_i}{-}\mathrm{OH} + \mathrm{EO} \xrightarrow{k_i} -\mathrm{C}_i\underset{Y_i}{-\mathrm{O}}\mathrm{EOH} \tag{1}$$

$$-\mathrm{C}_i\underset{Y_i}{-\mathrm{O}}\mathrm{EOH} + \mathrm{EO} \xrightarrow{k_x} -\mathrm{C}_i\underset{Y_{ii}}{-\mathrm{O}}\mathrm{EOEOH} \tag{2}$$

$$-\mathrm{C}_i\underset{Y_{ii}}{-\mathrm{OEO}}\mathrm{EOH} + \mathrm{EO} \xrightarrow{k_x} -\mathrm{C}_i\underset{Y_{iii}}{-\mathrm{OEO}}\mathrm{EOEOH} \tag{3}$$

$$-\mathrm{C}_i\underset{Y_{iii}}{-\mathrm{OEO}}\mathrm{EOEOH} + \mathrm{EO} \xrightarrow{k_x} -\mathrm{C}_i\underset{Y_{iiii}}{-\mathrm{OEO}}\mathrm{EOEOEOH} \tag{4}$$

and so on, where the mole fractions are indicated under each species.

Formation of cellulose ethers in reactions of the type similar to eq 1 was treated by Spurlin.[1] He has shown that the degree of substitution at each position, x_i, is given by

$$x_i = 1 - \exp(-Bk_i) \tag{5}$$

where B is a time factor. Thus, the probability, p_i, of having an unsubstituted hydroxyl at position i is

$$p_i = \exp(-Bk_i) \tag{6}$$

The total (average) degree of substitution of the glucosyl residues is

$$D = x_2 + x_3 + x_6 \tag{7}$$

$$D = 3 - \exp(-Bk_2) - \exp(-Bk_3) - \exp(-Bk_6) \tag{8}$$

The mole fraction, S_0, of unsubstituted glucosyl units is given by the product of the probabilities of having un-

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substituted hydroxyls at each of the three positions. Thus,

$$S_0 = \exp[-B(k_2 + k_3 + k_6)] \qquad (9)$$

Analogously, the mole fraction of unsubstituted vicinal diols (at positions 2 and 3) is

$$V_{23} = \exp[-B(k_2 + k_3)] \qquad (10)$$

The introduction of a pendent hydroxyethyl group by the reaction of eq 1 allows for chain extension by the reactions of eq 2–4. Thus, at any given position i, one may have pendent oxyethylene chains containing one, two, three, four, or more oxyethylene units. The mole fractions (of total units) of these are designated with Y_i, Y_{ii}, ..., Y_{ni}. The positional degree of substitution can be written as the sum

$$x_i = Y_i + Y_{ii} + Y_{iii} + ... \qquad (11)$$

The differential equations describing the time evolution of the mole fractions, Y_i, Y_{ii}, etc., have been set by Croon and Lindberg.[8] The equations are

$$\mathrm{d}Y_i/\mathrm{d}t = k_i(1 - x_i) - k_xY_i \qquad (12)$$

$$\mathrm{d}Y_{ii}/\mathrm{d}t = k_xY_i - k_xY_{ii} \qquad (13)$$

$$\mathrm{d}Y_{iii}/\mathrm{d}t = k_xY_{ii} - k_xY_{iii} \qquad (14)$$

and so on. It may appear that, in writing eq 12–14 in this form, it is tacitly assumed that the concentration of ethylene oxide remains constant throughout the process. However, as pointed out by Spurlin,[1] the model assumes that only the relative rate constants, rather than the actual reaction rates, remain unchanged. Thus, any change in the ethylene oxide concentration is incorporated as a change in the actual rates but has no effect on the values of the relative rate constants. In the final expressions, the factor B (which has the dimension of time) is introduced instead of the actual time, t. This underscores the fact that these expressions describe statistical distributions and related quantities characteristic of a final product rather than the actual kinetics of its formation.

