

Hydrolysis of Dextrin in a Reversed Micelle in Benzene: Dependence of the Hydrolysis Rate on Degree of Polymerization

INTRODUCTION

New catalysis systems for hydrolysis of carbohydrates have been investigated,¹⁻³ and recently an effective rate enhancement of the hydrolysis of dextrin in water solubilized in benzene with dodecylbenzenesulfonic acid (DBSH) was found.⁴ In the present paper, the dependence of the hydrolysis rate of dextrin on the degree of polymerization (DP) is described.

EXPERIMENTAL

Commercially available dextrin was dissolved in water and methanol was added as a precipitant in a stepwise manner to fractionate it into fractions with different DP. The fractions with number-average DP of 17, 51, 93, and 136 were selected and used as the substrates in the present experiment. Reagent grade maltose was also used as a substrate.

Commercially available sodium dodecylbenzenesulfonate (DBSNa) was dissolved in water and passed through a cation exchanger column to obtain the free acid form of the surfactant. DBSH, obtained as an aqueous solution, was concentrated under vacuum to a solid content of about 90%. A part of the jellied solid was neutralized with sodium hydroxide solution to estimate the acid content, and then dried at 110°C for 24 h to determine the water content of the jellied solid.

Measurements of the hydrolysis rate of dextrin and of the maximum amount of water solubilized in benzene were carried out according to the method previously reported.⁴

Viscosities of DBSNa benzene solutions containing 3.33 mol·L⁻¹ of water were measured with a Cannon-Fenske type viscometer at 30°C.

RESULTS AND DISCUSSION

The influence of DP of dextrin secondary-solubilized in water on the maximum amount of water solubilized in benzene with DBSH was investigated. Figure 1 shows the plots of the maximum amount of solubilized water as a function of concentration of DBSH for the selected fractions of

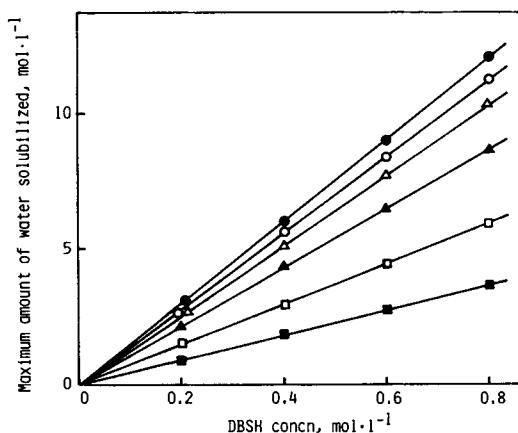


Fig. 1. Plots of the maximum amount of solubilized water as a function of concentration of DBSH for the selected fractions of dextrin in DBSH benzene solution, at room temperature. DP of dextrin: (●) 2; (▲) 17; (△) 51; (□) 93; (■) 136; (○) without dextrin. Concentration of dextrin, 0.154 mol·L⁻¹, as anhydroglucose unit (AGU) in water.

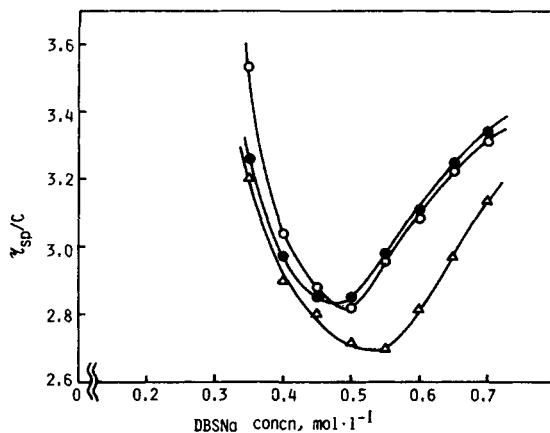


Fig. 2. Changes in plot of reduced viscosity, η_{sp}/C , of DBSNa benzene solution containing $3.33 \text{ mol}\cdot\text{L}^{-1}$ of water against concentration of DBSNa with addition of maltose or dextrin. (O) Without dextrin; (●) addition of maltose; (Δ) addition of dextrin (DP 93). Concentration of maltose and dextrin, $0.308 \text{ mol}\cdot\text{L}^{-1}$ as AGU in water.

