

The influence of 1-hexadecanol on the acid-catalysed hydrolysis of sodium dodecyl sulphate*

B. W. BARRY† AND E. SHOTTON

The kinetics at 60° of the acid-catalysed hydrolysis of sodium dodecyl sulphate in the presence of 1-hexadecanol above the critical micelle concentration showed the hydrolysis to be first order and the rate to depend on the molar ratio of alcohol to alkyl sulphate. Up to a ratio of 0.75 the rate increases; above this there is a steady decrease. The changes in rate have been correlated with phase changes and explained on the basis of the effect on the charge density on the micelle, and on the dielectric constant of the associated medium, in passing from a mixed spherical micelle to the lamellar structure and then to the expanded lamellar structure prevailing in liquid crystals.

SODIUM dodecyl sulphate in aqueous solution will hydrolyse to produce sufficient dodecanol to give a minimum in the surface tension curve after as short a period as 24 hr (Harrold, 1960). The hydrolysis of the lower alkyl sulphates in alkaline solution has been reported to follow a second order reaction (Green & Kenyon, 1950), a first order reaction (Burwell, 1952) and, for certain alkyl sulphates, first and second order reactions simultaneously (Calhoun & Burwell, 1955). Kurz (1962) showed that the rate of hydrolysis of sodium alkyl sulphates catalysed by hydrogen ions was strongly accelerated by the aggregation of the ester anions into micelles, the corresponding hydroxide ion catalysed rate was strongly suppressed and in neutral solution the rate was unchanged. Motsavage & Kostenbauder (1963) found that the hydrogen ion catalysed hydrolysis of sodium dodecyl sulphate was first order from pH 1 to 3.25 and from 30 to 70°. Solutions of the sulphate at concentrations above the critical micelle concentration (CMC) underwent hydrolysis at rates more than thirty times that for solutions below the CMC and the non-ionic agents dodecanol and Pluronic F-38 further increased the rate of hydrolysis. Nogami, Awazu & Kanakubo (1963) have shown that the rate of hydrolysis of sodium dodecyl sulphate in acid solution at high temperature increased markedly at the CMC whilst in alkaline solution the rate decreased. Nogami & Kanakubo (1963) studied the acid catalysed hydrolysis of long-chain alkyl sulphates, assuming a first order reaction to hold, and found that they were relatively stable below their CMC's but less stable above; the longer the chain length of the alkyl sulphate the more unstable the surfactant became.

Experimental and results

Materials. As used by Barry & Shotton (1967). The perchloric acid (71-73%) was Analar grade.

From the Department of Pharmaceutics, The School of Pharmacy, University of London, Brunswick Square, London, W.C.1.

* This work forms part of a thesis accepted for the degree of Ph.D. in the University of London.

† Present address: School of Pharmacy, Portsmouth College of Technology, Portsmouth.

PREPARATION AND ANALYSIS OF SYSTEMS

The systems were of the general formula: sodium dodecyl sulphate 12 g; 1-hexadecanol varied; perchloric acid 5 ml; water 1200 g.

The 1-hexadecanol concentration was varied from a molar ratio (alcohol to sulphate) of 0 to 1.75. Water, heated to 70–75°, was weighed (1200 g) and the sodium dodecyl sulphate, perchloric acid and 1-hexadecanol added and vigorous mixing accomplished using a Silverson mixer fitted with an axial flow head. The systems were rapidly cooled to room temperature with running water, a pump head attachment fitted to the mixer and previously washed and dried 20 ml ampoules were filled with the mixture using a tube fitted with a wide bore canula. The pH of the mixture was 1.7, as determined by a glass electrode.

The ampoules were sealed and stored at $60^\circ \pm 0.01^\circ$ in a thermostat bath. At set time intervals two ampoules were removed, rapidly cooled, the contents bulked and two 20 ml quantities titrated against 0.1N NaOH to pH 7.0, using an E.I.L. Model 24 Automatic Titrimeter, and the average titre taken.

MICROSCOPY

Microscopic observations were made using a microscope fitted with a Kofler micro hot stage. Systems were stored for not less than 12 hr at 60° and transferred after mixing to a slide with fused-on glass cell, which was maintained at 60° on the hot stage. Examination was carried out between crossed polars at a magnification of $\times 200$. Systems were clear up to a molar ratio in the region of 0.26–0.28 when they became opalescent and increased in opacity with increased molar ratio. Characteristic anisotropic spherulites showing the well-formed extinction cross of uniaxial crystals were visible in this region. This new phase was considered to be liquid crystal composed of sodium dodecyl sulphate–1-hexadecanol–water (containing perchloric acid). By the time the molar ratio had reached two, many small isotropic globules were present, presumably emulsified globules of excess alcohol in equilibrium with the liquid crystal phase. Further increase in the molar ratio led to an increase in the number of isotropic globules in the field of view, and a reduction in the number of spherulites.

