The Hydrolysis of Carbohydrates in the Presence of a Reversed Micelle. II. The Hydrolysis of Sucrose in Benzene

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The formation of a reversed micelle by dodecylbenzenesulfonic acid in benzene containing a certain amount of water was examined by means of the absorption spectra of the Methylene Blue added to the system. The hydrolysis of the sucrose secondary-solubilized in the system was then investigated. The maximum rate enhancement of 400-fold was obtained in the presence of the micelle on the basis of the reaction in an aqueous solution in the presence of hydrochloric acid, whereas the addition of ethanesulfonic acid to the system showed only a little effect on the reaction rate. The reaction rates were found to show behavior similar to that of the stability of the micelle with respect to changes in the substrate concentration and in the amount of solubilized water. From these results, the greater part of the rate enhancement obtained in the present system might be concluded to result from some effects due to the formation of the reversed micelle.

Numerous studies have been made of new catalysis systems in the presence of a polymer catalyst[1] or a micelle[2] showing interactions with the substrate. However, there is only a little information on the system for the hydrolysis of such carbohydrates as cellulose, starch, and their low-molecular-weight analogues. Although some attempts have been made to employ a polymeric acid[3-9] or a reversed micelle[10] as catalysts for the hydrolysis, the rate enhancements thus obtained were small.

In a previous paper,[10] the hydrolysis of sucrose in the presence of a dodecylbenzenesulfonic acid (DBSH)-reversed micelle in dioxane–water mixed solvents was investigated; rate enhancements up to 21-fold were observed on the basis of the reaction in an aqueous solution. The rate enhancement, however, had been inferred to result from the solvent effect of dioxane, related to the structuredness of water (*ca.* 10-fold), which was also effective in the catalysis in the presence of sulfuric acid, and from the substrate-binding effect by the reversed micelle (*ca.* 2.1-fold).

In the present experiment, the formation of a reversed micelle by DBSH in benzene containing a certain amount of water is examined, and then the hydrolysis of sucrose secondary-solubilized in the system is investigated.

Experimental

Materials. Reagent-grade sucrose, benzene, ethanesulfonic acid, and hydrochloric acid were used. De-ionized and distilled water was used. Commercially available sodium dodecylbenzenesulfonate (Tokyo Chemical Co., Tokyo) was passed through a cation-exchange column in order to obtain a free acidic surfactant.

UV Spectrum. The UV spectra were obtained with a Hitachi Spectrophotometer 124 (Hitachi Seisakusho Co., Tokyo) at various concentrations of DBSH in benzene containing a certain amount of water and a very small amount of Methylene Blue (cationic dye); the shifts of an absorbance peak in the range of 660—690 nm were measured.

Maximum Amount of Solubilized Water. Water was added, drop by drop with a bulet into the DBSH benzene solution, and the amount of water just before turbidity appeared was estimated as the maximum amount of solubilized water.

Measurement of the Reaction Rate. DBSH was dissolved in benzene, and a sucrose aqueous solution was added. The resulting reaction mixture was then quickly poured into a cell and the optical rotatory powers were measured at intervals at 20 °C by means of a polarimeter (Polax, Atago Kogaku Co., Tokyo). The logarithm of the difference in the optical rotatory powers between that at a reaction time $t (m_t)$ and that at infinity (m_∞) (practically, the optical rotatory power of the corresponding 1:1 mixture of glucose and fructose, because the precise value of m_∞ cannot be obtain in an organic solvent) was plotted against the reaction time, and the pseudo-first-order rate constant was estimated from the slope of the straight line thus obtained.

Results and Discussion

The absorption spectra of Methylene Blue added to a DBSH benzene solution containing a certain amount of water were investigated at various concentrations of DBSH, water, and sucrose. Figure 1 shows typical changes in the spectrum with the concentration of DBSH. Two absorbance peaks are observed in the figure, and one of them, on the left-hand side, is found to shift to a longer wave length with an increase in the concentration of DBSH. This sort of red shift is well known as methachromasis and may suggest the forma-

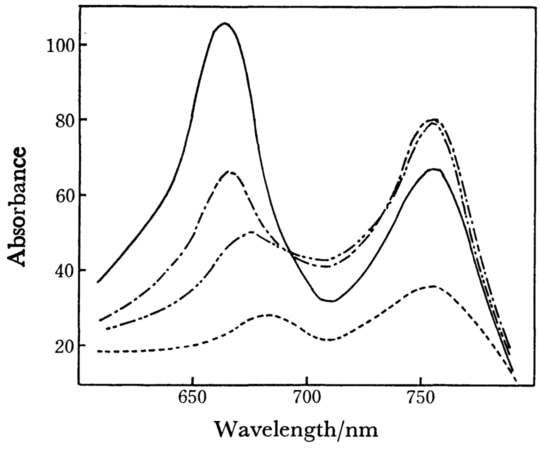

Fig. 1. Typical changes in absorption spectrum of Methylene Blue added to DBSH benzene solution with changing concentration of DBSH. Solubility water, 5 vol%. DBSH concn, N: ——; 0.03, —-—; 0.45, — — —; 0.50, ----; 0.70.

