

## The hydrolysis of propyl benzoate in aqueous solutions of surface-active agents

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The effect of cetrimide and sodium lauryl sulphate on the alkaline hydrolysis of emulsions and solutions of n-propyl benzoate has been investigated and compared with results obtained previously in cetomacrogol solutions. Evidence is presented to show that the rate of reaction depends on the degree of saturation of the dispersion expressed as a "Saturation Ratio", which is the ratio of ester concentration to its solubility in a given concentration of surface-active agent. The hydrolysis rate of solubilised ester decreases with increase in surface-active agent concentration while the effect of such an increase in concentration on the hydrolysis rate of emulsified ester depends on the nature of the surface-active agent. The initial rate in sodium lauryl sulphate and cetomacrogol is independent of concentration, but in cetrimide the rate increases with cetrimide concentration until sufficient is present to solubilise the ester.

**S**TUDIES on the hydrolysis of n-propyl benzoate in the non-ionic surface-active agent cetomacrogol (Mitchell, 1963) and the oxidation of aldehydes in various non-ionic surface-active agents (Carless & Mitchell, 1962) have shown that rates of reaction in aqueous solutions of non-ionic surface-active agents depend on the degree of saturation of the dispersion. The degree of saturation can be expressed as a saturation ratio  $R$ , in which

$$R = c/c_s \quad \dots \quad (1)$$

where  $c$  is the concentration of reactant and  $c_s$  its solubility in the solution of surface-active agent. For a given saturation ratio the rate of reaction divided by the concentration of reactant is a constant, i.e.

$$\text{rate} = kc \quad \dots \quad (2)$$

where from (1)  $c = Rc_s$ .

The relation between saturation ratio and reaction rate is valid for reactions in aqueous solutions of non-ionic surface-active agents, but does not appear to hold for the oxidation of aldehydes in cationic and anionic surface-active agents (Mitchell, 1960) nor for dispersions in the ampholytic betaines (Carless & Swarbrick, 1962). The present paper reports an investigation into the relation between saturation ratio and the alkaline hydrolysis of n-propyl benzoate in aqueous solutions of cetrimide, a cationic surface-active agent, and sodium lauryl sulphate, an anionic surface-active agent. The results are compared with those obtained earlier using cetomacrogol (Mitchell, 1963).

### Experimental

#### MATERIALS

Cetrimide B.P. 1958 containing 96.8% alkytrimethyl ammonium bromides calculated as  $C_{14}H_{29}(Me)_3N,Br$ , sodium lauryl sulphate B.P. containing the equivalent of 59.8% of total alcohols (B.P. assay), n-propyl benzoate fractionally distilled under reduced pressure, b.p  $231^\circ$ ,  $[n]_{D}^{22} 1.499_1$ .

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## DETERMINATION OF SOLUBILITY AND HYDROLYSIS

The experimental procedures have been described previously (Mitchell, 1962, 1963).

## Results

The solubilities of *n*-propyl benzoate in cetrimide and sodium lauryl sulphate solutions at 35° are shown in Fig. 1. The influence of concentration of surface-active agent on the alkaline hydrolysis of a fixed amount

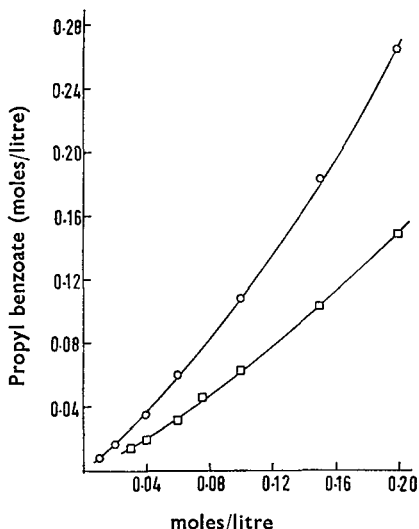


FIG. 1. Solubility of propyl benzoate in cetrimide and sodium lauryl sulphate solutions at 35°.

○ cetrimide. □ sodium lauryl sulphate

of the ester is shown in Figs 2 and 3 and Tables 1 and 2. Hydrolysis in cetrimide solutions followed the pattern reported for emulsions and solutions of ethyl benzoate and diethyl phthalate in cetrimide (Mitchell, 1962).

In the initial stage of the reaction the hydrolysis rate of emulsified ester increased with cetrimide concentration reaching a maximum when sufficient cetrimide was present for complete solubilisation (Fig. 2, curve 3). Addition of cetrimide in excess of that needed for solubilisation caused a fall in the initial rate. As hydrolysis takes place, emulsions become solutions and solutions become progressively less saturated with ester and in the final stages of the reaction the rate decreased with increase in cetrimide concentration.

Ester dispersed in sodium lauryl sulphate solutions was hydrolysed in a manner similar to that found in cetomacrogol (Mitchell, 1963). The initial hydrolysis rate of emulsions was independent of sodium lauryl sulphate concentration and was the same as suspensions of ester in water. In the solubilised state the initial rate of reaction decreased with increase

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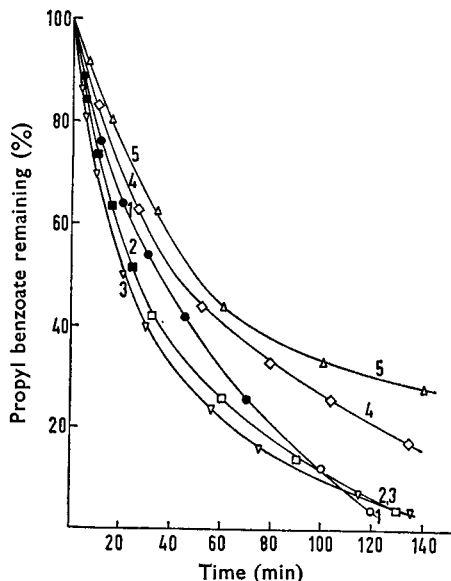


FIG. 2. Influence of cetrimide concentration on the alkaline hydrolysis of propyl benzoate (0.05 moles/litre) at 35°.

