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Research Article

Kinetic pH Titration to Predict the Acid and Hydrothermal Conditions for the Hydrolysis of Disaccharides: Use of a Microcapillary System

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The hydrolysis of disaccharides was conducted using a microcapillary system under hydrothermal conditions (up to 190°C at 10 MPa and pH 4–11). The hydrolysis reaction showed a sigmoidal progression with time, especially under alkaline conditions. Analysis using a kinetic model yielded the reaction induction period. The specific pH value (pH^{amb}) at the induction time, which is the pH value corresponding to the progression of disaccharide hydrolysis, was peculiar to each disaccharide. Finally, the calculation of the electron density around the oxygen atom of the glycosidic bond between saccharides was found to roughly predict the pH^{amb} value required for the progression of hydrolysis.

1. Introduction

Sugar production is an indispensable technology in food and chemical engineering. Many researchers have reported that cellulose and oligo- and disaccharides are hydrolyzed to monosaccharides [1–7]. Because cellulose is present in plant biomass [1], it is a useful resource for the preparation of sugars and other value-added materials. The hydrolysis of cellulose is, in principle, based on the cleavage of the glycosidic bond between monosaccharides and requires acidic conditions [8]. In recent years, a variety of methods including the use of metal catalysts, enzymatic treatment in ionic liquids [9–11], and hydrothermal treatment [1–3, 6, 7] have been reported to improve hydrolysis. However, the deterioration of metal catalysts and their poor reusability limit their use. In addition, enzymes and ionic liquids are expensive. Thus, the hydrolysis of sugar is not always an environmentally benign process and can be economically risky.

Water that maintains its liquid state under pressurized conditions in the temperature range of 100–374°C is called subcritical water. Subcritical water has two unique features: (i) a low relative dielectric constant [12–14] and (ii) a high ion product [15]. Because there is evidence of a high hydroxide ion concentration in supercritical water [16], the concentrations of hydrogen and hydroxyl ions in subcritical water should be also higher than those in water at room temperature. Therefore, subcritical water has been investigated for its application as acid and base catalysts [17–19]. However, there is no direct evidence of the physicochemical properties of subcritical water mentioned above, and the further application of subcritical water requires the clarification of its physicochemical property.

Recently, it has been reported that subcritical water can catalyze the hydrolysis [2–4, 6, 7, 20–24] and isomerization [25] of saccharides, as well as the hydrolysis of vegetable oil [26]. These findings demonstrate the use of subcritical water for the treatment of biomass. Further clarification of the

physicochemical properties of subcritical water would result in the effective treatment of solid biomass, such as used wood. The decomposition mechanism of sucrose has been clarified to some extent, and the decomposition of sucrose is affected by the acidity of the reaction medium [21]. It is expected that the variation in the hydrolysis behavior of disaccharides under hydrothermal conditions at different pHs is related to the physicochemical property of subcritical water.

The hydrothermal process can be carried out in a microcapillary system. Microcapillary systems permit the rapid shifting of the liquid temperature between room temperature and hydrothermal temperature [20–22, 27–29]. Therefore, the monitoring of the reaction under the hydrothermal conditions can be achieved. In particular, a shift in the pH to the acidic region occurs with increasing hydrolysis. If the pH that induces the hydrolysis of materials can be predicted from the physicochemical properties, the use of excess acid could be avoided.

In this study, we selected disaccharides as the target materials because the minimum unit process in cellulose hydrolysis is considered to be the hydrolysis of disaccharides. Then, we examined the hydrolysis behavior of disaccharides at various pHs and temperatures. From the kinetic analysis of hydrolysis under the hydrothermal conditions involving hydrochloric acid, the apparent decomposition rate constant was estimated to determine the specific pH value for hydrolysis. As a related parameter, the hydration structure of disaccharides was examined using dielectric measurements. Moreover, the relationship between the pH value and the hydration structure of disaccharides is discussed.

2. Materials and Methods

2.1. Materials. Sucrose, palatinose monohydrate, meribiose, cellobiose, turanose, trehalose, maltose, and lactose were used as disaccharides, and their general formula is $C_{12}H_{22}O_{11}$ (M_w = 342.296 g/mol). The disaccharides and other chemicals were purchased from Wako Pure Chemical Industries, Ltd. (Osaka, Japan), except trehalose, which was obtained from Hayashibara Co. Ltd. (Okayama, Japan). Other chemicals were of analytical grade.

2.2. Thermogravimetric Analysis. The thermogravimetric analysis was carried using a TG-60A (Shimadzu, Kyoto, Japan). A platinum crucible loaded with 2 to 3 mg of sucrose was first heated to 300°C from the room temperature at a heating rate of 20°C/min. N_2 gas was used as carrier gas at a flow rate of 100 mL/min.

2.3. Preparation of the Disaccharide Solutions. The disaccharides were dissolved in distilled water to adjust the final concentration to 0.5–5 wt%. To adjust the pH of the disaccharide solution, either HCl or NaOH was used. The disaccharide solution without pH adjustment had a pH of 6. The disaccharide solution was degassed for 10 min and purged with nitrogen gas to avoid the variation in pH caused by dissolving carbon dioxide in the disaccharide solution.