DETERMINATION OF CRITICAL MICELLE CONCENTRATION

The determination of the CMC of sodium dodecyl sulphate using the conductivity method was not possible in the presence of the strongly ionized perchloric acid. The dye method of Corrin & Harkins (1947) was used with the cationic dyes rhodamine 6G and acriflavine at a concentration of $10^{-5}M$ (Shinoda, Nakagawa & others, 1963). Both dyes gave the CMC of sodium dodecyl sulphate at 60° as 0.076–0.078% w/w in the presence of a molal concentration of perchloric acid of 0.0508; the CMC at 60° in the presence of perchloric acid and an equimolecular ratio of 1-hexadecanol to sodium dodecyl sulphate was 0.035% w/w. These results were used to ensure that the experimental work was at concentrations above the CMC.

ACID-CATALYSED HYDROLYSIS OF SODIUM DODECYL SULPHATE

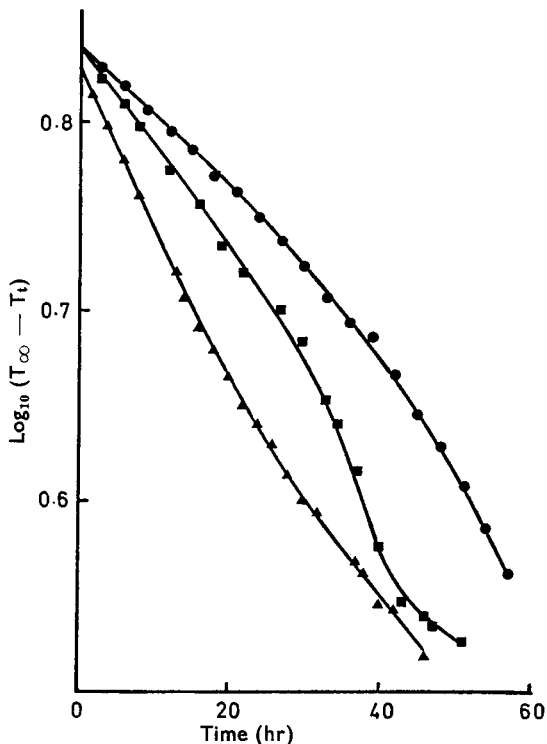


FIG. 1. $\text{Log}_{10}(T_{\infty} - T_t)$ versus time for systems of molar ratio (1-hexadecanol to sodium dodecyl sulphate) of 0 (—●—), 0.25 (—■—) and 0.75 (—▲—). Temperature 60°C .

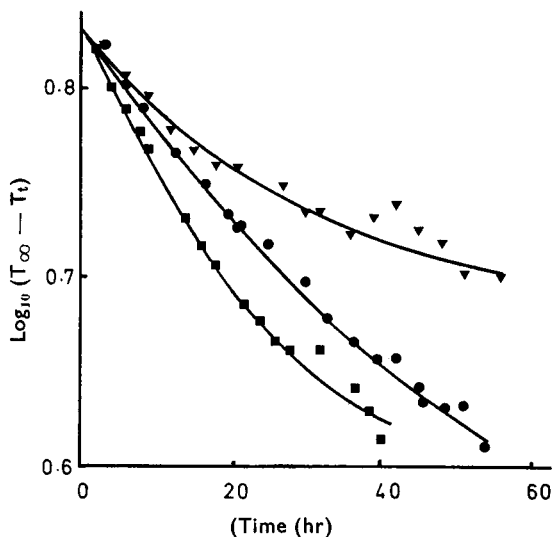


FIG. 2. $\text{Log}_{10}(T_{\infty} - T_t)$ versus time for systems of molar ratio (1-hexadecanol to sodium dodecyl sulphate) of 1 (—■—), 1.5 (—●—) and 1.75 (—▼—). Temperature 60°C .