In order to simplify the solution of the differential equations, Croon and Lindberg[8] (and subsequently Stratta[5]) assumed that $1 - Y_i \ll Y_{ii} + Y_{iii}$. The assumption implies that (see eq 11) $x_i \ll 1$. This assumption is not valid for most HEC products of interest. Positional degrees of substitution as high as 0.8 are not uncommon.[6]

Exact solutions of eq 12–14 were obtained by the method of integrating factors.[9] The solutions are

$$Y_i = k_i(k_x - k_i)^{-1}[\exp(-Bk_i) - \exp(-Bk_x)] \qquad (15)$$

$$Y_{ii} = k_ik_x(k_x - k_i)^{-2}\exp(-Bk_i) - k_ik_x(k_x - k_i)^{-1}[B + (k_x - k_i)^{-1}]\exp(-Bk_x) \qquad (16)$$

$$Y_{iii} = k_ik_x^2(k_x - k_i)^{-3}\exp(-Bk_i) - k_ik_x^2(k_x - k_i)^{-1}[B(k_x - k_i)^{-1} + B^2/2 + (k_x - k_i)^{-2}]\exp(-Bk_x) \qquad (17)$$

The molar substitution, M, i.e., the average number of oxyethylene units per glucosyl unit, is given by

$$M = \sum_i (Y_i + 2Y_{ii} + 3Y_{iii} + ...) \qquad (18)$$

The molar substitution, M_i, at position i is

$$M_i = Y_i + 2Y_{ii} + 3Y_{iii} + ... \qquad (19)$$

The time evolution of M_i is

$$\mathrm{d}M_i/\mathrm{d}t = \mathrm{d}Y_i/\mathrm{d}t + 2\mathrm{d}Y_{ii}/\mathrm{d}t + 3\mathrm{d}Y_{iii}/\mathrm{d}t + ... \qquad (20)$$

Substituting eq 12–14 into eq 20, one obtains

$$\mathrm{d}M_i/\mathrm{d}t = k_i(1 - x_i) + k_x(Y_i + Y_{ii} + Y_{iii} + ...) \qquad (21)$$

and, using eq 11

$$\mathrm{d}M_i/\mathrm{d}t = k_i(1 - x_i) + k_xx_i \qquad (22)$$

With the use of eq 5, eq 22 reduces further to

$$\mathrm{d}M_i/\mathrm{d}t = k_x + (k_i - k_x)\exp(-k_it) \qquad (23)$$

The solution of this equation is

$$M_i = Bk_x + (1 - k_x/k_i)[1 - \exp(-Bk_i)] \qquad (24)$$

where the factor B has replaced the actual time. Summing over the three positions, one has the final form

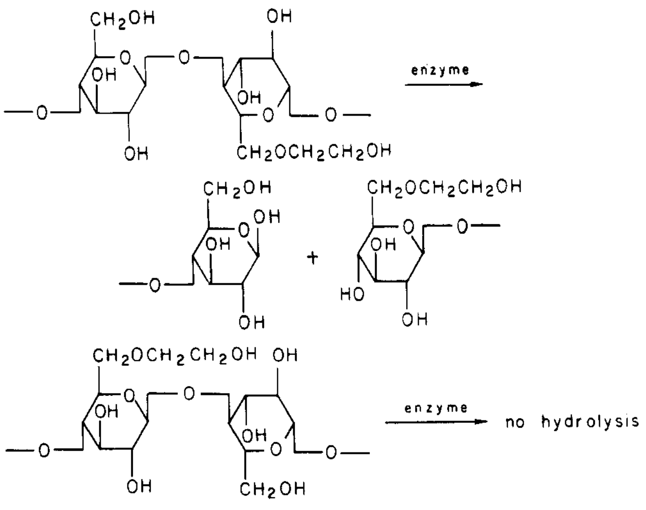
$$M = 3Bk_x + 3 - k_x\sum_i(1/k_i) + \sum_i[(k_x/k_i - 1)\exp(-Bk_i)] \qquad (25)$$

Using eq 5 and 7, one obtains the form

$$M = 3Bk_x + D - k_x\sum_i(x_i/k_i) \qquad (26)$$

The remarkable feature of eq 24–26 is that they provide in a closed form[10] explicit functional dependencies of the molar substitution on the kinetic parameters and on the degree of substitution. Also, no assumptions (excepting those of the model) were involved in the derivation. The system of equations (5)–(10), (15)–(17), and (24)–(26) can serve as a framework for the treatment of analytical data and for the description of HEC.[11] On the basis of these equations, rate constants and oxyethylene chain-length distributions can be readily calculated with a pocket calculator.

