Bull. Chem. Soc. Jpn., *59*, *935—936 (1986)*

Influence of Higher Alcohols on Acid-Catalyzed Hydrolysis of Sodium Dodecyl Sulfate. Effect of Complex Formation

Masayuki Nakagaki and Shoko Yokoyama*
Faculty of Pharmaceutical Sciences, Kyoto University, Yoshida-Shimoadachi-cho,
Sakyo-ku, Kyoto 606

(Received September 20, 1985)

Synopsis. The order of effectiveness of 1-alkanols for increasing the rate of acid-catalyzed hydrolysis of sodium dodecyl sulfate is 1-dodecanol>1-tetradecanol ≫ 1-decanol. The effect of 1-alkanols on this hydrolysis is discussed from the viewpoint of formation of complexes composed of SDS and 1-alkanol.

In our preceding paper,[1)] we reported the influence of 1-dodecanol ($C_{12}OH$) on the acid-catalyzed hydrolysis of sodium dodecyl sulfate (SDS) at concentrations above and below the critical micelle concentration (cmc). The hydrolysis of SDS at a concentration below the cmc is accelerated by addition of $C_{12}OH$ due to formation of a complex (SDS:$C_{12}OH$=2:1), and at concentrations above the cmc is initially suppressed by addition of $C_{12}OH$ due to reduction in surface charge density of the SDS micelle.

On the other hand, it has been known that complexes are formed not only between $C_{12}OH$[2–6)] and SDS but also between other 1-alkanols[7,8)] and SDS.

In this paper, therefore, we will deal with the influence of higher alcohols on the acid-catalyzed hydrolysis of SDS at concentrations below the cmc from the viewpoint of complex formation.

Experimental

Normal higher alcohols, 1-octanol (C_8OH), 1-decanol ($C_{10}OH$), 1-dodecanol ($C_{12}OH$), and 1-tetradecanol ($C_{14}OH$) obtained from Nakarai Chemicals Co. were of guaranteed reagent grade and used without further purification. Sodium dodecyl sulfate (SDS) was the same as that specified in our preceding paper.[1)] Solutions were prepared by adding 1-alkanol to an aqueous 0.5 mmol dm^{-3} solution of SDS, followed by stirring for 20 h at 25 °C. The hydrolysis of SDS was carried out at pH 3.22±0.01 and 25±0.2 °C, and second-order rate constants were estimated as previously described.[1)]

Results and Discussion

Effects of C_8OH, $C_{10}OH$, $C_{12}OH$, and $C_{14}OH$ on the Hydrolysis of SDS. Figure 1 shows rate constants for the hydrolysis of SDS against concentrations of 1-alkanols (or mole ratios of 1-alkanol to SDS). The relationship between $C_{12}OH$ and SDS which has been given in the preceding paper[1)] is also included in Fig. 1. When the solution contains only premicellar SDS, the rate constant for the hydrolysis is very small but is increased markedly by addition of $C_{12}OH$ or $C_{14}OH$. Above mole ratio 0.5 of 1-alkanol to SDS, the rate constant is independent of the 1-alkanol concentration, which suggests formation of a complex of SDS with $C_{12}OH$[5,6)] or $C_{14}OH$.[7)]

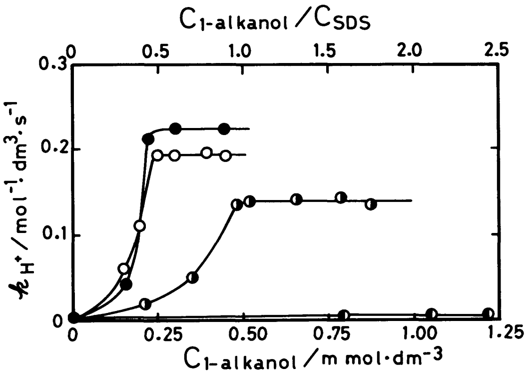

Fig. 1. Effect of 1-alkanols on the rate constant for hydrolysis of SDS at a concentration below the cmc
1-alkanol: ◐ C_8OH, ◑ $C_{10}OH$, ● $C_{12}OH$, ○ $C_{14}OH$
C_{SDS}: 0.50 mmol dm^{-3}
pH: 3.22

In the case of $C_{10}OH$, the rate constant increases with increasing concentration of $C_{10}OH$ and assumes a constant value at mole ratios of $C_{10}OH$ to SDS above 1.0. This tendency is consistent with formation of a 1:1 complex of SDS with $C_{10}OH$.[8)]

The rate constants in the presence and absence of C_8OH do not so much differ from each other, even if C_8OH is added above mole ratio 2.0 to SDS. This suggest that there is no characteristic interaction between SDS and C_8OH. It has been reported[9)] that a liquid crystal is formed in the C_8OH–SDS–water ternary system at a SDS concentration of 40 w/v%. We used too low a concentration of SDS for the formation of micelle (cmc values of SDS in the presence of 1-alkanols have been reported[8)]). Therefore, it may be concluded that neither liquid crystal nor surfactant-alcohol complex is formed in this C_8OH system.