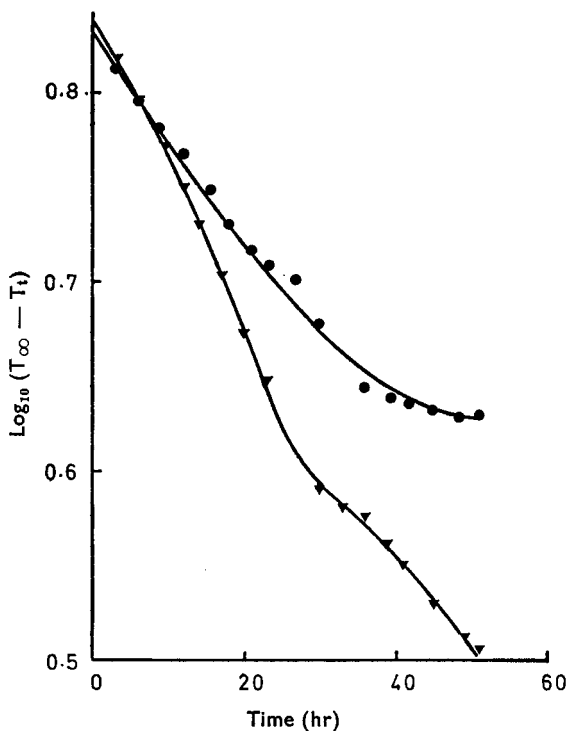


FIG. 3. $\text{Log}_{10}(T_{\infty} - T_t)$ versus time for systems of molar ratio (1-hexadecanol to sodium dodecyl sulphate) of 0.5 (\blacktriangledown) and 1.25 (\bullet). Temperature 60°C .

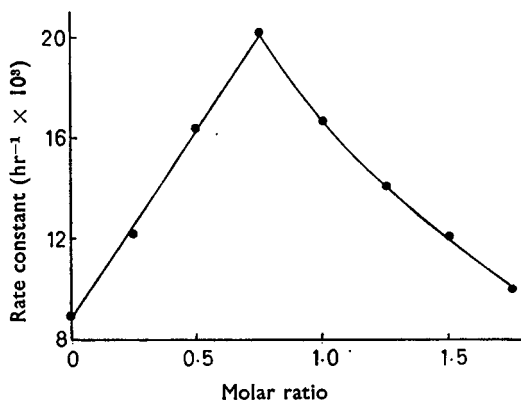


FIG. 4. Rate constant versus molar ratio (1-hexadecanol to sodium dodecyl sulphate) Temperature 60°C .

ACID-CATALYSED HYDROLYSIS OF SODIUM DODECYL SULPHATE

Figs 1, 2 and 3 are plots of $\log_{10}(T_{\infty} - T_t)$ against time, where T_{∞} is the theoretical titre after infinite time of hydrolysis and T_t the titre at successive time intervals (Glasstone & Lewis, 1960). In all systems examined, some deviation from an initial straight line takes place after approximately 18 hr hydrolysis; the linear relationship confirms that at least in the first hours of hydrolysis the reaction is first order. Rate constants derived from the linear region of the graphs are plotted against molar ratio 1-hexadecanol to sodium dodecyl sulphate in Fig. 4. This graph shows a pronounced maximum in the rate of reaction at a molar ratio of 0.75.

Discussion

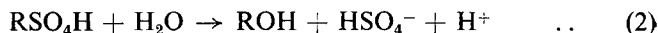
In making a kinetic study of this nature, it is desirable to keep the environmental conditions constant. The temperature was kept uniform and the pH low and constant using perchloric acid, which in concentrations greater than 0.01M depresses the ionization of the bisulphate ion produced by the hydrolysis of sodium dodecyl sulphate (Kurz, 1962). However, during hydrolysis the ratio of alcohol to alkyl sulphate increases. The rate of hydrolysis was dependent on this ratio and the rate will therefore change during an experiment. In addition, the hydrolysis of the alkyl sulphate results in the production of dodecanol, which will have a qualitatively similar effect to the 1-hexadecanol on the hydrolysis rate. With systems which have a molar ratio less than the maximum in Fig. 4, the rate constant will increase as hydrolysis proceeds, due to the molar ratio increasing. The rate constants of systems which have a ratio equal to or greater than 0.75 will decrease, due to the same cause. These changes in rate become apparent in Figs 1, 2 and 3 where the deviation from linearity of the plots for systems of molar ratio 0.25 and 0.5 results in these plots becoming convex to the time axis, whereas the plots for systems of molar ratio 0.75, 1, 1.25, 1.5 and 1.75 become concave to this axis. The plot for the system of molar ratio zero becomes convex as the sodium dodecyl sulphate hydrolyses and produces dodecanol, showing that dodecanol has a similar effect to 1-hexadecanol on the hydrolysis rate of the alkyl sulphate. The experimental points for the system of molar ratio 1.75 show much scatter. It was difficult to obtain consistent end-points in the titrations for this system, and experiments at higher molar ratios were therefore not attempted.

Attempts to correlate the maximum in Fig. 4 with any phase changes observed microscopically or macroscopically were unsuccessful, and it must be assumed in the absence of evidence to the contrary that no new phase appeared at molar ratio 0.75.

The complication of the changing molar ratio due to hydrolysis does not appear to affect significantly the rate of decomposition during the initial hours of reaction. Thus rate constants have been calculated for all eight experimental systems by assuming that first order reaction kinetics hold, at least during the first 18 hr hydrolysis. Nogami & Kanakubo (1963) obtained initial linear periods of hydrolysis for sodium

octyl, myristyl, cetyl and pentadecane-8 sulphates of 24, 10, 8 and 10 hr respectively. The value of 18 hr for dodecyl sulphate falls between the octyl and myristyl values.

