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Hydrolysis of Carbohydrates in the Presence of a Reversed Micelle. III. Hydrolysis of Dextrin in Benzene

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The secondary solubilization of dextrin in a dodecylbenzenesulfonic acid (DBSH) reversed micelle in benzene containing a small amount of water was examined; a perfectly clear solution was obtained. The solution showed a CMC of DBSH, estimated by the method of Methylene Blue methachromasis, just like that of sucrose-containing similar reversed-micelle system. The hydrolysis of the dextrin in the system was investigated; the maximum rate enhancement of 285-fold was obtained on the basis of the reaction in DBSH aqueous solution. The CMC and the reaction rate showed changes similar to those in the case of sucrose-containing similar reversed-micelle system with changing the amount of water solubilized, but they showed different changes with changing the concentration of the substrate. These different changes were supposed to result from the differences in the molecular weights of the substrates. These results suggested that the rate enhancement mechanism due to solvent effect and micelle effect which was proposed for the hydrolysis of sucrose in the presence of a DBSH reversed micelle operates in the hydrolysis of the high molecular weight substrate such as dextrin.

Recently, the effective use of carbohydrates as renewable resources has again been recognized to be important. Many modifications of carbohydrates-containing raw and waste materials to, for example, a raw material for preparation of ethanol and livestock feed have been the subject of numerous investigations. In these cases, an effective and economical and if possible, selective depolymerization of the polysaccharides such as cellulose and starch in the raw material is essential.[1]

In previous papers, the hydrolysis of sucrose in the presence of dodecylbenzenesulfonic acid (DBSH) reversed micelles in a dioxane–water mixed solvent[2] and in benzene[3] was investigated. Rate enhancements up to 400-fold were observed on the basis of the reaction in an aqueous solution in the presence of hydrochloric acid. The greater part of the rate enhancement resulted from the formation of the reversed micelle.[3]

In the present paper, we report the hydrolysis of dextrin as a model of polysaccharides, which was carried out to investigate the effect of high molecular weight of the substrate on the reaction in the presence of the reversed micelle.

Experimental

Materials. Commercially available dextrin was purified by pouring a 20% aqueous solution into 5-fold volume of methanol to cause it to precipitate. The number-average molecular weight of the purified dextrin, estimated by the method of end group determination, was 66. Commercially available sodium dodecylbenzenesulfonate was passed through a cation exchange resin column to obtain a free acidic surfactant. Deionized and distilled water was used.

UV Spectrum and Maximum Amount of Solubilized Water. The UV spectra and the maximum amounts of solubilized water in benzene were obtained with the methods previously reported.[2,3]

Measurement of Reaction Rate. DBSH was dissolved in benzene and a dextrin aqueous solution was added with vigorous stirring to get a clear solution. The resulting reaction mixture was maintained at 60 °C in a thermostat, and aliquots were taken out at intervals to determine the amount of reducing sugar according to the method of Somogyi.[4] The logarithm of the ratio of [the amount of reducing sugar at reaction time infinity (r_∞)] to [the difference in the amount of reducing sugar at a reaction time t (r_t) and at infinity (r_∞)] was plotted against the reaction time. A pseudo-first-order rate constant was estimated from the slope of the straight line obtained.

Results and Discussion

In the present experiment, the first problem was whether polysaccharides such as dextrin could be solubilized in benzene in the presence of DBSH or not; polysaccharides could hardly be supposed to be solubilized easily because of their high molecular weights, at least in the same manner as occurs for low molecular weight analogs. In a preliminary experiment, however, addition of dextrin aqueous solution drop by drop to benzene with vigorous stirring was found to give a perfectly clear solution.

Then, we measured the maximum amount of solubilized water containing dextrin. Figure 1 shows the plots of the maximum amount of solubilized water containing dextrin at several concentrations in DBSH

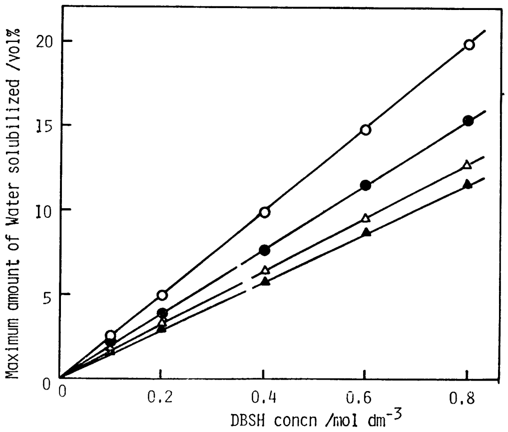

Fig. 1. Plots of maximum amount of solubilized water containing dextrin at several concentrations in DBSH benzene solution against concentration of DBSH, at room temperature.
Concentration of dextrin, %: ○, 0; ●, 2.49; △, 5.79; ▲, 17.7.

