April, 1976] BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 49(4), 1059—1062 (1976) 1059

Hydrolysis of Carbohydrates in the Presence of a Reversed Micelle. I. Hydrolysis of Sucrose in a Dioxane–Water Mixed Solvent

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(Received April 18, 1975)

Formation of a reversed micelle by dodecybenzenesulfonic acid (DBSH) in a dioxane-water mixed solvent was discussed in terms of the behavior of critical micelle concentration and NMR study. Hydrolysis of sucrose in the presence of the reversed micelle was then investigated. The pseudo-first-order rate constant of the reaction showed a tendency to increase with decreasing substrate concentration and increasing dioxane composition, and the maximum rate acceleration obtained in the present experiment was 21-fold on the basis of the reaction in aqueous solution. The rate acceleration may result from the solvent effect of dioxane relating to the structuredness of water and the substrate binding effect due to the formation of the reversed micelle.

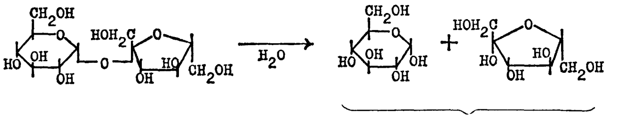
The hydrolysis of carbohydrates in the presence of catalysts has been studied.[1–3] Numerous studies have been made on catalysis in the presence of a micelle[4] and also in the presence of a reveresed micelle.[5–9] In the present work the hydrolysis of sucrose as a model substance of carbohydrates in the presence of a reversed micelle was investigated. First the formation of the reversed micelle in the dioxane–water mixed solvent was examined, since carbohydrates are not sufficiently soluble in a polar solvents such as benzene and cyclohexane for the reaction rate to be followed accurately. If dodecylbenzenesulfonic acid (DBSH) can form a reversed micelle in the mixed solvent and the carbohydrates are bound into the micelle, it can be expected that the hydrolysis rates of sucrose are affected; the carbohydrates bound into the micelle are hydrolyzed in the presence of locally concentrated protons in the interior of the micelle.

There is little information on the reversed micelle in a mixed solvent, and its behavior was predicted to be very complicated.[10] The analyses were therefore carried out with emphasis on the rate enhancement.

Experimental

Materials. Reagent grade sucrose, dioxane and hydrochloric acid (Wako Chemical Co., Tokyo) were used. Deionized and distilled water was used. Commercial sodium dodecybenzenesulfonate (Tokyo Chemical Co., Tokyo) was passed through a cation-exchange resin column in order to obtain free acidic surfactant.

Measurement of the Reaction Rate. DBSH was dissolved in a dioxane-water mixture and added to a sucrose aqueous solution, and the resulting mixture was kept at 40 °C. Aliquots of the mixture were taken out at intervals and the optical rotatory powers were measured by an automatic digital polarimeter (Nippon Bunko Co., Tokyo, DIP-180; accuracy ±0.002°). The logarithm of the difference between the optical rotatory powers, m_t at a reaction time t and m_∞ at infinite time (practically at ten times half life), was plotted against the reaction time, and the pseudo-first-order rate constant, k_1, was estimated from the slope (Fig. 1).



$[\alpha]_D^{20} = 66.45$ $[\alpha]_D^{20} = -19.7 + 0.36C$

C; concentration in g·dl^{-1}

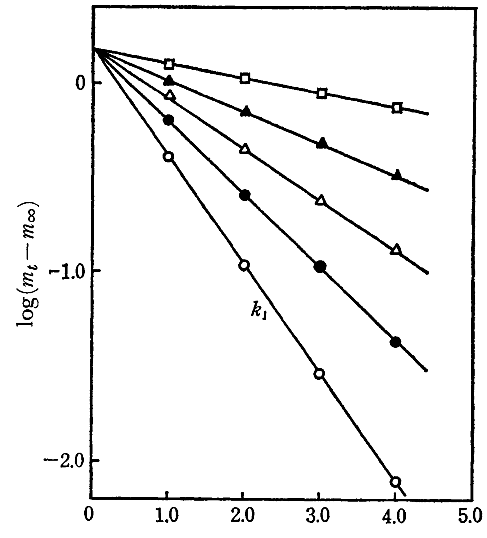


Fig. 1. Typical first-order plots of the changes in the optical rotatory power of sucrose at 40 °C.
m_t and m_∞ are the optical rotatory powers at a reaction time t and infinity. Dioxane composition, 70 vol%. DBSH concn, mM: ○; 100, ●; 80, △; 60, ▲; 40, □; 20.

