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Application of a modified rate equation to the acetylation of wood

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Abstract A modified rate equation, in which the diffusion of reagent was taken into consideration, was proposed and applied to results reported previously for the acetylation of wood. The equation was fitted more successfully to the prolonged as well as the early stage of the reaction than a common first-order rate equation. Although the conclusions were virtually unchanged, the reliability was enhanced because reaction parameters such as the rate constant, ultimate extent of the reaction, and activation energy calculated for the modified equation were based on much more data than those reported previously. The equation proposed here may be applicable not only to acetylation but to other chemical modifications of cellulosic materials in heterogeneous systems.

Key words Acetylation · Rate equation · Kinetics · Diffusion

Introduction

In previous work,¹ a pseudo first-order rate equation was applied to the acetylation of wood, which was carried out in various reaction systems, and the reaction kinetics were discussed. Notably, we compared the activation energy of acetylation with that reported by Hill et al.,² and explained the difference. In the kinetic analysis, the applicability of the rate equation to the data was not always satisfactory for us or for Hill et al. Therefore, we were obliged to discuss the kinetics by using less reliable reaction parameters estimated by excluding the data for the later stage of the reaction.

Because the chemical modifications of wood or cellulosic materials proceed in a heterogeneous system, the reaction is controlled by the diffusion of reagent. Therefore, only the data for the early stage was used for the application of the

rate equation. Such a procedure can be used to estimate the reaction parameters at the initial stage of the reaction, but not to predict those for the overall reaction.

In this article, a modified rate equation, which is applicable to the prolonged as well as initial stage of the reaction, was proposed and applied to previously presented data.

Theory

In the previous study,¹ a first-order rate equation,

$$x = a \times (1 - e^{-kt}), \quad (1)$$

was applied to the data under the assumption that acetic anhydride exists in the reaction system in excess of the numbers of hydroxyl groups accessible for the reaction. x (%) is the weight gain at reaction time t (h), a (%) is the ultimate weight gain, and k (h^{-1}) is the rate constant. The compatibility of the equation was not good, and the regression curve deviated from the observed values, especially when the reaction was conducted with an elevated temperature and/or catalyzed system. This was attributable to a diffusion-controlled reaction, in which the supply of reagent to the reaction sites cannot follow the real reaction rate.

In this article, a modified rate equation in which the influence of diffusion is taken into consideration,

$$x = a \times (1 - e^{-kt})^{1/n}, \quad (2)$$

was applied. Here, n is a measure of the hindrance to the diffusion of reagent to the reaction site. Generally, the chemical reactions of wood or cotton fiber occur heterogeneously in the solid–liquid interface, and the reaction proceeds in a concentric circle from the peripheral region of the cell wall and the surface of the cell lumen. Moreover, it is said that the reaction products progressively hinder the diffusion of the reagent into the unreacted portion.³ The x value, which was underestimated because of the retardation of the diffusion, is adjusted by an exponent, n , in Eq. 2.

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Sakurada⁴ applied another diffusion-controlled rate equation,

$$dx/dt = K'(1/x^n), \quad (3)$$

to the acetylation or nitration of cotton fiber. x is the reaction level (e.g., weight gain) at reaction time t . The integrated form is

$$x = Kt^m, m = 1/(n + 1), K = (K'/m)^m \quad (4)$$

where, K is the reaction level per unit time, namely a rate constant, and n is a measure of the hindrance to the diffusion. Also in this case, the hindrance to the diffusion is adjusted using an exponent. Therefore, Eqs. 2 and 4 are conceptually similar.

The actual regression was achieved with the following two criteria:

1. Weight gain above 30% is not used for the regression, because it is unreasonable to fit the regression curve to the data at a markedly prolonged reaction time and/or near the ultimate value.
2. When a does not converge because of a lack of data at a moderate reaction level, k and n are estimated while fixing a at 30%. As long as a does not diverge, it becomes roughly 30% for wood meal, and thus the value is neither unreasonable nor assertive.

Results and discussion

Figure 1 shows an example of the regression of the modified rate equation along with that of a previous one. Under

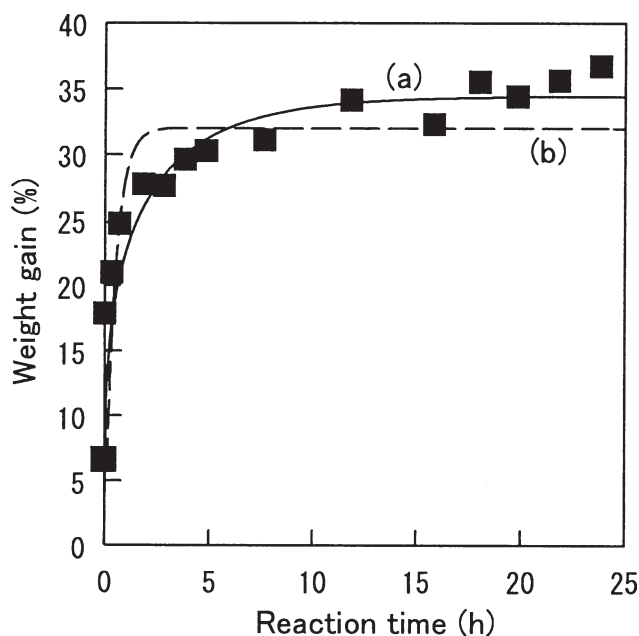


Fig. 1. Regressions of the modified rate equation (a) and the first-order rate equation (b) applied to the pyridine-catalyzed reaction of wood meal at 100°C