Enzymatic Hydrolysis. In the presence of moisture, cellulose and its derivatives are hydrolyzed and degraded by a class of enzymes called cellulases. Many of the uses of HEC demand that the product be stable toward enzymatic (and microbial) degradation. Therefore the problem of enzymatic degradation has been of interest among industrial researchers.[6,12] Other workers have used HEC as a model substance in studies of the mechanism of action of the cellulases.[13] It is generally accepted in the literature that cellulase breaks the polymer chain at points containing adjacent unsubstituted glucosyl residues.[6,12,13] However, it has been observed that the experimentally determined number of such points is larger than statistical estimates based on the fraction of unsubstituted anhydroglucose.[6,12,13] A detailed analysis of the products of enzymatic hydrolysis led Klop and Kooiman[13] to suggest that additional chain breaks occur at points containing the sequence of unsubstituted and substituted-only-at-position-6 glucosyl residues, i.e., β-glucosyl (1→4)-6-*O*-(substituted)glucosyl. The reversed sequence of β-6-*O*-(substituted)glucosyl (1→4)glucosyl is resistant to enzymatic hydrolysis.



The probability of occurrence of pairs of unsubstituted glucosyl residues is S_0^2. Only one break in the polymer chain will result if there are more than two consecutive residues of this kind. Therefore, the number of chain breaks at such points, C_0, is the sum of isolated sequences containing two, three, etc. unsubstituted residues, i.e.

$$C_0 = S_0^2(1 - S_0)^2 + S_0^3(1 - S_0)^2 + ... = S_0^2(1 - S_0) \quad (27)$$

The probability of occurrence of sequences of the second type is

$$C_6 = \tfrac{1}{2}S_6S_0(1 - S_0)^2 \quad (28)$$

where $S_0(1 - S_0)^2$ is the probability of having isolated unsubstituted residues, S_6 is the fraction of residues substituted only at position 6, and the factor $^1/_2$ accounts for the fact that only one of the two possible permutations of these sequences is susceptible to enzymatic hydrolysis. Thus, the total number of polymer chain breaks (per monomer unit) is

$$C = S_0^2(1 - S_0) + \tfrac{1}{2}S_6S_0(1 - S_0)^2 \quad (29)$$

It should be emphasized that eq 29 applies to polymeric materials of high degrees of substitution and low fractions of unsubstituted glucosyl residues.[14] Having in mind that[1]

$$S_6 = p_2p_3(1 - p_6) \quad (30)$$

and (see eq 6 and 9)

$$p_2p_3 = S_0/p_6 \quad (31)$$

one obtains the expression

$$C = S_0^2(1 - S_0) + \tfrac{1}{2}S_0^2(1 - S_0)^2(1/p_6 - 1) \quad (32)$$

Wirick, in his interpretation of enzymatic hydrolysis data,[12] used a similar algorithm, but without the factor of $^1/_2$ in the last term of eq 32. As a result his conclusions, while essentially correct, remain incomplete. This apparent failure of the model might be what compelled Glass et al.[6] to postulate that enzymatic hydrolysis occurs between adjacent residues both of which are unsubstituted at position 2. It can be shown that this alternative often predicts numbers of chain breaks, which are larger than experimentally observed.

Varying Reactivity Ratios. Glass et al.[6] have reported on HEC made under conditions of varying reactivity ratios (achieved by varying the alkali concentration). The description of materials made in this way is complicated since upon changing the reactivity ratios, one must consider as a starting material HEC of a given composition, rather than cellulose composed of unsubstituted residues with a mole fraction of unity. For convenience, all quantities and parameters pertaining to this starting material or to the initial phase of the process will be indicated by a prime. Thus, p_i' is the probability of having an unsubstituted hydroxyl at position i on the glucosyl unit at the point of change. It is given by

$$p_i' = \exp(-B'k_i') \quad (33)$$

where k_i' is the rate constant for reaction at this position in the initial phase and B' is a time factor. In the final product, one will have

$$p_i = p_i' \exp(-Bk_i)$$

or

$$p_i = \exp(-B'k_i' - Bk_i) \quad (34)$$

Already at this point, it becomes clear that, even if the three quantities p_2, p_3, and p_6 could be determined, one could not separate the sum $B'k_i' + Bk_i$. Thus, whereas for constant reactivity ratios, measurements of p_i' yield the relative rate constants, viz.