2.4. Apparatus of the Flow-type Reactor. A continuous flow-type reactor (Figure 1) was used to monitor the decomposition of the disaccharides following a previous report [21]. The reactor was made of stainless steel (SUS 316, GL Science, Tokyo, Japan) tubing (1.6 mm o.d. × 0.8 mm i.d.) and was immersed in an oil bath (160–190°C). The temperature of the oil bath was monitored using a thermal detector TXN-400 (AS ONE, Osaka, Japan). To terminate the reaction rapidly, the reaction mixture leaving the reactor was passed through a water bath. The pressure in the system was regulated at 10 MPa by a valve (P-880, Upchurch Scientific). The effluent was collected in a sampling vessel to analyze the sucrose concentration by high-performance liquid chromatography (HPLC).

To investigate the pH decrease during the hydrolysis, the pH of the reactor effluent of all samples was measured using a pH meter.

2.5. HPLC Analysis. The concentration of the remaining sucrose in the effluent was determined by a liquid chromatograph (LC-20AD, Shimadzu, Kyoto, Japan) equipped with a refractometer RI-8010 (TOSO, Osaka, Japan). A COSMOSIL Sugar-D packed column (4.6 mm i.d. × 250 mm) was used for the analysis of the sucrose and its hydrolysates. The 20 μL sample was injected into the column and incubated at 38°C by the column oven. The eluent was an acetonitrile/water mixture (80/20 v/v), and its flow rate was 1.6 mL/min. The determination was repeated at least three times and then averaged.

2.6. Dielectric Measurement. Dielectric dispersion analysis permits the monitoring of the dipole moment such as that of water. A network analyzer (Agilent, N5230 C; 500 MHz to 50 GHz) was used to monitor the bulk water and the water bound to disaccharides. The sample solution at a constant mixing ratio of water to disaccharide was used and maintained for 30 min at a constant temperature before starting the measurement. Thereafter, the relative permittivity (ε') and dielectric loss (ε'') of the liposome suspension were measured as a function of frequency at each temperature following previous reports [30–32]. The frequency dependence of ε' and ε'' (500 MHz to 50 GHz) was analyzed using Debye's equations:

$$\varepsilon' - \varepsilon_h' = \sum_{i=1}^{2} \frac{\Delta\varepsilon_i}{1 + \left(f/f_{ci}\right)^2}, \tag{1}$$

$$\varepsilon'' - \frac{G_{dc}}{2\pi f C_0} = \sum_{i=1}^{2} \frac{\Delta\varepsilon_i \left(f/f_{ci}\right)}{1 + \left(f/f_{ci}\right)^2}, \tag{2}$$

where ε_h' and G_{dc} are the limit of relative permittivity at higher frequency and direct current conductivity of the solutions, respectively. C_0 is the cell constant obtained by calibration using distilled water. It has been reported that aqueous

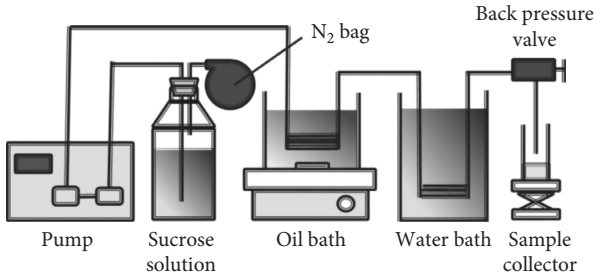

Figure 1: Schematic illustration of the reaction system for sucrose decomposition under hydrothermal conditions.

solutions have two different characteristic relaxations of water molecules: the water bound to saccharides ($i = 1$; third step, 1–3 GHz) and bulk water ($i = 2$, second step, *ca.* 20 GHz) [30, 32]. Therefore, equations (2) and (3) were assumed to be a summation of the two relaxation terms. Samples were prepared by mixing 0.5 g of disaccharide with 0–1.3 g of water. The number of water molecules to disaccharide is defined as N_w. $N_w = (m_w/M_w)/(m_d/M_d)$, where m_w and m_d are the masses of water and disaccharide (g), respectively. M_w and M_d are the molecular weights of water and disaccharide, respectively.

3. Results and Discussion

3.1. Thermal Stability of Disaccharides. In the first series of experiments, the thermal stability of the disaccharides was investigated to rule out the possibility of the thermal decomposition of the disaccharides. For this, differential scanning calorimetry (DSC) and thermal gravimetric (TG) analysis were used. Figure 2(a) shows typical DSC and TG curves for sucrose. In the temperature range between 150 and 170°C, an endothermic heat flow was observed, but no weight change was observed. The sucrose was considered to be melted in this temperature range. The weight change in sucrose was observed above 200°C from the TG curve. The DSC curve shows an endothermic adsorption in the same temperature range. These results indicated that the sucrose thermally decomposed above 220°C. The temperatures required to induce the decomposition for other disaccharides were measured to be 270°C (maltose), 24°C (trehalose), 240°C (cellobiose), 195°C (turanose), and 215°C (meribiose). For lactose, the decomposition temperature has been reported to be 220°C [33]. Thus, it is considered that the hydrolysis of disaccharides should be examined below 190°C, although data for palatinose was not obtained in this study.