tion of a micelle. In general, the micelle formed in an apolar solvent such as benzene is known to be a reversed micelle,[11] so the micelle formed in the present system is inferred also to be a reversed one. Figure 2 shows typical changes in the wavelength corresponding to the peak in the spectrum with the concentration of DBSH. A sigmoidal curve is obtained, and the inflection point of the curve is presumed to be a critical micelle concentration of DBSH (CMC).

The maximum amounts of solubilized water in the DBSH benzene solution were measured at various concentrations of DBSH. Figure 3 shows the plots of the maximum amount of water against the concentration of DBSH; the amount of water is found to increase proportionally with the increase in the concentration of DBSH. The slope of the straight line obtained corresponding to 9.3 mol of water/mol of DBSH, which is comparable to the water-solubilizability of Aerosol OT.[12]

The hydrolysis of sucrose secondary-solubilized in the reversed micelle system containing a certain amount of water was investigated at various concentrations of acid, water, and sucrose. Figure 4 shows some typical first-order plots of the changes in the optical rotatory power of sucrose at 20 °C. 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 5 shows the plots of the k_1 against the concentration of acid, the total concentration of DBSH and ethanesulfonic acid. The plots shown with a solid line are those of the k_1 in the presence of DBSH alone; a straight line is obtained for each plot in the concentration range of DBSH higher than a certain concentration, which is nearly in accord with the corresponding CMC presumed from the changes in the absorption spectrum. The slope of the straight line gives an apparent second-order rate constant, $k_{2\mathrm{obsd}}$, when the amount of solubilized water is not considered. The $k_{2\mathrm{obsd}}$'s are far larger than that of the reaction in water

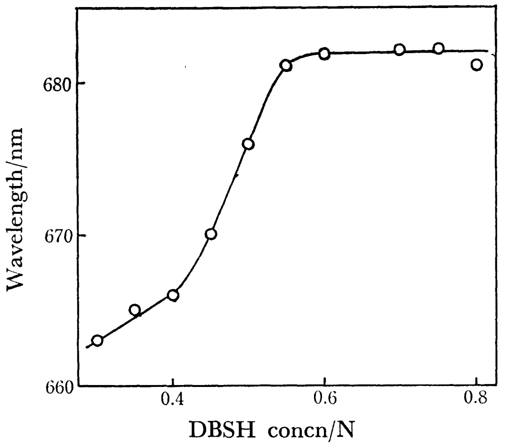

Fig. 2. Typical changes in wavelength corresponding to the peak in absorption spectrum of Methylene Blue added to DBSH benzene solution with changing concentration of DBSH. Solubilized water, 5 vol%.

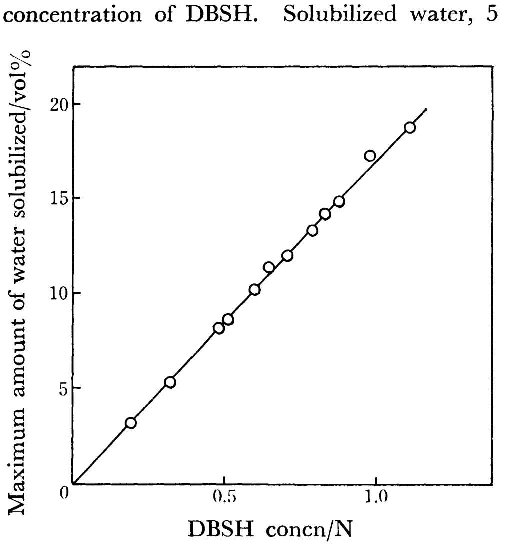

Fig. 3. Plot of maximum amount of water solubilized in DBSH benzene solution against concentration of DBSH.