$$k_i'/k_j' = \ln p_i'/\ln p_j' \quad (35)$$

under conditions of varying reactivity ratios, this becomes impossible. Now one has

$$\ln p_i/\ln p_j = (B'k_i' + Bk_i)/(B'k_j' + Bk_j) \quad (36)$$

Many quantities of interest can be expressed with the probabilities given by eq 34. These include the positional degree of substitution (eq 5), the average degree of substitution (eq 7), the mole fraction of unsubstituted glucosyl units (eq 9), and the mole fraction of vicinal diols (eq 10). In order to derive an expression for the molar substitution, M, of the final product, the set of differential equations (eq 12–14) must be written for the appropriate conditions. Thus

$$\mathrm{d}Y_i/\mathrm{d}t = k_ip_i - k_xY_i \quad (37)$$

$$\mathrm{d}Y_{ii}/\mathrm{d}t = k_xY_i - k_xY_{ii} \quad (38)$$

and so on, where

$$p_i = p_i' \exp(-k_it) \quad (39)$$

with p_i' now being a constant. The solution of eq 37 is

$$Y_i = p_i'k_i(k_x - k_i)^{-1}[\exp(-Bk_i) - \exp(Bk_x)] + Y_i' \exp(-Bk_x) \quad (40)$$

where the factor B has replaced the actual time and

$$Y_i' = k_i'(k_x' - k_i')^{-1}[\exp(-B'k_i') - \exp(B'k_x')] \quad (41)$$

For the molar substitution at position i, one has (see eq 23)

$$\mathrm{d}M_i/\mathrm{d}t = k_x + p_i'(k_i - k_x) \exp(-k_it) \quad (42)$$

The solution of eq 42 is

$$M_i = M_i' + Bk_x + p_i(k_x/k_i - 1)[\exp(-Bk_i) - 1] \quad (43)$$

where M_i' is the molar substitution at position i before the reactivity ratios are changed. For the total (average) molar substitution, we sum over the three positions and obtain

$$M = M' + 3Bk_x + \sum_i\{p_i'(k_x/k_i - 1)[\exp(-Bk_i) - 1]\} \quad (44)$$

Data Analysis

The monomer composition and substituent distribution of HEC can be fully described by five parameters: the four rate constants k_2, k_3, k_6, and k_x and the factor B. However, because the latter parameter appears in all equations as the product with a rate constant, only relative rate constants can be dtermined.[1] Therefore, since the reactivity of the hydroxyl at position 3 is the lowest, it is assumed that $k_3 = 1$. Thus, one is left with four unknown parameters. At least four independent observations are needed for their determination.

Results on molar substitution (M), unsubstituted glucosyl units (S_0), and vicinal diols (V_{23}) have been reported by Glass et al.[6] These authors claim that the set of relative rate constants can be *uniquely* determined from such measurements and provide stochastic simulations in support of this contention. We note, however, that four parameters cannot be determined with only three observations. The data given in Figure 1 of ref 6 are analyzed in the following fashion. The logarithms of V_{23} and of S_0/V_{23} are plotted against the logarithm of S_0 in Figure 1. The first line in Figure 1 is described by (see eq 9 and 10)

$$\ln V_{23} = (\ln S_0)(k_2 + k_3)/(k_2 + k_3 + k_6) \quad (45)$$

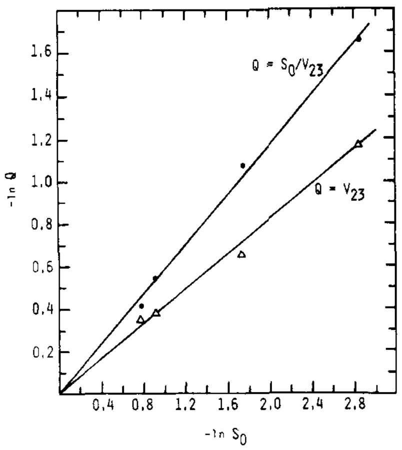


Figure 1. Graphical analysis according to eq 45 and 46 of the data from ref 6 on unsubstituted glucosyl units (S_0) and vicinal diols (V_{23}).