3.2. Influence of Inorganic Acids on Hydrothermal Hydrolysis Behavior of Disaccharides. To select the acid in this study, sucrose was examined as a typical disaccharide. It has been reported that sucrose is susceptible to hydrolysis by acids because it has a glycosidic oxygen atom with a large electrostatic potential charge [21].

To confirm the influence of the acid species, HCl, H_2SO_4, and HNO_3 were used to induce the hydrolysis of sucrose. Each acid was mixed with sucrose to adjust the pH to 5 to initiate hydrolysis under the hydrothermal condition (185°C and 10 MPa). The change in the remaining sucrose (C/C_0) with time in the presence of each acid is shown in Figure 2(b). It is obvious that the changes in C/C_0 with time in the presence of each acid are identical. The same was true for the variation of pH (Figure 2(c)). In general, all the strong acids form H_3O^+ (H^+), known as the *leveling effect*. Therefore, the results in Figures 2(b) and 2(c) strongly indicate that the protons dissociated from the inorganic acids triggered the hydrolysis of sucrose. Thus, HCl was used for the hydrolysis of disaccharides.

3.3. Kinetic Analysis of the Hydrolysis of Disaccharides. Sucrose solutions at various pH values, adjusted by HCl, were prepared to investigate its hydrolysis under subcritical conditions (180°C and 10 MPa). The change in the remaining sucrose concentration was monitored at various pHs (Figure 3(a)). Sigmoidal curves were observed above pH 4. This indicates the presence of an induction period [34]. Following previous reports [34], we analyzed the change in the remaining sucrose (C/C_0) with time using the following equation:

$$\frac{C}{C_0} = 1 - \frac{1}{1 + \exp\left(-\left(t - t_m\right)/\tau\right)}, \tag{3}$$

where the induction time is $t_d = t_m - 2\tau$ and the apparent rate constant is $k^{app} = \tau^{-1}$. In Figure 3(a), $t_d = 25 - 160$ s and $k^{app} = 0.01 - 0.058\ s^{-1}$ were estimated from the curve fitting of equation (3) with the experimental data obtained in this study. Overall, the induction time, t_d, increased with the increasing pH. The corresponding apparent rate constant, k^{app}, also reduced with the increasing pH.

To confirm the general relationship between both, the k^{app} values were plotted against the corresponding t_d value obtained under various temperatures and pH conditions. A good correlation between both was observed at all pH values and temperatures (Figure 3(b)), which is a typical relationship often seen in the time development involving an induction period. The negatively correlated relationship between t_d and k^{app} implies a lag time for the hydrolysis of sucrose.

In a previous report, a production of organic acids such as formic acid and acetic acid associated with the hydrolysis of sucrose resulted in a pH reduction [21]. The pH variation during sucrose hydrolysis was monitored at various initial pH values. The pH converged to pH 4 regardless of the initial pH (Figure 3(c)). The reason for the convergence to the same pH appears to be due to the production of organic acids, as previously reported [21]. The pH corresponding to the induction time (t_d) is denoted as pH^{amb}. pH^{amb} was then plotted against the corresponding t_d value (Figure 3(d)). It was found that the pH^{amb} was 5 at all temperatures and initial pHs, suggesting that proton accumulation is required for the progression of sucrose hydrolysis. The pH^{amb} value for other disaccharides was also measured, as shown in Figure 4. The pH condition required to progress hydrolysis depended on the disaccharides. Overall, the pH^{amb} values