A fairly good straight line was obtained for each plot. The changes in optical rotatory powers in water are as above.

Critical Micelle Concentration (CMC). Electric conductances of DBSH–dioxane–water mixed solutions were measured with an electric conductance titrator (Mitamura Riken Co., Tokyo) at various concentrations of DBSH, specific electric conductances being plotted against the concentration of DBSH. The maximum experimental error of specific conductance was ±0.001 S. The CMC was estimated from the break in the plots.

NMR Study. NMR spectra were obtained with an analytical NMR spectrometer (Nichiden-Varian Co., Varian A-60D, 60 MHz) at various concentrations of DBSH and hydrochloric acid, the chemical shifts of water-proton being measured. Sodium 3-trimethylsilylpropanesulfonate was used as a reference.

Results and Discussion

Formation of Reversed Micelle. First we examined whether reversed micelle could be formed by DBSH. Figure 2 shows the plots of the electric conductance of DBSH–dioxane–water mixtures against the con-

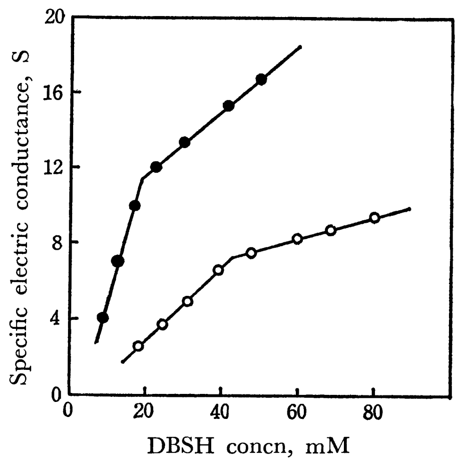


Fig. 2. The plots of the specific electric conductance of DBSH in dioxane-water mixtures against the concentration of DBSH at 40 °C.
Solvent: ○; dioxane 70 vol%, ●; dioxane-free.

centration of DBSH at compositions of dioxane 0 and 70 vol%. The concentration of surfactant corresponding to the break point of the straight lines obtained is considered to be CMC. The break point of the straight line can be clearly seen for the mixture with dioxane composition of 70 vol% as well as in the dioxane-free medium (Fig. 2), although it has been reported that the CMC of a reversed micelle is not clear.[11] This suggests the formation of a micelle even at higher dioxane composition.

Figure 3 shows the temperature dependence of the CMC estimated by the electric conductance method. It was found that the CMC is scarcely influenced by temperature. This behavior is in approximate agreement with the general characteristics of the micelle of ordinary alkylbenzenesulfonates.

Figure 4 shows the changes in CMC with the concentration of added sucrose. The CMC in the mixed solvent of dioxane 70 vol% decreases with addition of sucrose up to about 50 mM, and then levels off, but hardly changes in the dioxane-free solvent. The decrease in CMC with the addition of polar substrate was also found by Fendler *et al.*[6] in the reversed micelle system, and might indicate substrate binding into the micelle. The leveling off of the CMC with increasing sucrose concentration at higher dioxane compositions might be due to the fact that the amount of sucrose bound into the micelle does not increase any more with increasing concentration of sucrose under the conditions.