The slope of this line gives $(k_2 + k_3)/(k_2 + k_3 + k_6)$. The second line in Figure 1 is described by

$$\ln (S_0/V_{23}) = (\ln S_0)k_6/(k_2 + k_3 + k_6) \qquad (46)$$

The slope of this line gives $k_6/(k_2 + k_3 + k_6)$. Assuming $k_6 = 1$, a relative value of B can be obtained from ln (S_0/V_{23}). Thus we have a set of values for B and the relative value of $k_2 + k_3$ from the ratio of two slopes. With these, the data on M were analyzed with eq 26 and a set of equations of the type of eq 5 to yield values of k_x for different ratios of k_2/k_3. As could be anticipated, k_x was rather insensitive to the value of k_2/k_3, since none of the measured quantities separates k_2 and k_3. The only parameters that can be determined from the data of Glass et al. are $k_x/k_6 = 1.471$, which is in excellent agreement with the value of 1.50 in ref 6, and $k_6/(k_2 + k_3) = 1.424$, which should be compared with 1.333 in ref 6. In the present treatment, analytical data were used to calculate a set of parameters with the equations describing the relationships between these quantities. Glass et al.,[6] on the other hand, had to make a decision regarding the preference of one set of parameters over another from the conformity of the data to computer-simulated curves. In order to obtain an accurate set of parameters with this procedure a large number of simulated curves is required.

Measurements on HEC made under variable alkali conditions were carried out by Glass et al.[6] They reported molar substitution (M) and mole fraction of unsubstituted glucosyl units (S_0) for seven samples with M values in the range 2.2–4.4, with additional data on the fraction of vicinal diols (V_{23}) for four of the samples. In the following treatment of these data, it is assumed that initially $k_2':k_3':k_6':k_x' = 4:1:7:10$, as determined above (the k_2/k_3 value is assumed), and that before reactivity ratios were changed the material had $M' = 1.0$.[6] The treatment proceeds as described above for the normal process. First, the values of B are determined from the values of ln (S_0/V_{23}), assuming $k_6 = 1.0$. Then values of $(k_2 + k_3)/k_6$ are obtained from ln V_{23}/ln (S_0/V_{23}). The average value for the four samples is $(k_2 + k_3)/k_6 = 5.48$. Then assuming $k_2/k_3 = 3.0$, values of k_x are calculated from the values of M by solving eq 44 for k_x. The average value thus obtained is $k_x = 3.03$. Finally, the results are expressed relative to k_3, giving $k_2:k_3:k_6:k_x = 3:1:0.73:2.21$. Using a trial-and-error procedure, i.e., comparison of data with computer-simulated curves, Glass et al.[6] report $k_2:k_3:k_6:k_x = 3:1:1:2$. The experimental data along with the curves calculated with the parameters determined here are presented in Figure 2. It is emphasized that these curves are not very sensitive to the values of k_2/k_3 and that the assumption $k_2/k_3 = 3.0$ is an operative one.

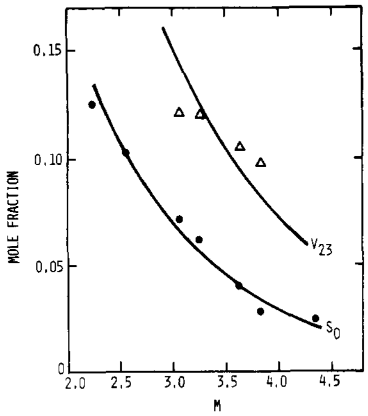


Figure 2. Plots of the mole fractions of unsubstituted glucosyl units (S_0) and vicinal diols (V_{23}) against the molar substitution (M) for HEC made under variable alkali conditions. Data are from ref 6. The curves are calculated with $k_2:k_3:k_6:k_x = 3:1:0.73:2.21$ (see text).

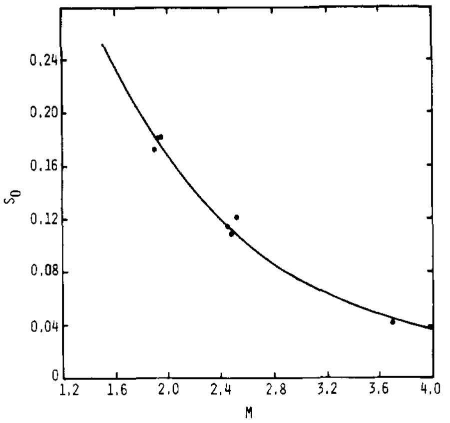


Figure 3. Mole fraction of unsubstituted glucosyl units (S_0) plotted against the molar substitution (M). Data are from ref 12. The curve is calculated with $k_2:k_3:k_6:k_x = 4.0:1.0:12.37:12.44$.