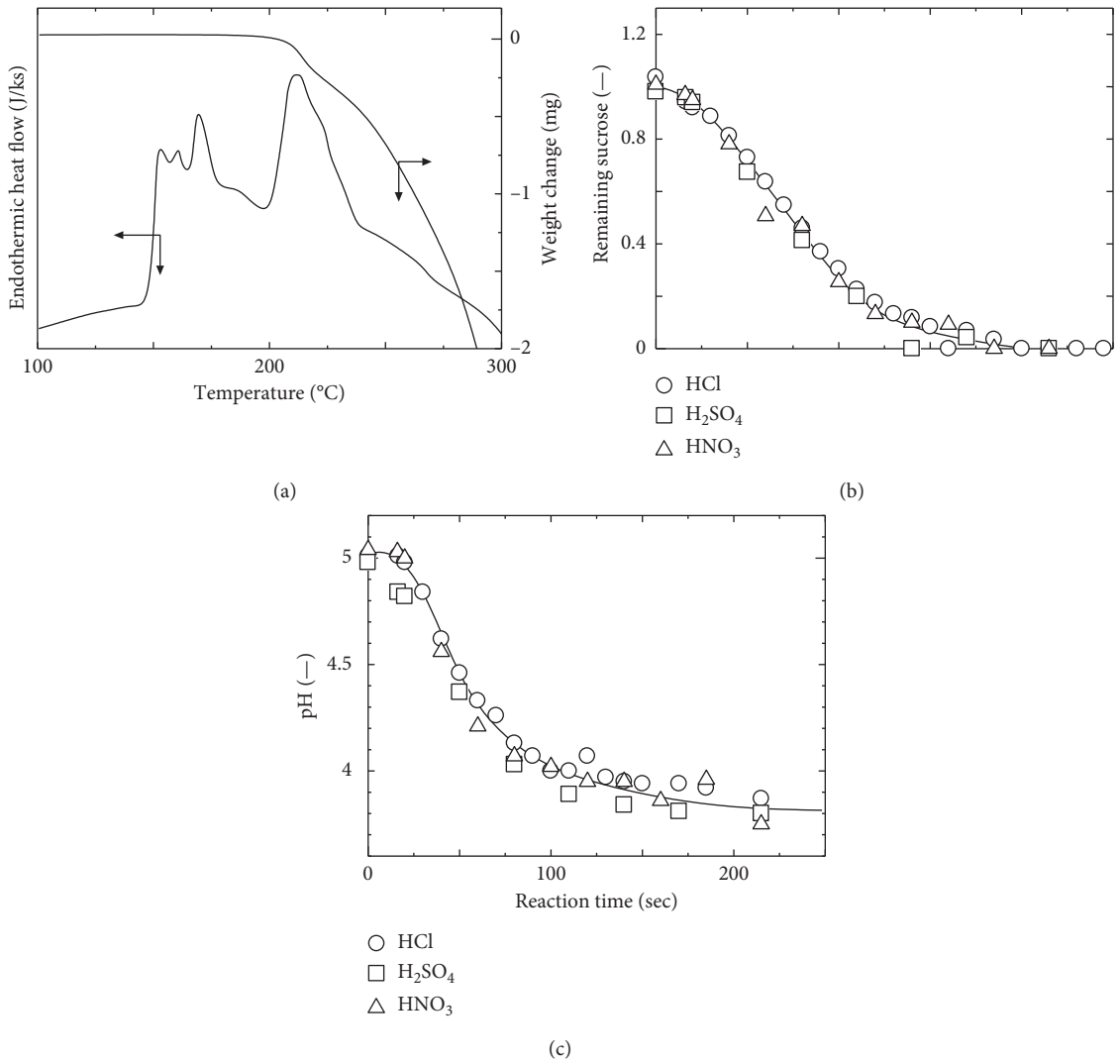

Figure 2: (a) Thermal gravimetric and differential thermogram of sucrose. Effect of acids on sucrose decomposition under the subcritical water condition. Time course of (b) remaining sucrose concentration and (c) pH. All the experiments were performed at 185°C, 10 MPa, initial pH 5, and C_0 = 0.5 wt%.

ranged between 4 and 5, suggesting that the hydrolysis of disaccharides occurred under acidic conditions in the hydrothermal reaction.

3.4. Simple Implications for the Hydrolysis Mechanism of Disaccharides. To clarify the hydrolysis mechanism of sucrose associated with the accumulation of protons, the activation energy of the sucrose hydrolysis at various pHs was investigated. Figure 5(a) shows the temperature dependencies of sucrose hydrolysis at pH 6. When the temperature was increased to 190°C, a rapid hydrolysis of sucrose was observed with a corresponding decrease in the induction period. The apparent rate constant (k^{app}) at various temperatures was estimated using equation (3) and plotted against the corresponding temperature, as shown in Figure 5(b). The slope of the plot of $\ln k^{app} - 1/T$ gives $\Delta E/R$ (Arrhenius plot), and the ΔE value was subsequently plotted against the initial pH of the sucrose solution (Figure 5(c)). Overall, the ΔE values are below 100 kJ/mol. The ΔE values for radical reactions have been reported to be about 400 kJ/mol [35]. These results indicate that the sucrose was hydrolyzed via an ionic reaction. In addition, in the range below pH 5, the ΔE value was reduced as compared with those above pH 5. The accumulation of protons appeared to be advantageous for the hydrolysis of sucrose. The same was true for other disaccharides regarding the pH dependency of the ΔE value (data not shown).

From the results, the electronic environment of the oxygen atom in the glycosidic bond of the disaccharide (where the cleavage of disaccharides occurred) played an important role in the hydrolysis reaction.