dextrin. The maximum amount of solubilized water is found to increase proportionally with an increasing concentration of DBSH, and to decrease with the increasing DP of dextrin, except that with the least DP, maltose. The secondary solubilization of maltose makes the maximum amount higher in comparison with that without the secondary solubilizate, somewhat similar to the case of sucrose.⁵

Changes in viscosity of the reversed micelle system with secondary solubilization of dextrin were investigated. In this case, DBSNa was used instead of DBSH in order to prevent hydrolysis of the substrate. Figure 2 shows plots of the reduced viscosity of the reversed micelle system containing $3.33 \text{ mol}\cdot\text{L}^{-1}$ of water against concentration of DBSNa for the systems with dextrin (DP 93), with maltose, or with no secondary solubilizate. In each plot the existence of a minimum value of the reduced viscosity is found. Behavior similar to that of the reduced viscosity has also been found for the aqueous solution of surfactant, a normal micelle system. Sata and Tyuzyo⁶ suggested that the concentration of the surfactant corresponding to the minimum of the reduced viscosity is a critical

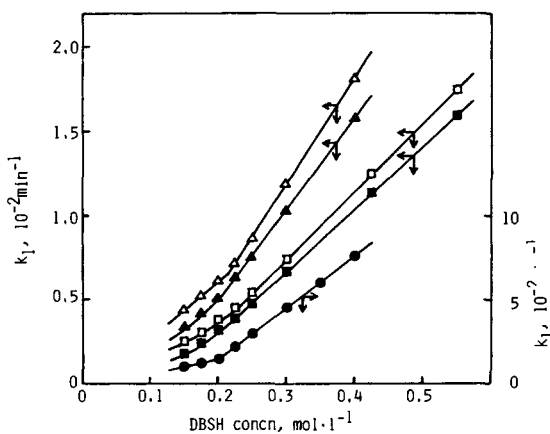


Fig. 3. Plots of pseudo-first-order rate constant k_1 of hydrolysis of dextrans with different DP against concentration of DBSH at 60°C . DP of dextrin: (●) 2; (Δ) 17; (\blacktriangle) 51; (\square) 93; (\blacksquare) 136. Solubilized water, $1.33 \text{ mol}\cdot\text{L}^{-1}$. Concentration of dextrin, $3.7 \text{ mmol}\cdot\text{L}^{-1}$ as glucoside bond in whole volume.

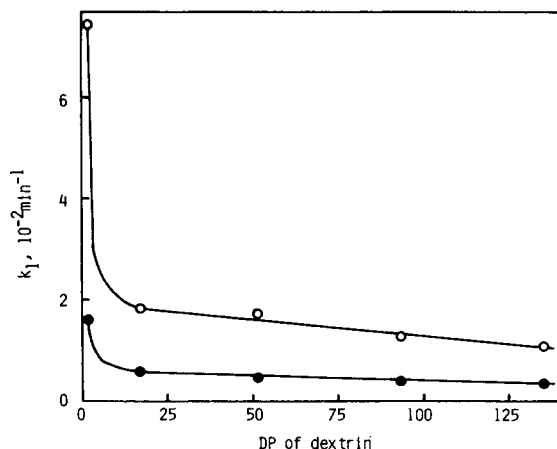


Fig. 4. Plots of k_1 against DP of dextrin. Concentration of DBSH ($\text{mol}\cdot\text{L}^{-1}$): (O) 0.40; (●) 0.20. Solubilized water, $1.33 \text{ mol}\cdot\text{L}^{-1}$. Concentration of dextrin, $3.70 \text{ mmol}\cdot\text{L}^{-1}$ as glucoside bond.

micelle concentration (cmc). In Figure 2, the cmc is found to decrease slightly with secondary solubilization of maltose and to increase with secondary solubilization of dextrin (DP 93). These changes in the reduced viscosity qualitatively agree with that in the maximum amount of water solubilized, and may suggest that the dextrin with higher DP makes the reversed micelle less stable at a given concentration of DBSNa.