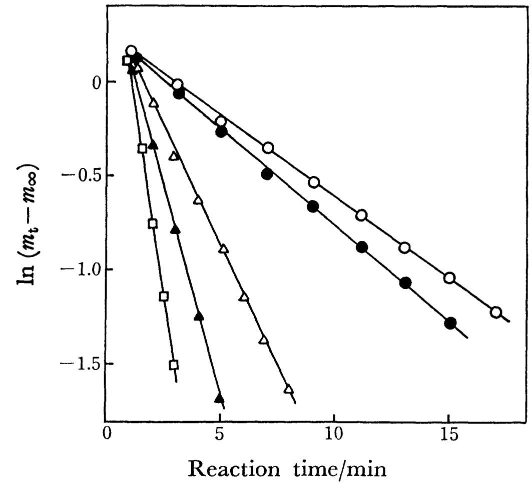

Fig. 4. Typical first-order plots of the changes in the optical rotatory power of sucrose at 20 °C. m_t and m_∞ are the optical rotatory powers at a reaction time t and infinity. Sucrose concn, 32 mM. DBSH concn, N: ○; 0.55, ●; 0.61, △; 0.68, ▲; 0.77, □; 0.86. Solubilized water, 7.5 vol%.

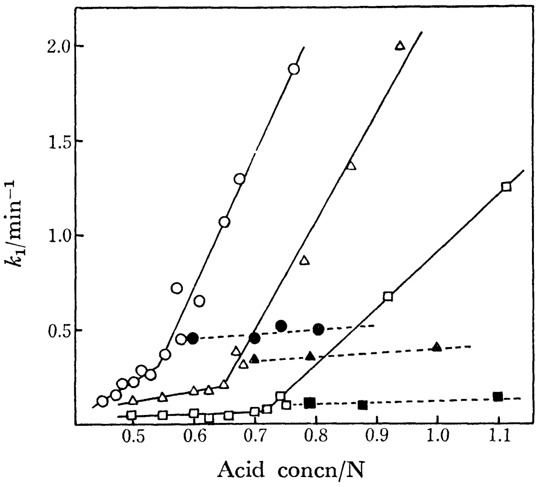

Fig. 5. Plots of pseudo-first-order rate constant, k_1, of sucrose hydrolysis against acid concentration. Sucrose concn, 32 mM. Solubilized water, vol%: ○, ●; 5.0, △, ▲; 7.5, □, ■; 10.0. Acid: ——; DBSH only, ----; ethanesulfonic acid added to DBSH.

in the presence of hydrochloric acid (the plot is omitted in the figure to avoid complexity, and the second-order rate constant, $k_{2\mathrm{HCl}}$, is 0.016 $\mathrm{l\,mol^{-1}\,min^{-1}}$) and is found to decrease with an increase in the amount of solubilized water. The plots shown with dotted line are those of the k_1 in the presence of the ethanesulfonic acid added to the system after DBSH formed the micelle. Ethanesulfonic acid is presumed not to form any micelle, and in fact, CMC was not influenced by the addition of ethanesulfonic acid to the system. In the figure the slopes of the dotted straight lines are found to be far smaller than those in the presence of DBSH alone in a higher concentration range at the same acid concentration.

Figure 6 shows the plots of CMC presumed from the absorption spectrum and of the ratio of the sucrose hydrolysis rates with the DBSH micelle to those with hydrochloric acid, $k_{2\mathrm{obsd}}/k_{2\mathrm{HCl}}$, against the concentration of sucrose. Again, for each reaction with different concentrations of sucrose, the DBSH concentration at the break point of the plots of k_1 against the DBSH concentration were nearly in accord with the corresponding CMC. It can be seen in Fig. 6 that CMC decreases with an increase in the concentration of sucrose and that $k_{2\mathrm{obsd}}/k_{2\mathrm{HCl}}$ also increases in the concentration range higher than 40 mM. It may be explained qualitatively that the more stable the micelle is, the larger $k_{2\mathrm{obsd}}/k_{2\mathrm{HCl}}$ is given, although the larger values of $k_{2\mathrm{obsd}}/k_{2\mathrm{HCl}}$ in a concentration range lower than 40 mM cannot be explained at the present time. Figure 7 shows the plots of the CMC and $k_{2\mathrm{obsd}}/k_{2\mathrm{HCl}}$ against the amount of solubilized water. It is found that the CMC increases proportionally with the amount of solubilized water and that the $k_{2\mathrm{obsd}}/k_{2\mathrm{HCl}}$ decreases. Again, from these plots it may be possible to explain qualitatively that the more stable the micelle is, the larger $k_{2\mathrm{obsd}}/k_{2\mathrm{HCl}}$ is given.