Figure 5 shows the relationship between the CMC and dioxane composition in the mixed solvents. DBSH was found to be insoluble in the range 20—50 vol% of dioxane. This suggests that the micelle formed at above 60 vol% of dioxane is the reversed micelle. The CMC is scarcely influenced by the dioxane composition in the lower range. In the higher range of dioxane composition, however, the CMC increases with increasing dioxane composition, and then shows a maximum at 80 vol% of dioxane. In the higher range of dioxane composition than those shown in Fig. 5, measurement of CMC was impossible because of the phase separation. The increase in CMC with increasing dioxane composition does not necessarily rule out the possibility of the reversed micelle formation, since the size of the micelle in the mixed solvent probably changes remarkably with changing solvent composition.[10]

The proton magnetic resonance shifts of water-proton in the presence of DBSH and hydrochloric acid in the dioxane-water mixed solvent at various concentrations were measured in order to investigate the reversed micelle formation. It has been established that the chemical shift of the proton magnetic resonance is concentration-dependent in the solutions of electrolytes which yield hydrogen-containing ions. The chemical exchange averages the chemical shifts in the proton resonance position over the different chemical species, and the averaged shifts observed are correlated with the dissociation of the solute.[12–15] Figure 6 shows the plots of averaged chemical shift *vs.* acid concentrations in the aqueous solution and in the dioxane-water mixed solvent with 70 vol% of dioxane. In the aqueous solution, the changes in the chemical shift with addition of acids were relatively small and

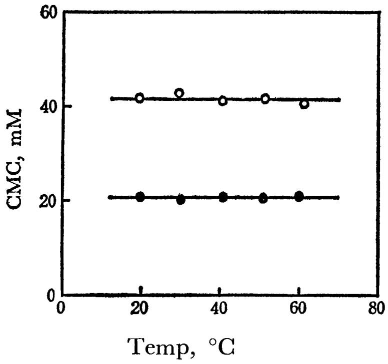


Fig. 3. Temperature dependence of CMC. Solvent: ○; dioxane 70 vol%, ●; dioxane-free.

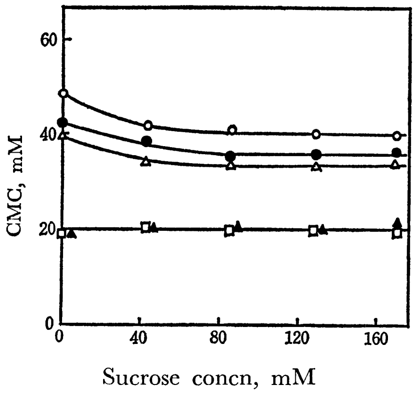


Fig. 4. Changes in CMC with addition of surcose at 40 °C. Dioxane compositions, vol%: ○; 80, ●; 70, △; 60, ▲; 10, □; 0.

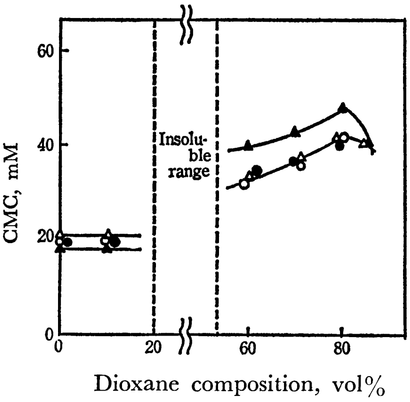


Fig. 5. Relationships between CMC and dioxane composition in the mixed solvents at 40 °C. Sucrose concn, mM: ○: 124.8, ●; 83.2, △; 41.6, ▲; 0.

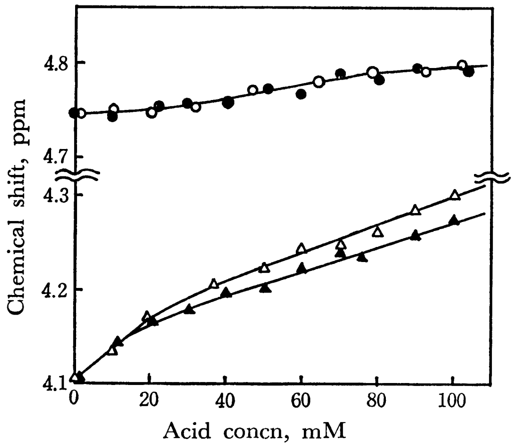


Fig. 6. The plots of averaged chemical shift of water-proton magnetic resonance *vs.* acid concentration. Acid: DBSH, ▲; dioxane 70 vol%, ●; dioxane free: hydrochloric acid, △; dioxane 70 vol%, ○; dioxane-free.