The actual mechanism of the acid-catalysed hydrolysis of monoalkyl sulphates was considered by Kurz (1962) to proceed through the equilibrium protonation of the alkyl sulphate followed by attack of water on the sulphur atom.



Kurz (1962) considered that the sharp increase in the rate constant which occurred when micelles were formed was due to the electrostatic potential between the micelle and the bulk solution. The sulphate groups became stronger bases due to the presence of a negative potential on the micelle and there was a resulting shift to the right in the prior protonation equilibrium (eqn 1). The reaction of the protonated ester molecules (eqn 2) then occurred with a specific rate essentially unchanged from its value in bulk solution, that is, where the ester molecules are not aggregated into micelles.

Motsavage & Kostenbauder (1963) explained the further increase in rates of hydrolysis consequent on the incorporation of non-ionic molecules in the micelle as follows. Although the charge density of the micellar surface was reduced by the polar heads of the alcohol molecules and hence, on Kurz's theory, the sulphate groups should now become weaker bases, the heads of the alkyl sulphate ions may now be regarded as being adjacent to a region of lower dielectric constant, i.e. the alcohol has lowered the dielectric constant along the surface of the micelle. Electrostatic interactions in this region should be strengthened and the rate of hydrolysis increased. However, it would seem probable that charge density did not fall as Motsavage & Kostenbauder (1963) assumed. An examination of the results quoted by Osipow (1962) shows that in a micellar solution of an alkyl sulphate only about 20% of the surfactant molecules are ionized. Introduction of a nonionic molecule would dilute the micellar surface concentration of alkyl sulphate and also allow increased ionization. The charge density would be restored and the rate of hydrolysis maintained. Any effect of lower dielectric constant would then be in addition to this.

The above considerations may explain the increase in rates of hydrolysis with increase in molar ratio in the systems examined, up to the appearance of a liquid crystal phase, i.e. up to a molar ratio of 0.26-0.28. The continuation of the increase into the liquid crystalline region may be ascribed to a radical change in the packing of the molecules. They are now held in a lamellar structure, and are closer together than in the original spherical micelle. A further decrease in dielectric constant at the surface of the micelle causes an increase in hydrolysis rate. To explain the fall in the rate of hydrolysis after a molar ratio of 0.75 it is postulated that the increased number of alcohol molecules forces the

ACID-CATALYSED HYDROLYSIS OF SODIUM DODECYL SULPHATE

alkyl sulphate heads further apart than they were in aqueous solution, i.e. before the appearance of smectic phase.

In addition, 1-hexadecanol has an alkyl chain which is four carbon atoms longer than the dodecyl sulphate chain, and this will modify the packing in the micelles. This effect will become more pronounced the higher the alcohol concentration. The hydroxyl group of the alcohol will protrude further into the aqueous environment than the sulphate group. In systems of alcohol content greater than molar ratio 0.75 the result may be a partial shielding of the sulphate ion, resulting in a lowering of the rate of hydrolysis.

References

- Barry, B. W. & Shotton, E. (1967). *J. Pharm. Pharmac.*, **19**, *Suppl.*, 110S–120S.
Burwell, R. L. (1952). *J. Am. chem. Soc.*, **74**, 1462–1466.
Calhoun, G. M. & Burwell, R. L. (1955). *Ibid.*, **77**, 6441–6447.
Corrin, M. L. & Harkins, W. D. (1947). *Ibid.*, **69**, 679–683.
Glasstone, S. & Lewis, D. (1960). *Elements of Physical Chemistry*, pp. 603–608, London: Macmillan.
Green, G. H. & Kenyon, J. (1950). *J. chem. Soc.*, 1389–1391.
Harrold, S. P. (1960). *J. Colloid Sci.*, **15**, 280–281.
Kurz, J. L. (1962). *J. phys. Chem., Ithaca*, **66**, 2239–2246.
Motsavage, V. A. & Kostenbauder, H. B. (1963). *J. Colloid Sci.*, **18**, 603–615.
Nogami, H., Awazu, S. & Kanakubo, Y. (1963). *Chem. pharm. Bull., Tokyo*, **11**, 13–18.
Nogami, H. & Kanakubo, Y. (1963). *Ibid.*, **11**, 943–947.
Osipow, L. I. (1962). *Surface Chemistry. Theory and Industrial Applications*, p. 180, New York, Reinhold.
Shinoda, K., Nakagawa, T., Tamamushi, B. & Isemura, T. (1963). *Colloidal Surfactants. Some Physicochemical Properties*, p. 10, New York: Academic Press.