3.5. Dielectric Measurement. The hydration of disaccharides is a possible factor affecting their hydrolysis. Dielectric measurements under an alternating electric field are a

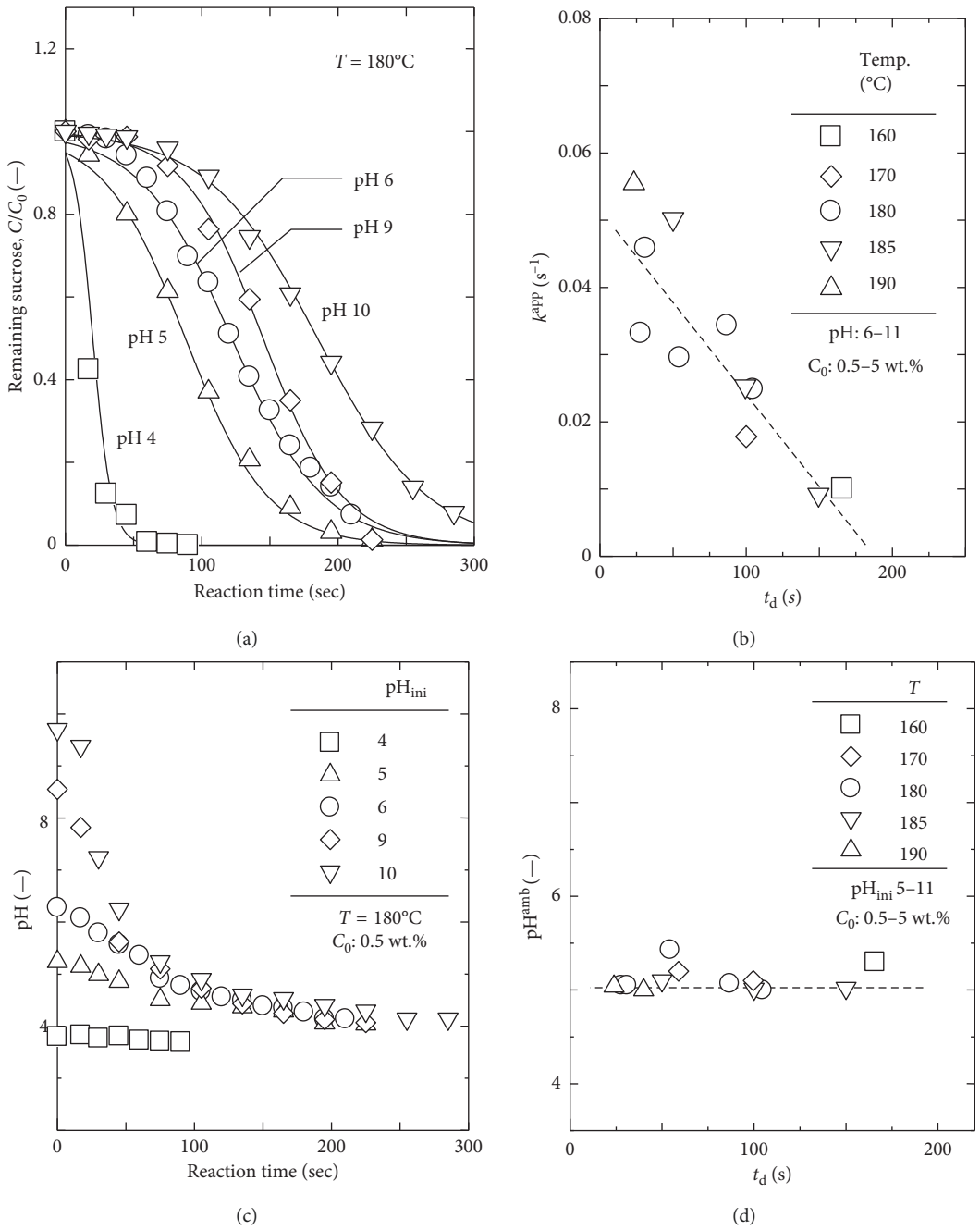

Figure 3: Kinetic pH titration. (a) Time course of remaining sucrose concentration under various pH conditions at 180°C. The experiment was performed at 180°C, 10 MPa, C_0 = 0.5 wt%, and initial pH 4–10. (b) Relationship between the induced time (t_d) and apparent rate constant (k^{app}). (c) Time course of the pH at the outlet of reaction system. (d) Relationship between t_d and the corresponding pH (pH^{amb}).

powerful tool to estimate the hydration structure [30–32]. The frequency range between 500 MHz and 20 GHz was selected because this range involves the relaxation originating from hydration [30, 32].

Typical dielectric spectra between 500 MHz and 20 GHz measured at 25°C are shown in Figures 6(a) and 6(b). In the cases of sucrose and maltose, dielectric relaxation was observed at around 1–3 and 8–20 GHz, respectively. The former relaxation was attributed to the bound water to disaccharide and the latter to that of bulk water [30, 32]. On varying the water to disaccharide content (N_w = 6.84–30.7), definite relaxation was observed for both disaccharides. The relaxation amplitude at around 1–3 GHz ($\Delta\varepsilon$) was estimated by fitting Debye-type equations (1) and (2) to the experimental data. For sucrose, the first relaxation, $\Delta\varepsilon$ = 20.3 and f = 1.2 GHz, and the second relaxation, $\Delta\varepsilon$ = 16 and f = 8 GHz, occurred at N_w = 6.84 (r^2 = 0.960); the first relaxation, $\Delta\varepsilon$ = 21.5 and f = 1.2 GHz, and the second relaxation, $\Delta\varepsilon$ = 23; and f = 8 GHz, occurred at N_w = 13.6 (r^2 = 0.955); and the first relaxation, $\Delta\varepsilon$ = 11.3 and f = 1.5 GHz, and the second