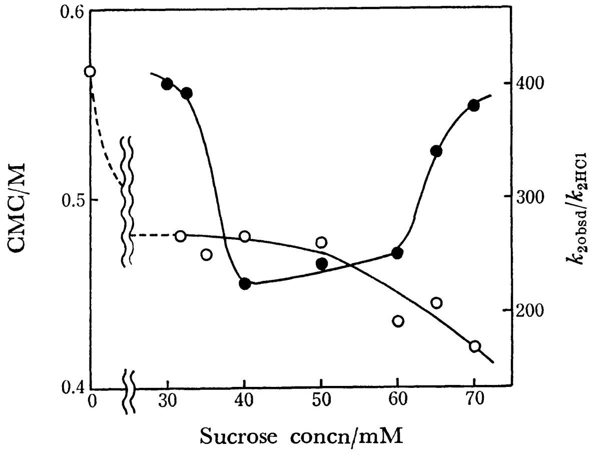

Fig. 6. Plots of CMC (○) and the ratio of sucrose hydrolysis rates with the DBSH micelle to those with hydrochloric acid, $k_{2\mathrm{obsd}}/k_{2\mathrm{HCl}}$ (●), against sucrose concentration. Solubilized water, 5 vol%.

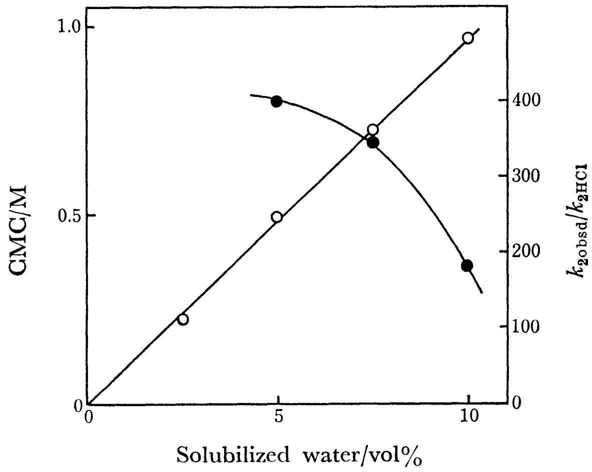

Fig. 7. Plots of CMC (○) and the ratio of sucrose hydrolysis rates with the DBSH micelle to with hydrochloric acid, $k_{2\mathrm{obsd}}/k_{2\mathrm{HCl}}$ (●), against the amount of solubilized water. Sucrose concn, 32 mM.

Conclusion

The hydrolysis of sucrose secondary-solubilized in a DBSH benzene solution containing a certain amount of water was investigated, and rate enhancements up to 400-fold were obtained on the basis of the reaction in an aqueous solution in the presence of hydrochloric acid. Some facts observed in the present investigation, which show the existence of a close relationship between the changes in the reaction rate and the micelle formation, suggest that the greater part of the rate enhancement is related to the formation of the reversed micelle; in contrast to the corresponding reaction in a dioxane–water mixed solvent,[10] the micelle effect may be far larger than the solvent effect. The micelle effects obtained in the present system are supposed to arise from a substrate-binding effect into the micelle, from the increase in the activities of the water molecules and hydronium ions, from a more suitable conformation of transition state for the reaction, and from other factors. At the present time, however, the details are not apparent.

References

1) For example: I. Sakurada, *Pure Appl. Chem.*, **16**, 263 (1968); C. Overberger, *Acc. Chem. Res.*, **2**, 217 (1969); H. Morawetz, *Acc. Chem. Res.*, **3**, 354 (1970); N. Ise, *Adv. Polym. Soc.*, **7**, 536 (1971).

2) For example: J. Albrizzio, J. Archila, T. Rudulfo, and E. H. Cordes, *J. Org. Chem.*, **37**, 871 (1972); J. R. Cho and H. Morawetz, *J. Am. Chem. Soc.*, **94**, 345 (1972); J. H. Fendler and R. R. Liechti, *J. Chem. Soc., Chem. Commun.*, **1972**, 1041; S. Friberg and S. I. Ahmad, *J. Am. Chem. Soc.*, **94**, 5196 (1972).

3) W. Kern, W. Herold, and B. Scherhag, *Makromol. Chem.*, **17**, 231 (1955).

4) T. J. Painter and W. T. J. Morgan, *Chem. Ind. (London)*, **1961**, 437.

5) N. Hartler and K. Hyllengren, *J. Polym. Sci.*, **55**, 779 (1975).

6) K. Arai and N. Ise, *Makromol. Chem.*, **176**, 37 (1975).

7) K. Arai and Y. Ogiwara, *Makromol. Chem.*, **176**, 2491, 2501 (1975); **177**, 367 (1976).

8) K. Arai, Y. Ogiwara, and N. Ise, *Makromol. Chem.*, **176**, 2871 (1976).

9) K. Arai and Y. Ogiwara, *J. Appl. Polym. Sci.*, **20**, 1989 (1976).

10) K. Arai and Y. Ogiwara, *Bull. Chem. Soc. Jpn.*, **49**, 1059 (1976).

11) A. Kitahara, T. Kobayashi, and T. Tachibana, *J. Phys. Chem.*, **66**, 363 (1962).

12) A. Kitahara, *Yukagaku*, **9**, 169 (1960).