Regarding the relationship between the formation of liquid crystal and the rate constant for the hydrolysis of SDS, Barry and Schotten[10)] reported that the rate constant was increased by an addition of 1-hexadecanol ($C_{16}OH$) due to formation of a liquid crystal in the $C_{16}OH$–SDS–water ternary system.

Effect of Complex Formation on Rate Constant. It has been suggested[4,6,7)] that these complexes are formed by hydrogen bonding between the oxygen atom of sulfate and the OH group of alcohols. Therefore, the faster hydrolysis of SDS in the complexed state than in the noncomplexed state may be considered due to a proton being supplied by hydrogen bonding from $C_{12}OH$ to SDS in the first step of the hydrolysis mechanism:[11,12)]

First step

$$C_{12}H_{25}OSO_3^- + H^+ \longrightarrow C_{12}H_{25}OSO_3H,$$

Second step

$$C_{12}H_{25}OSO_3H + H_2O \longrightarrow C_{12}H_{25}OH + HSO_4^- + H^+.$$

Moroi et al.[6] suggested that alkyl alcohol is more strongly bound to alkyl sulfate in a complex with alcohol to sulfate mole ratio 0.5 than in one with mole ratio 1.0. It is, therefore, considered that the complex with mole ratio 0.5 is more easily supplied with a proton in the first step of the hydrolysis than the one with mole ratio 1.0, which facility leads to the order of rate constants of hydrolysis: $k_c(C_{10}OH) < k_c(C_{12}OH)$, $k_c(C_{14}OH)$. In addition, the smaller k_c of the $C_{14}OH$–SDS complex than that of the $C_{12}OH$–SDS complex is considered due mainly to the steric effect. It is further considered that the aggregation of $C_{14}OH$ with SDS is more difficult than that of $C_{12}OH$ with SDS, because the two carbon atoms of $C_{14}OH$ protrude from the alkyl chain of SDS. This is consistent with the fact[4] that the complex between alkyl sulfate and 2-alkanol cannot be formed because of a difficulty of the aggregation.

Conclusion

The rate constant for the hydrolysis of SDS is increased by addition of $C_{10}OH$, $C_{12}OH$, or $C_{14}OH$ due to formation of complex ($SDS:C_{10}OH=1:1$), ($SDS:C_{12}OH=2:1$), or ($SDS:C_{14}OH=2:1$), respectively. Furthermore, the order of effectiveness of 1-alkanols for increasing the rate constant is $C_{12}OH > C_{14}OH > C_{10}OH$. This is due to the strength of hydrogen bonding between SDS and 1-alkanols and the steric effect of the complex.

In conclusion, we call attention to the difference in the effects of 1-alkanols on the hydrolysis of SDS (with respect to the formation of complex between SDS and 1-alkanols, and the rate constant for the complexed state), in contrast to the suggestion of Barry and Schotten[10] that $C_{16}OH$ and $C_{12}OH$ have a similar effect on the hydrolysis.

References

1) M. Nakagaki and S. Yokoyama, *J. Pharm. Sci.*, **74**, 1047 (1985).

2) M. B. Epstein, A. Wilson, C. W. Jakob, L. E. Conroy, and J. Ross, *J. Phys. Chem.*, **58**, 860 (1954).

3) J. N. Phillips and K. J. Mysels, *J. Phys. Chem.*, **59**, 325 (1955).

4) H. C. Kung and E. D. Goddard, *J. Colloid Sci.*, **20**, 766 (1965).

5) M. Abe and K. Ogino, *J. Colloid Interface Sci.*, **80**, 146 (1981).

6) Y. Moroi, K. Motomura, and R. Matuura, *Bull. Chem. Soc. Jpn.*, **44**, 2078 (1971).

7) H. C. Kung and E. D. Goddard, *J. Phys. Chem.*, **67**, 1965 (1963).

8) K. Ogino, M. Abe, and N. Takesita, *Bull. Chem. Soc. Jpn.*, **49**, 3679 (1976).

9) Y. Kasai and M. Nakagaki, *Nippon Kagaku Zasshi*, **91**, 19 (1970).

10) B. W. Barry and E. Schotten, *J. Pharm. Pharmacol.*, **19**, 785 (1967).

11) R. L. Bullwell, *J. Am. Chem. Soc.*, **74**, 1462 (1952).

12) J. H. Fendler and E. J. Fendler, "Catalysis in Micellar and Macromolecular Systems," Academic Press, New York (1975), p. 131.