benzene solution against concentration of DBSH. The maximum amount of solubilized water was found to increase proportionally with an increasing concentration of DBSH. Figure 2 shows changes in the maximum amount of solubilized water with changing concentration of dextrin in the water. The maximum amounts of solubilized water are found to decrease with an increasing concentration of dextrin, especially in the lower range of the concentration.

The critical micelle concentration (CMC) was estimated with the method of methachromasis of Methylene Blue solubilized in the micelle; we measured the red shift of a peak in the UV spectrum of the added Methylene Blue with changing concentration of DBSH.[2)] Figure 3 shows a typical change in the wavelength corresponding to the left-hand side peak in an absorption spectrum of Methylene Blue (shown in the figure), with changing concentration of DBSH. The inflection point of the sigmoidal curve obtained was presumed to be the CMC of DBSH, just as the case of a sucrose-containing reversed-micelle system. Figure 4 shows the plot of the CMC against the amount of water solubilized in the DBSH benzene solution. The CMC is found to increase proportionally with the increasing amount of solubilized water. This result does not conflict with the relationship between the maximum amount of solubilized water and the concentration of DBSH, and agrees with the change in the CMC obtained in the case of a sucrose-containing reversed-micelle system.[2)] Figure 5 shows plots of the CMC against concentration of dextrin in water solubilized and the CMC's are found to increase slightly with increasing concentration of dextrin. This tendency is contrary to that observed in the case of the sucrose-containing reversed-micelle system,[3)] and is supposed to result from the high molecular weight of dextrin; the higher molecular weight of the substrate is inferred to need more DBSH molecules to form the reversed micelle.

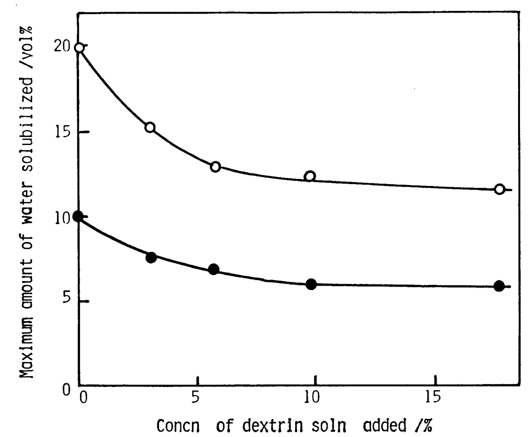

Fig. 2. Changes in maximum amount of solubilized water in DBSH benzene solution, with changing concentrations of dextrin contained in the water, at room temperature.
Concentration of DBSH, mol dm^{-3} as acid: ○, 0.80; ●, 0.40.

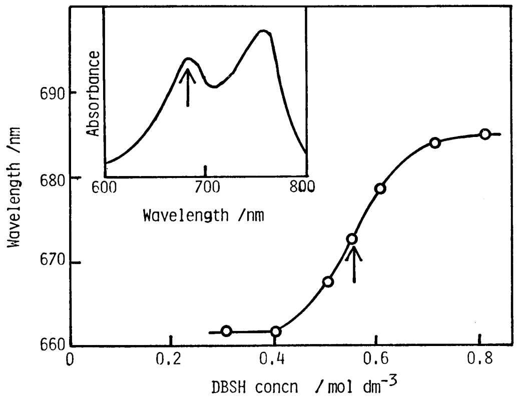

Fig. 3. Typical change in wavelength corresponding to the left-hand side peak in an absorption spectrum of Methylene Blue added to DBSH benzene solution (shown above), with changing concentrations of DBSH. Solubilized water, 5.50 vol%. Concentration of dextrin, 3.68%.