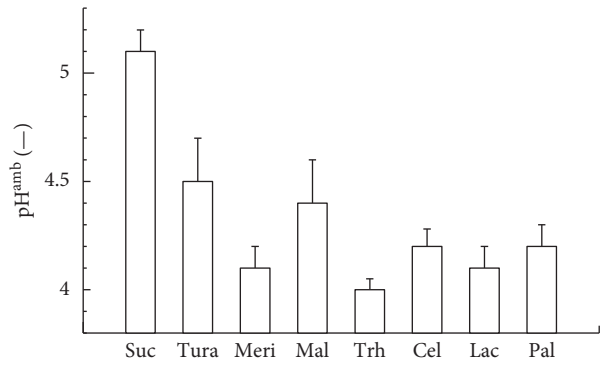

Figure 4: Specific pH value to progress the decomposition reaction of disaccharides. Suc: sucrose; Tura: turanose; Meri: meribiose; Mal: maltose; Trh: trehalose; Cel: cellobiose; Lac: lactose; Pal: palatinose. Error was calculated from the three independent experiments.

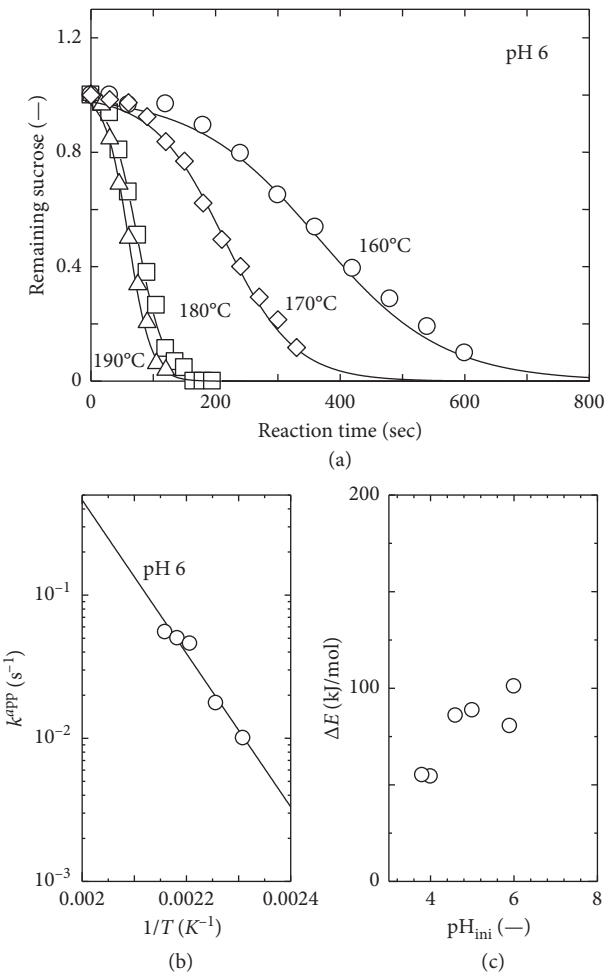

Figure 5: (a) Time course of sucrose decomposition at various temperatures. Arrhenius plot of the apparent rate constant ((b) pH 6) and (c) pH dependency of activation energy for sucrose decomposition.

relaxation, $\Delta\varepsilon = 57$ and $f = 12$ GHz, occurred at $N_w = 30.7$ ($r^2 = 0.982$). As N_w increased beyond 13.6, the characteristic frequency increased from 8 to 12 GHz, indicating the generation of free bulk water. In addition, the increase in water content increased the $\Delta\varepsilon$ value of the second relaxation. This resulted from the contribution of bulk water. The same was true for maltose.

The $\Delta\varepsilon$ value at the first relaxation, in principle, depends on the number and strength of the dipole moment derived from the bound water. The strength of the dipole moment of water reflects the extent of polarization of water. Thus, the $\Delta\varepsilon$ value as an index for the bound water was plotted against the N_w value. The $\Delta\varepsilon$ value monotonously increased up to $N_w = 10$–15 and, subsequently, decreased in the case of sucrose, turanose, and meribiose (Figure 6(c)). On the contrary, the $\Delta\varepsilon$ value monotonously increased up to $N_w = 20$–30 and then plateaued in the case of the other disaccharides (Figure 6(d)). Thus, the critical point in the $\Delta\varepsilon$ vs. N_w curve might correspond to the number of bound water molecules; thus, the critical N_w value is 15–30. However, computational studies [36, 37] have indicated that a hydration number of 13–16 is lower than the critical N_w value. This difference in the number of bound water molecules might result from the principle of the dielectric measurements: both strongly and weakly bound water are detectable. Alternatively, considering that $\Delta\varepsilon$ depends on the number and strength of dipole moment, a $\Delta\varepsilon/N_w$ value in the range between 0 and 10 might be defined as the hydration structure. The $\Delta\varepsilon/N_w$ value indicates the average strength of the dipole moment (polarization) of bound water. This definition is similar to the conventional method used to discuss the hydration of substrates, e.g., a plot of the melting enthalpy of substrates to the water content of the substrate (mol/mol) [38]. Thereby, the $\Delta\varepsilon/N_w$ values for each disaccharide are summarized in Figure 6(e). Four disaccharides (sucrose, turanose, meribiose, and maltose) had significantly higher $\Delta\varepsilon/N_w$ values than the other disaccharides. Therefore, these four disaccharides could have strongly bound hydration structures.