the difference in the chemical shifts of DBSH and hydrochloric acid appeared to be within the error limit. In the mixed solvent the chemical shift shifted to higher magnetic field with addition of dioxane, the changes in the chemical shift with addition of acids being greater than those in aqueous solution. The shifts may be related to the changes in structuredness of water. The changes in chemical shift were found to become smaller with addition of DBSH than with that of hydrochloric acid with an increase in acid concentration above 30 mM. The difference may result from the decrease in dissociation of DBSH due to "concentration" of sulfonic acid groups in the interior of the reversed micelle.

It seems that DBSH could form a reversed micelle in a dioxane–water mixed solvent with dioxane above 60 vol%, although the micelle might be less stable than the typical reversed micelle formed in neat apolar solvents.

Hydrolysis of Sucrose in the Presence of the Reversed Micelle. Hydrolysis of sucrose in dioxane–water mixed solvents in the presence of the reversed micelle mentioned above was investigated. Figure 7 shows the plots of the pseudo-first-order rate constant, k_1, estimated from the changes in the optical rotatory power of the reaction mixture (see Fig. 1) *vs.* the concentration of DBSH. Above 60 vol% of dioxane each plot gives two half lines, whereas below 10 vol% it gives only one straight line. In the hydrolysis of sucrose in the presence of hydrochloric acid, each similar plot of k_1 gives only one straight line independent of dioxane composition in the mixed solvent. Since k_1 was defined as the pseudo-first-order rate constant at a constant concentration of DBSH, the slope of the straight lines gives the apparent second-order rate constant, k_2, when the changes in the amount of water in the mixed solvent are not considered. Above 60 vol% of dioxane, k_2's in the lower and higher concentration ranges of DBSH are denoted by k_{2L} and k_{2H}, respectively. k_2 for the hydrolysis of sucrose in the presence of hydrochloric acid is denoted by k_{2HCl}.

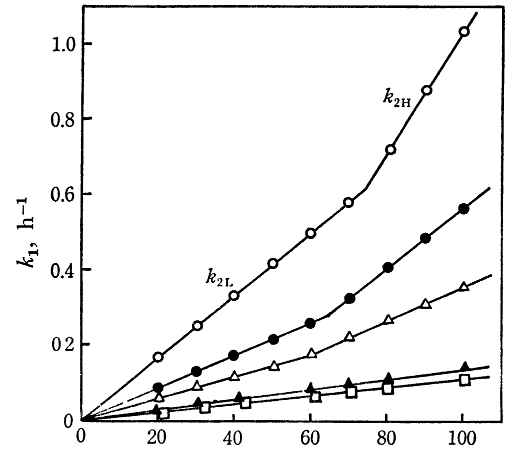


Fig. 7. Plots of the pseudo-first-order rate constant, k_1, *vs.* DBSH concentration at 40 °C. Sucrose concn, 83.2 mM. Dioxane composition, vol%. ○; 80, ●; 70, △; 60, ▲; 10, □; 0.

Although the concentration of DBSH corresponding to the break point on the straight line was slightly higher than the CMC estimated by the electric conductance method under the same conditions, the concentration may be considered as CMC, since CMC is known to be slightly affected by the measuring method and also the changes in concentration corresponding to the break point with change in concentration of DBSH and sucrose qualitatively agree with those of the CMC estimated by the electric conductance method (Table 1). Fendler *et al.*[7] also found a change in rate constant at a certain concentration by changing the concentration of surfactant. The hydrolysis of sucrose seems to be accelerated with formation of reversed micelle.