The hydrolysis of dextrin in water solubilized in DBSH benzene solution was investigated. In this case, the concentration of dextrin was expressed as moles of anhydroglucose repeating unit in the total volume, not in water alone. Figure 6 shows typical first-order plots of the amount of reducing sugar in

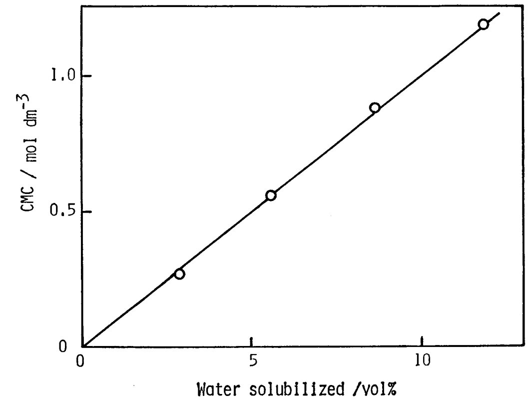

Fig. 4. Plot of CMC estimated with the Methylene Blue methachromasis method against the amount of water solubilized in DBSH benzene solution. Concentration of dextrin, 3.68%.

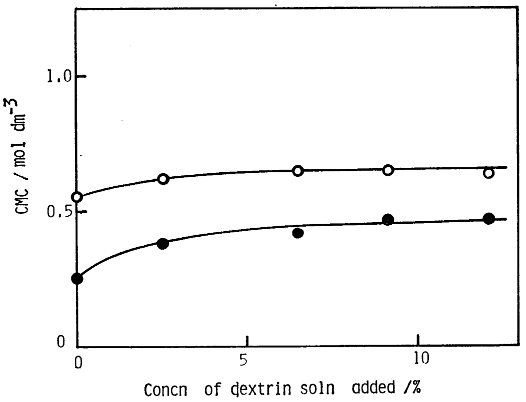

Fig. 5. Plots of CMC against concentration of dextrin in water solubilized in DBSH benzene solution. Water solubilized, vol%: ○, 5.50; ●, 3.50.

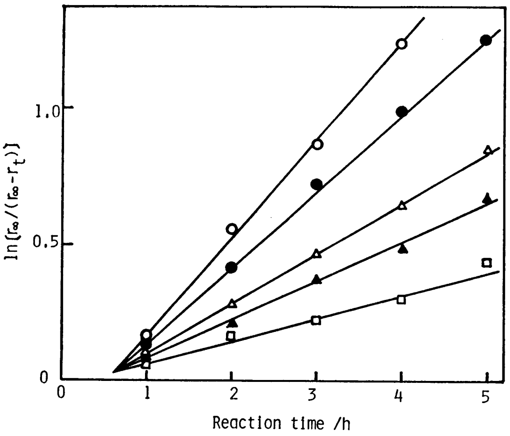

Fig. 6. Typical first-order plots of the changes in the amount of reducing sugar in the reaction mixture at 60 °C.
r_t and r_∞ are the amounts of reducing sugar at a reaction time t and infinity. Concentration of dextrin, 3.29×10^{-3} mol dm^{-3}. Concentration of DBSH, mol dm^{-3}: ○, 0.45; ●, 0.40; △, 0.35; ▲, 0.30; □, 0.25. Solubilized water, 5.50 vol%.

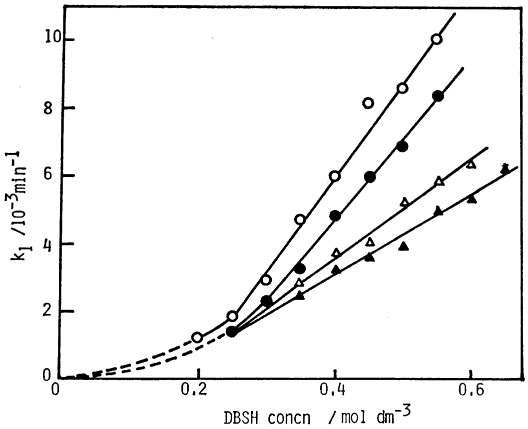

Fig. 7. Plots of pseudo-first-order rate constant, k_1, of dextrin hydrolysis against concentration of DBSH, at 60 °C.
Solubilized water, 4.77 vol%. Concentration of dextrin, 10^{-3} mol dm^{-3}: ○, 1.63; ●, 3.29; △, 4.53; ▲, 6.05.