Wirick reported molar substitution (M), unsubstituted glucosyl units (S_0), and number of enzymatically effected polymer chain breaks (C) for a series of commercial samples.[12] His data were analyzed in the following fashion. First, values of p_6 were calculated from the experimental values of C and S_0 by solving eq 32 for p_6. Then the ratio (see eq 6 and 9)

$$(k_2 + k_3)/k_6 = \ln S_0/\ln p_6 - 1$$

was calculated. Finally, the value of k_x was obtained by solving eq 25 and using the experimental value of M. For this purpose an assumption had to be made regarding the value of k_2/k_3. This assumption, however, is not serious, since the value of k_x is not very sensitive to the k_2/k_3 ratio. The results, averaged over all samples, are $(k_2 + k_3)/k_6 = 0.404$ and $k_x/k_6 = 1.006$. The experimental data on S_0 and C along with curves calculated with $k_2/k_3 = 4.0$ are plotted in Figures 3 and 4, respectively. This analysis shows that the number of enzymatically effected polymer chain breaks, in addition to being an important property of HEC, is a useful analytical quantity.

Discussion

A complete description of HEC requires a set of four parameters. Therefore, at least four analytical quantities are necessary for the determination of these parameters. With only three quantities such as, e.g., the molar substitution (M), the fraction of unsubstituted glucosyl units (S_0), and the fraction of vicinal diols (V_{23}), or M, S_0, and

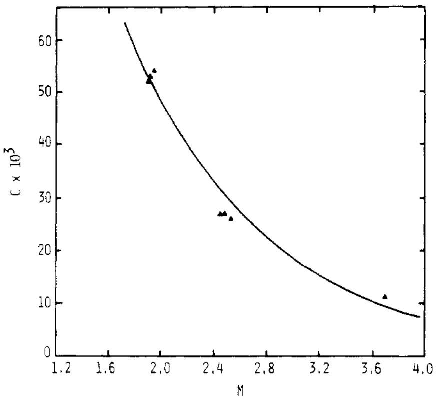


Figure 4. Number of enzymatically effected polymer chain breaks (C) plotted against the molar substitution (M). Data are from ref 12. The curve is calculated with k_2:k_3:k_6:k_x = 4.0:1.0:12.37:12.44.

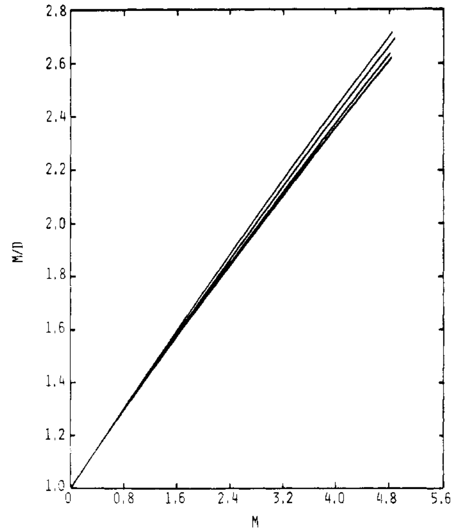


Figure 5. Computer simulation of the average length of the oxyethylene side chains (M/D) as a function of the molar substitution (M) at constant ratios of $(k_2 + k_3)/k_6 = 5/7$ and $k_x/k_6 = 10/7$ and a different k_2/k_3 ratio of (from top to bottom) 4.0, 3.0, 2.0, and 1.0.

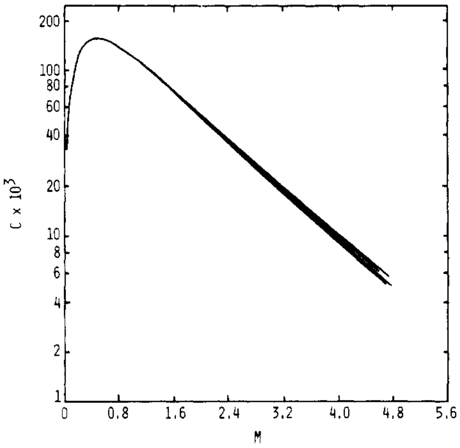


Figure 6. Computer simulation of the number of enzymatically effected polymer chain breaks (C) as a function of the molar substitution (M) at constant ratios of $(k_2 + k_3)/k_6 = 5/7$ and $k_x/k_6 = 10/7$ and a different k_2/k_3 ratio of (from top to bottom) 4.0, 3.0, 2.0, and 1.0.