harsh conditions such as in uncatalyzed reactions above 120°C and in pyridine-catalyzed reactions above 100°C, Eq. 1 did not satisfactorily fit the data. In such cases, the regression curve deviated upward of the observed values especially in the early stage of the reaction, and thus the rate constants were overestimated and the ultimate values were underestimated. Furthermore, in the pyridine-catalyzed reaction at 120°C, the ultimate value did not converge to a definite value with the application of Eq. 1.

The modified equation was successfully applied to the data which did not fit Eq. 1. Equation 2 was applicable even to the data obtained for the wood block, although a was fixed to 30% when applying the regression equation because it was extremely low when the regression was carried out while a is variable. However, the amount of accessible hydroxyl groups, namely the ultimate weight gain, should not differ between wood meal and blocks. Therefore, the a value estimated for wood meal (*ca.* 30%) was also used for block samples. Table 1 summarizes the reaction parameters estimated by the application of the modified equation and statistical data for the regression.

Concerning the ultimate weight gain of the reaction, a , the estimated value was near 30% except when fixed. This is valid because the data for the early stage of the reaction was used for the regression whereas that above 30% was excluded. Meanwhile, the a values obtained at a prolonged reaction time rose above 30%. However, when all the data was used for the regression, the a value became large without a remarkable deviation from the observed value. An example where all the data was used for the regression is shown in Fig. 2.

Figure 3 shows an Arrhenius plot in which the natural logarithm of k was plotted against the reciprocal absolute temperature. Table 2 summarizes the apparent activation

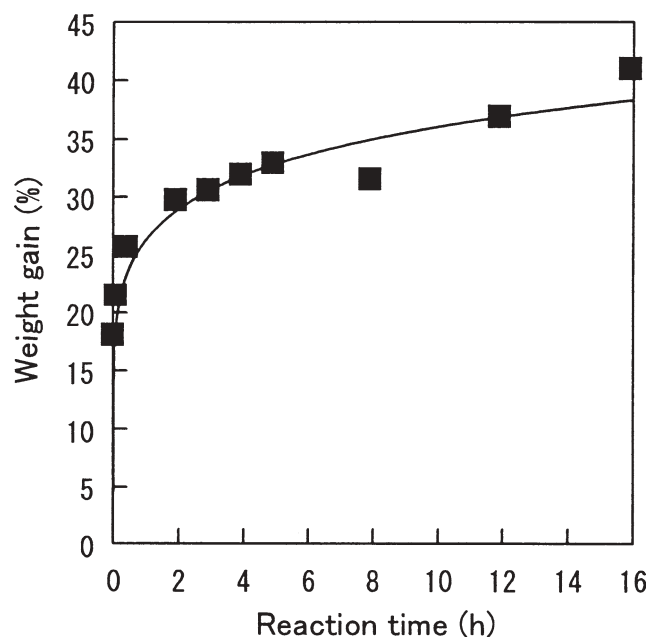


Fig. 2. Regression of the modified rate equation applied to the data observed for pyridine-catalyzed reaction of wood meal at 120°C