k_2's estimated at various concentrations of sucrose and dioxane are summarized in Table 2. It was found that k_2's increased with increasing dioxane composition in the mixed solvents for all of the k_{2H}, the k_{2L} and the k_{2HCl}. The increase may arise from the increase in activities of proton and water molecules due to the decrease in structuredness of water with addition of dioxane.[16] At the same composition of dioxane, k_{2L}'s were always smaller than k_{2HCl}. These differences may be due to the differences in the degree of dissociation. Above 60 vol% of dioxane and higher concentration range of DBSH, however, k_{2H}'s were greater than k_{2L}'s and even greater than k_{2HCl}. This rate enhancement might result from the substrate binding into the reversed micelle in which protons

TABLE 1. DBSH CONCENTRATION CORRESPONDING TO THE BREAK POINT OF THE STRAIGHT LINES OBTAINED IN THE PLOTS OF k_1 *vs.* DBSH CONCENTRATION, mM

Dioxane composition, vol%	Sucrose concn, mM		
	41.6	83.2	124.8
80	77	74	68
70	67	65	65
60	67	61	61

TABLE 2. SECOND-ORDER RATE CONSTANTS, k_2'S, IN $M^{-1}\,h^{-1}$, FOR SUCROSE HYDROLYSIS IN THE PRESENCE OF DBSH OR HYDROCHLORIC ACID AT 40 °C

Catalyst	Sucrose concn, mM		Dioxane composition, vol%					
			85	80	70	60	10	0
DBSH	41.6	k_{2L}	13.0	8.3	4.5	2.6	1.4	1.3
		k_{2H}	27.0	19.0	9.5	4.5		
		k_{2H}/k_{2L}	2.1	2.3	2.1	1.7	—	—
	83.2	k_{2L}	—	8.3	4.5	3.0	1.4	1.3
		k_{2H}	—	16.8	7.9	4.6		
		k_{2H}/k_{2L}	—	2.0	1.8	1.5	—	—
	124.8	k_{2L}	—	10.7	5.3	3.4	1.6	1.4
		k_{2H}	—	16.5	8.0	5.1		
		k_{2H}/k_{2L}	—	1.6	1.5	1.5	—	—
Hydrochloric acid	124.8	k_{2HCl}	—	14.0	6.5	3.5	1.6	1.5

were concentrated. The ratio k_{2H}/k_{2L} could be regarded as a measure of rate enhancement produced by the formation of reversed micelle. The ratios were found to increase with increasing dioxane composition. It is presumed that the stability of reversed micelle increases with lowering polarity of the mixed solvent or increasing dioxane composition, the effect leading to rate enhancement. The ratio k_{2H}/k_{2L} was also found to decrease with increasing sucrose concentration. The decrease could be explained as the result of averaging of reaction rates in and out of the reversed micelle, since the amount of sucrose bound into the micelle was presumed not to change, at least remarkably, with increasing total amount of sucrose, while the amount of sucrose existing out of the micelle increased, and the averaged reaction rate or the rate enhancement decreased with increasing total amount of sucrose. This explanation is supported by some investigations published so far. For example, Konno and Kitahara[17] reported that a small amount of water solubilized in reversed micelle is firmly bound into the micelle, but the binding become more loose, even less than that of free water, with the increase in amount of water solubilized. Kitahara[18] found that the change in the amount of water solubilized in the anionic surfactant reversed micelle scarcely influences the amount of micelle. The value of k_{2H}/k_{2L} corresponding to the sucrose concentration 41.6 mM and dioxane 85 vol% was found to deviate from the tendency mentioned above (Table 2). A similar deviation of the value of CMC estimated by the electric conductance method under the same conditions is shown in Fig. 5.

It may be concluded that DBSH forms a reversed micelle in dioxane–water mixture with above 60 vol% of dioxane and the micelle accelerates the hydrolysis of sucrose by binding the substrate inside. The maximum rate enhancement obtained in the present investigation was *ca.* 21-fold, and it was predicted to increase with decreasing sucrose concentration. The rate enhancement may result from the solvent effect of dioxane relating to the structuredness of water and the substrate binding effect due to the formation of reversed micelle.

We are very grateful to Professor Norio Ise, Kyoto University, Kyoto, for his helpful discussion.

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