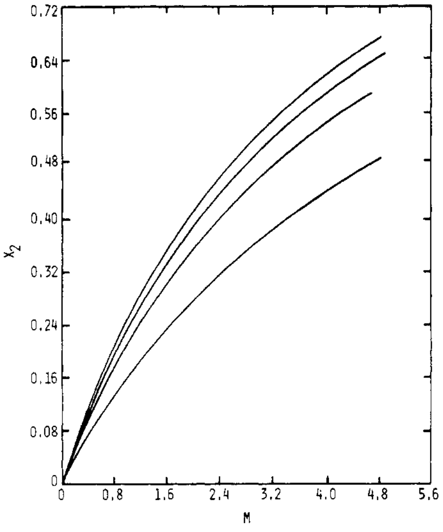


Figure 7. Computer simulation of the degree of substitution at position 2 on the glucosyl unit (x_2) as a function of the molar substitution (M) at constant ratios of $(k_2 + k_3)/k_6 = 5/7$ and $k_x/k_6 = 10/7$ and a different k_2/k_3 ratio of (from top to bottom) 4.0, 3.0, 2.0, and 1.0.

the number of enzymatically effected chain breaks (C), one can obtain a partial description. Specifically, in these examples, the ratios $(k_2 + k_3)/k_6$ and k_x/k_6 can be determined. The ratio k_2/k_3 is needed in order to complete the description. Nevertheless, with only three parameters, a number of important quantities can be predicted with sufficient accuracy. Thus, as shown in Figure 5, for a given M value the average length of the oxyethylene side chain (given by M/D) is almost independent of the k_2/k_3 ratio at constant $(k_2 + k_3)/k_6$ and k_x/k_6 ratios. Figure 6 shows the similar behavior for the number of enzymatically effected polymer chain breaks. It was also found that, for a given M value, the values of S_0, V_{23}, and x_6 are similarly insensitive to variations in the k_2/k_3 ratio.

As could be anticipated, the degrees of substitution at positions 2 and 3 on the anhydroglucose unit, x_2 and x_3, are very sensitive to variations in the k_2/k_3 ratio [at constant $(k_2 + k_3)/k_6$ and k_x/k_6 ratios]. The results of the computer simulation for x_2 are shown in Figure 7. Thus, a complete characterization of HEC must include measurements of either x_2 or x_3.

It is of interest to note that the mole fraction of vicinal diols (V_{23}) and the number of enzymatically effected polymer chain breaks (C) are related quantities and contain similar, rather than complementary, information. The latter quantity (see eq 32) is a function of S_0 and $1/p_6$. Similarly, from eq 9 and 10, one has $V_{23} = S_0/p_6$. Thus, the value of C can be calculated from data on S_0 and V_{23}.

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expression, probably because of its restricted nature. Brown, W. *Ark. Kemi* **1961**, *18*, 227.
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(14) Equation 29 describes the number of chain breaks as measured conveniently by the change in the degree of polymerization.[12,13] It can be shown by computation that as S_0 increases C will increase to a maximum of 0.144 at $S_0 \simeq 0.6$. However, C will decrease with further increase in S_0, reaching zero at $S_0 = 1$. Thus, the applicability of this treatment is limited to materials with $S_0 < 0.6$. HEC products of interest have fairly high degrees of substitution,[5] and the mole fraction of unsubstituted glucosyl residues is usually $S_0 < 0.3$.[6,12]

Model Reaction Pathways in Kraft Lignin Pyrolysis

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ABSTRACT: Kraft lignin pyrolysis was analyzed in terms of the experimental thermolyses of 1,2-diphenylethane, *cis*- and *trans*-stilbene, diphenylmethane, and triphenylethylene, all compounds mimicking prevalent Kraft lignin structural moieties. The experiments revealed five first-order diphenylethane pyrolysis pathways, the most important of which led to formation of toluene. Degradative pyrolysis of either stilbene isomer was equivalent to decomposition of a near-equilibrium mixture in which trans was prevalent. Diphenylmethane pyrolysis yielded benzene, toluene, and fluorene, and triphenylethylene pyrolyzed to these three and also diphenylmethane, diphenylethane, stilbene, and phenanthrene. All Arrhenius parameters of the pyrolysis pathways were determined. The present results are used in analysis of the thermal reactions of Kraft lignin. Of note, reaction pathways for the formation of methyl-substituted phenolics and hydroxyl-substituted fused-ring aromatics are developed.