3.6. Implications for the pH Condition Required for the Hydrolysis of Disaccharides. It is considered that a hydration structure is formed at the hydroxyl group of monosaccharides and the glycosidic bond. The glycosidic bond is affected by hydrolysis under hydrothermal conditions. If the hydration is caused by the water bound to the glycosidic bond, the hydration structure can be considered to be related

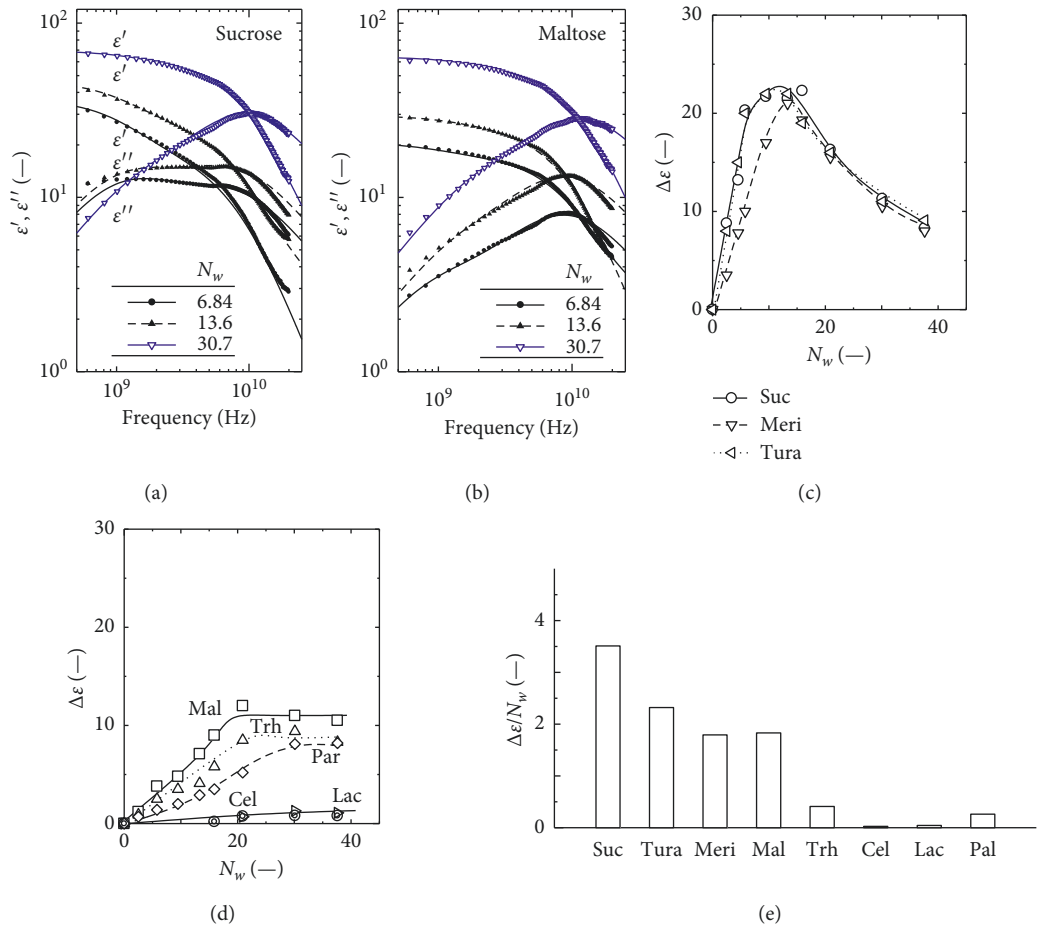

Figure 6: Dielectric spectra for (a) sucrose and (b) maltose in the frequency range between 500 MHz and 20 GHz. (c, d) The dielectric amplitude at first relaxation (at around 1–3 GHz) as a function of N_w. (e) Hydration index for various disaccharides. Suc: sucrose; Tura: turanose; Meri: meribiose; Mal: maltose; Trh: trehalose; Cel: cellobiose; Lac: lactose; Pal: palatinose.

to the electronic charge in the glycosidic bond (oxygen atom). Thus, theoretical calculations using the molecular orbital calculation program MOPAC 2000 were performed according to a previous report [21], and the results are summarized in Figure 7(a). Sucrose had the most negative Q value of the disaccharides used, indicating the high electron charge in the glycosidic bond of the electron-rich α-glucose-(1⟶4)-α-fructose bond [21]. Trehalose, cellobiose, lactose, and palatinose had relatively low Q values. The obtained order of Q values is likely comparable to the trend in hydrolysis (Figure 4).