Figure 3 shows the plots of pseudo-first-order rate constant k_1 of hydrolysis of dextrans with different DP against the concentration of DBSH. In these cases, the concentrations of the substrate are expressed as the concentration of glucoside bond in the whole volume, not only in the water. It is found in the figure that in the higher range of concentration of DBSH above $0.25 \text{ mol}\cdot\text{L}^{-1}$ each plot shows a straight line, whereas in the lower range the plot shows a tendency to curve. For the substrate with the least DP, maltose, an inflection point is clearly shown, but a definite inflection is less clear with increasing DP of the substrate. This lack of clarity of the inflection point may be due to polydispersity of the DP for the substrate; fractionated dextrin still contains molecules with different DP, especially as the DP is higher.

Figure 4 shows the plots of k_1 against DP of dextrin. k_1 's are found to decrease with increasing

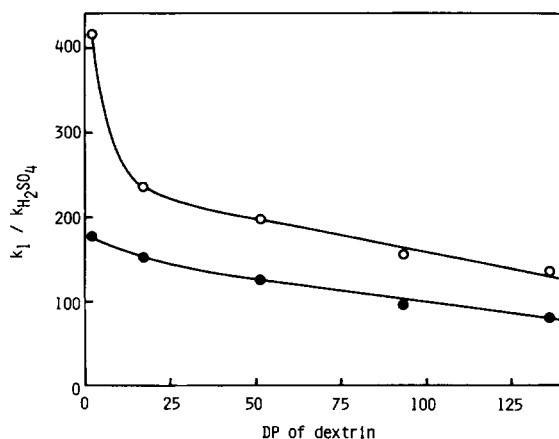


Fig. 5. Plots of relative reaction rate, $k_1/k_{\text{H}_2\text{SO}_4}$, of dextrin hydrolysis in the present reversed micelle system on the basis of that in sulfuric acid aqueous solution against DP of dextrin at 60°C . Concentration of DBSH and sulfuric acid, $\text{eq}\cdot\text{L}^{-1}$ as acid: (O) 0.80; (●) 0.40. Solubilized water, $1.33 \text{ mol}\cdot\text{L}^{-1}$. Concentration of dextrin, $3.70 \text{ mmol}\cdot\text{L}^{-1}$, as glucoside bond.

DP of dextrin. In general, a similar dependence of the hydrolysis rate of dextrin on the DP has also been found in the aqueous solution of mineral acid.⁷ As shown in Figure 5, however, even for the plots of the relative reaction rate on the basis of that in aqueous solutions of sulfuric acid, again a dependence of the relative reaction rate on DP is found, although the influence of the DP of dextrin on the reaction rate is smaller than that on absolute reaction rate. One of the reasons of the dependence of the relative reaction rate on DP may be the limiting diffusibility of protons into the long chain coils of the substrate. In the micelle protons are placed near the periphery of the water pool solubilized under influence of dodecylbenzenesulfonate anions. Lower DP substrate molecules can easily interact with the proton by diffusion, whereas higher DP substrate molecules have less probability to interact with the proton because of their limited diffusibility. It is also found in the figure that DBSH in the reversed micelle system shows a catalytic activity 80–400 times higher, depending on the DP of dextrin and the water content, than that for sulfuric acid in water for hydrolysis of dextrin, at a given concentration of acid ($\text{eq}\cdot\text{L}^{-1}$).

From these results, it may be concluded that the effect of DP on k_1 for hydrolysis of dextrin in the present system is a result of the decrease in stability of the reversed micelle, the lower diffusibility of protons into the long chain coils with increasing bulkiness of the substrate molecules, and the decrease in susceptibility of the glucoside bond itself to hydrolyze with the increasing chain length.

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Received February 7, 1983
Accepted May 9, 1983