Introduction

Conversion of macromolecular resources to lower molecular weight chemicals will be enhanced through elucidation of the process-controlling reaction pathways, kinetics, and mechanisms. Lignin pyrolysis to gas, liquid, tar, and char product fractions, for example, yields both useful and undesirable components, and strategies for selective production of useful products remain unclear on account of the complexity of both the lignin structure and its pyrolysis product spectra. These complexities motivate the use of simple model compounds whose chemical structures mimic structural residues found in the macromolecule. The relatively simple product spectra obtained from model compound pyrolyses allow inference of a macromolecule's operative pyrolysis pathways, kinetics, and, in favorable cases, mechanisms. The present analysis of Kraft lignin pyrolysis, then, is as discerned through the experimental pyrolyses of the model compounds 1,2-diphenylethane (DPE), *cis*- and *trans*-stilbene, diphenylmethane (DPM), and triphenylethylene (TPE).

Structural analyses (Freudenberg, 1968; Glasser, 1981) show native lignin to be a copolymer of single-ring phenolic units that can be characterized by the bonds that connect them and also by the substituents each ring possesses (Klein and Virk, 1981). For the present analysis the influence of Kraft pulping on the types and proportions of substituents and interunit links that a Kraft lignin comprises was inferred from the structural scenario presented by Marton (1971).

Comparison of native and Kraft lignin structural information shows that the α- and β-aryl alkyl ether linkages so prevalent in native lignins are scarce in Kraft lignins and are replaced, in large part, by diphenylethane, diphenylmethane, stilbene, and triphenylethylene linkages; other Kraft lignin linkages are akin to biphenyl, diphenyl ether, and phenethyl phenyl ether (PPE) molecules. Since only one PPE linkage appears in the Marton structure and biphenyl and diphenyl ether linkages are thermally stable (Klein, 1981), the present analysis was formulated in terms of the pyrolyses of the hydrocarbons diphenylethane, stilbene, diphenylmethane, and triphenylethylene. By extending similar analyses of native lignins and the oxygen-containing interunit linkages contained therein (Klein and Virk, 1983) to include hydrocarbon reactions, this analysis should therefore reveal the essential differences between native and Kraft lignin pyrolysis.

Previous Kraft lignin pyrolyses provided a framework for the analysis. Iatridis and Gavalas (1979) reported the yields of permanent gases, methanol, acetone, and five single-ring phenolics as a function of pyrolysis temperature and time. Connors et al. (1980) found phenols, guaiacols, catechols, char, methane, and carbon dioxide from pyrolysis in tetralin. Chan and Krieger (1981) detailed the yields and components of gas, aqueous distillate, phenolic, and carbonaceous residue product fractions obtained from microwave pyrolysis, and their identification of fused-ring fluorene, anthracene, and naphthalene products from the single-ring lignin substrate is noteworthy. Graef et al. (1979) found the fused-ring naphthalene, anthracene, and acenaphthene products from microwave-induced plasma pyrolysis of lignin. These pyrolyses of actual lignins have provided useful product spectra information but have yet to reveal the operative reaction pathways and intrinsic chemical kinetics involved. This motivated the present approach.

Previous pyrolyses of the model compounds are also informative. Pyrolysis of diphenylethane (DPE) in hydrogen-donor solvent occurs with solvent-independent first-order kinetics and yields a rather simple solvent-dependent product spectrum in which toluene is the major component (Brower, 1977; Collins et al., 1977; Cronauer et al., 1978; Panvelker et al., 1982; Benjamin et al., 1978; Kamiya et al., 1979). Arrhenius parameters are similar for liquid- and gas-phase pyrolyses (Sato et al., 1978), although product spectra from the latter are more like those from thermolysis in the absence of donor solvent, where, in

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