To check the effect of the electronic charge of the glycosidic bond on the hydrolysis, both the pH^{amb} and $\Delta\varepsilon/N_w$ values for each disaccharide were plotted against the corresponding Q value. Figure 7(b) shows that a decrease in Q resulted in an increase in pH^{amb}, suggesting that the negative charge of the glycosidic bond is closely related to the progression of the hydrolysis reaction. The $\Delta\varepsilon/N_w$ value also indicates a negative correlation with the Q value, although some data were scattered away from the trendline (Figure 7(c)). This scattering might result from the configuration of water around the saccharides, which is dependent of the conformation of the disaccharides. Based on Figures 7(b) and 7(c), the Q value of a disaccharide could be used to determine the critical pH condition for the progression of hydrolysis.

4. Conclusion

A kinetic model taking into consideration the induction period was adopted to analyze the hydrolysis of disaccharides. Thereby, using our analysis technique, the pH value required to initiate the hydrolysis of disaccharides (pH^{amb}) can be calculated. The activation energy for the hydrolysis of disaccharides under hydrothermal conditions was calculated, and the reactions were found to be ionic reactions. Therefore, possible parameters relating to ionic reactions are (i) the hydration structure of disaccharides and (ii) the electronic charge of oxygen in the glycosidic bond. The hydration structure was determined using dielectric measurements. It was found that sucrose, turanose, and meribiose were well-hydrated relative to the other disaccharides. In addition, the calculations using MOPAC can give the Q value, and the hydration structure is roughly comparable to the Q value, although some deviations were observed. It is likely that the electronic environment of the

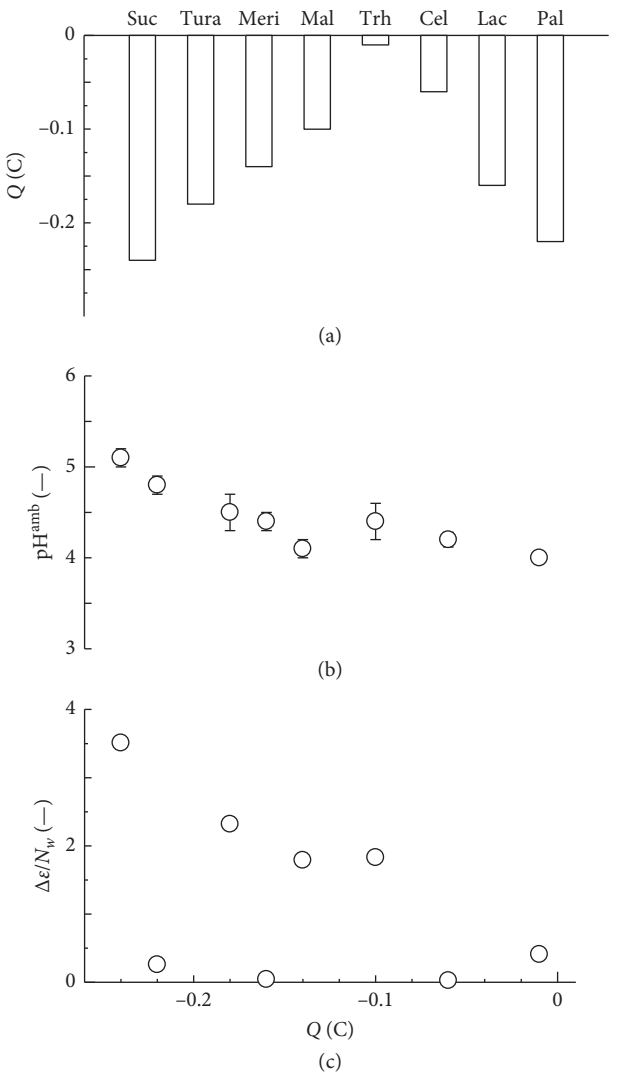

Figure 7: (a) Electronic charge around oxygen in the glycoside bond of disaccharides. Q dependency of (b) pH^{amb} and (c) $\Delta\varepsilon/N_w$. Suc: sucrose; Tura: turanose; Meri: meribiose; Mal: maltose; Trh: trehalose; Cel: cellobiose; Lac: lactose; Pal: palatinose.

oxygen atom in the glycosidic bond is related to the hydrolysis of disaccharides. Finally, the pH^{amb} value was roughly correlated with the Q value. Therefore, the method only requires knowledge of the electronic charge of the oxygen atom in the glycosidic bond of disaccharides obtained from calculation to predict the pH^{amb} of the target disaccharide. The prediction of pH^{amb} would avoid the use of excess quantities of acid to adjust the initial pH, which is of significant environmental benefit. Furthermore, a microcapillary system can be used to monitor the change in the pH with time to obtain the pH^{amb} value for the hydrothermal hydrolysis of disaccharides.

Data Availability

The data used to support the findings of this study are available from the corresponding author upon request.

Conflicts of Interest

The authors declare that there are no conflicts of interest regarding the publication of this paper.

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