Table 1. Estimated reaction parameters and statistical data for regression

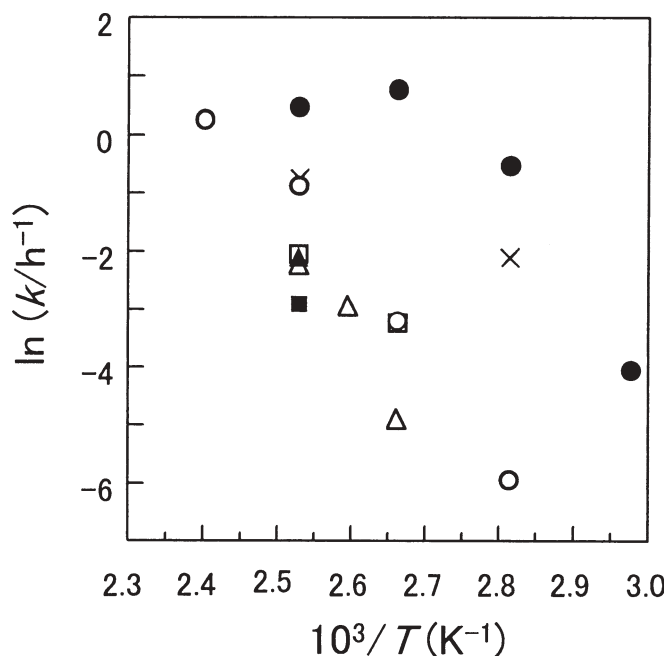
	Reaction system	Temperature (°C)	<i>a</i> (%)	<i>k</i> (h ⁻¹)	<i>n</i>	No. of data	Time range ^a (h)	<i>R</i> ²
Wood meal	Uncatalyzed	80	30 (fix)	2.39×10^{-3}	1.28	10	4–48	0.944
		100	28.8	3.70×10^{-2}	1.25	14	1–72	0.990
		120	26.4	3.79×10^{-1}	1.40	14	0.25–14	0.977
		140	27.2	1.19	1.46	11	0.08–5	0.988
	Xy/AA (v/v = 1:1)	100	30 (fix)	6.96×10^{-3}	0.750	5	4–25	0.990
		110	25.6	4.92×10^{-2}	0.784	9	5–72	0.997
		120	29.7	1.01×10^{-1}	1.13	9	3–42	0.974
		100	25.7	3.58×10^{-2}	0.822	10	4–96	0.968
	Xy/AA (v/v = 1:3)	120	30.4	1.18×10^{-1}	2.13	5	4–24	0.995
		60	30 (fix)	1.58×10^{-2}	0.727	5	3–24	0.971
	Py/AA (v/v = 1:4)	80	27.7	5.36×10^{-1}	0.874	6	0.5–8	0.994
		100	28.5	1.97	1.51	8	0.08–5	0.966
		120	29.8	1.46	4.30	4	0.08–2	0.998
		120	30 (fix)	1.16×10^{-1}	2.83	8	0.08–8	0.977
Wood block	Uncatalyzed	120	30 (fix)	5.26×10^{-2}	1.49	4	1–20	0.939
		80	30 (fix)	1.15×10^{-1}	3.21	4	0.25–7	0.973
	Py/AA (v/v = 1:4)	120	30 (fix)	4.42×10^{-1}	5.34	3	0.08–1	1

AA, acetic anhydride; Py, pyridine; Xy, xylene

^aTo which the regression was applied**Table 2.** Activation energy estimated for various reaction systems

Shape of sample	Reaction system	Activation energy (kJ/mol)
Wood meal	Uncatalyzed	129
	Xy/AA (v/v = 1:1)	165
	Xy/AA (v/v = 1:3)	74
	Py/AA (v/v = 1:4)	84
Wood block	Py/AA (v/v = 1:4)	39

AA, acetic anhydride; Py, pyridine; Xy, xylene

**Fig. 3.** Arrhenius plot. *Open circles*, uncatalyzed; *open triangles*, xylene/acetic anhydride (v/v = 1/1); *open squares*, xylene/acetic anhydride (v/v = 1/3); *filled circles*, pyridine/acetic anhydride (v/v = 1/4); *filled triangle*, uncatalyzed (block sample); *filled square*, xylene/acetic anhydride (v/v = 1/1, block sample); *crosses*, pyridine/acetic anhydride (v/v = 1/4, block sample)

energies obtained from the slope of the linear regression. Values were about 130 and 165 kJ/mol for the uncatalyzed and xylene/acetic anhydride (v/v = 1:1) reactions of wood meal, respectively, and are not that different from the previous value for the pyridine-catalyzed reaction of wood meal. Therefore, the conclusions did not change greatly on applying the newly proposed rate equation, but the reliability of the analysis was enhanced.

When the wood block was used, the activation energy was about 40 kJ/mol, which suggests a diffusion-controlled reaction as previously concluded. The modified rate equation presumes to exclude the influence of diffusion. Therefore, if the target functions perfectly, the activation energy that is not affected by the diffusion should be obtainable. In any case, the reliability was too low for proper interpretation, because the value was estimated using only two data.

The *n* value was not far from unity in the uncatalyzed and xylene/acetic anhydride systems, but was much larger in the pyridine/acetic anhydride systems. Notably, at an elevated temperature, *n* was larger than unity irrespective of the reaction system. Also, when the wood block was used, *n* was larger than unity. From these results, it may be concluded that the *n* value becomes large when the reaction is controlled by diffusion.

Concerning the difference between activation energies obtained by Hill et al.² and in our work,¹ the only explanation that is obvious is the difference in the dimensions of the wood samples.

Conclusions

A modified rate equation, in which the diffusion of the reagent was taken into consideration, was applied to data on acetylation reported previously. The equation was fitted more successfully than the simple first-order rate equation. Although the result did not change the previous conclusion,

the reliability was enhanced because the regression analysis was based on more data. Because the chemical modification of wood or cellulosic fiber proceeds in a heterogeneous system, it is impossible to entirely exclude the influence of the diffusion of reagent. Nevertheless, the modified equation reflected the statistical analysis as much as possible. The equation may be applicable not only to acetylation but to other chemical modifications in heterogeneous systems.

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