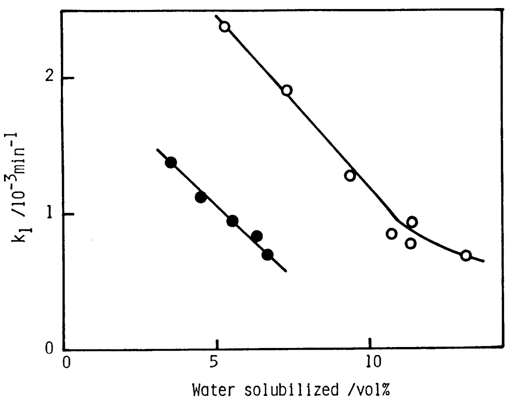

Fig. 8. Plots of k_1 against the amount of solubilized water.
Concentration of dextrin, 13.5×10^{-3} mol dm^{-3}. Concentration of DBSH, mol dm^{-3}: ○, 0.80; ●, 0.40.

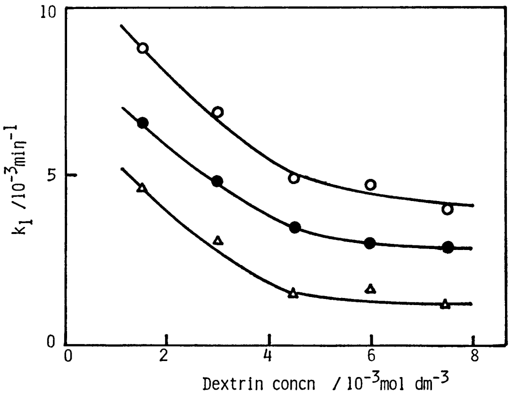

Fig. 9. Plots of k_1 against concentration of dextrin. Solubilized water, 4.77 vol%. Concentration of DBSH, mol dm^{-3}: ○, 0.50; ●, 0.40; △, 0.30.

the reaction mixture; a fairly good straight line is obtained for each plot. A pseudo-first-order rate constant, k_1, was estimated from the slope of the straight line. Figure 7 shows plots of k_1 against concentration of DBSH. The values of k_1 are found to increase proportionally with an increasing concentration of DBSH in the range of the concentration higher than 0.30 mol dm^{-3}. No break point, such as was found in the similar plot in the case of a sucrose-containing reversed-micelle system at CMC of DBSH, was found of the plots in this range, although the CMC of DBSH in this case is in a range of 0.45 to 0.60 mol dm^{-3}. The difference may be related to the solubilizing states of the substrates; the high molecular weight of the substrate may make the solubilizing state of the substrate less stable. The details are now under investigation. The maximum apparent second-order rate constant estimated from the slope of the straight line in Fig. 7, not considering the amount of solubilized water, is 2.8×10^{-2} dm^3 mol^{-1} min^{-1}, which is about 285-times larger than that of dextrin hydrolysis in aqueous solution in the presence of DBSH normal micelle, under similar conditions.

Figure 8 shows plots of k_1 against the amount of solubilized water. The k_1 is found to decrease considerably with increasing amounts of solubilized water. Figure 9 shows plots of k_1 against concentration of dextrin. The k_1 is found to decrease with an increasing concentration of dextrin, especially in the lower range of concentration. This change in k_1 is contrary in tendency to that observed in a sucrose hydrolysis in the same reversed-micelle system. The difference may result from the difference in molecular weights of the substrates; the higher molecular weight of the substrate is inferred to lead to the less stable reversed micelle.

Conclusion

Even an addition of water containing a higher molecular weight substrate such as dextrin to the DBSH benzene reversed-micelle system gave a perfectly clear solution. The CMC of DBSH estimated with the method of Methylene Blue methachromasis was observed in the solution, just like in the system containing the low molecular weight analogs. Furthermore in the hydrolysis reaction of the dextrin in this system, large rate enhancement, up to 285-fold, on the basis of the reaction in an aqueous DBSH solution, were observed. Some behaviors different from those in the case of sucrose in the same reversed-micelle system were found in the dependences of CMC and hydrolysis rate on the concentration of substrate and in that of k_1 on the concentration of DBSH. These different behaviors may be due mainly to the high molecular weight of dextrin; the high molecular weight of the substrate influences the stability of the reversed micelle, and consequently the association of the substrate and DBSH molecules and the activity of hydrogen ions. These results suggest that the rate enhancement mechanism due to the solvent effect and micelle effect which was observed in the hydrolysis of sucrose in the same reversed-micelle system operates also on the hydrolysis of the high molecular weight substrate such as dextrin, although the state of association of the substrate with water and DBSH is not apparent at the present time.

References

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4) M. Somogyi, *J. Biol. Chem.*, **195**, 19 (1952).