Cetrimide concentration (moles/litre): 1, 0.01; 2, 0.03; 3, 0.054; 4, 0.25; 5, 0.80. Closed symbols, emulsions. Open symbols, solutions.

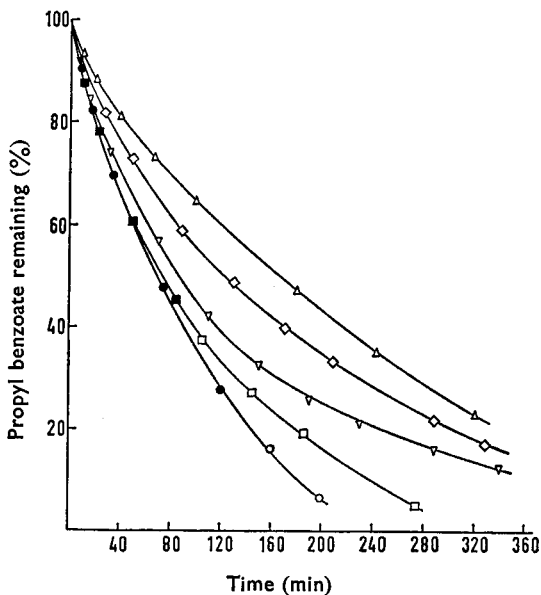


FIG. 3. Influence of sodium lauryl sulphate concentration on the alkaline hydrolysis of propyl benzoate (0.05 moles/litre) at 35°. Sodium lauryl sulphate concentration (moles/litre):  $\circ$  0.02;  $\square$  0.04;  $\nabla$  0.08;  $\diamond$  0.15;  $\triangle$  0.25. Closed symbols, emulsions. Open symbols, solutions.

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in the amount of surface-active agent. In the final stages the rate of hydrolysis decreased progressively with increase in sodium lauryl sulphate concentration as in cetrimide.

Unlike reactions in cetomacrogol the data could not be fitted to first order rate plots. Hence comparisons were made on the basis of half

TABLE 1. DEPENDENCE OF ALKALINE HYDROLYSIS OF PROPYL BENZOATE IN CETRIMIDE SOLUTIONS ON THE SATURATION RATIO

Saturation ratio R	Propyl benzoate moles/litre		Cetrimide moles/litre	Initial rate moles/litre/min $\times 10^4$	$K \frac{\text{min}^{-1} \times 10^3}{\left(\frac{\text{Initial rate}}{c}\right)}$	$t_{\frac{1}{2}}$ min
	c	$c_g$				
0.1	0.125	0.125	0.116	1.26	10	65
0.1	0.025	0.25	0.193	2.75	11	67
0.25	0.025	0.10	0.096	6.28	25	28
0.25	0.050	0.25	0.164	13.2	26	27
0.5	0.0125	0.025	0.029	3.74	30	22
0.5	0.0250	0.050	0.054	7.60	30	21
0.5	0.0375	0.075	0.077	11.7	31	22
0.5	0.050	0.100	0.096	18.5	37	19
1.0	0.025	0.025	0.029	10.4	42	25
1.0	0.050	0.050	0.054	19.2	38	24
1.0	0.075	0.075	0.077	31.2	42	22
1.0	0.100	0.100	0.096	40.0	40	25
2.0	0.05	0.025	0.029	13.2	26	30
2.0	0.10	0.050	0.054	22.7	23	31
2.0	0.15	0.075	0.077	34.1	23	34
2.0	0.20	0.100	0.096	50.0	25	34
4.0	0.05	0.0125	0.014	9.33	19	43
4.0	0.10	0.025	0.029	18.2	18	44
4.0	0.20	0.050	0.054	39.2	20	43

R =  $c/c_g$   
 where c = ester concentration  
 $c_g$  = solubility of ester in cetrimide.

TABLE 2. DEPENDENCE OF ALKALINE HYDROLYSIS OF PROPYL BENZOATE IN SODIUM LAURYL SULPHATE SOLUTIONS ON THE SATURATION RATIO

Saturation ratio R	Propyl benzoate moles/litre		Sodium-lauryl sulphate moles/litre	Initial rate moles/litre/min $\times 10^4$	Initial rate constant $K \frac{\text{min}^{-1} \times 10^3}{\left(\frac{\text{Initial rate}}{c}\right)}$	$t_{\frac{1}{2}}$ min
	c	$c_g$				
0.25	0.025	0.1	0.148	1.55	6.2	172
0.25	0.050	0.2	0.250	2.69	5.4	168
0.5	0.0125	0.025	0.049	1.03	8.3	120
0.5	0.0250	0.050	0.086	1.79	7.2	131
0.5	0.0375	0.075	0.120	2.50	6.7	120
0.5	0.050	0.10	0.148	3.82	7.6	124
1.0	0.025	0.025	0.049	2.43	9.7	86
1.0	0.050	0.050	0.086	4.67	9.4	89
1.0	0.075	0.075	0.120	6.75	9.0	88
1.0	0.10	0.10	0.148	9.90	9.9	88
2.0	0.05	0.025	0.049	4.76	9.5	72
2.0	0.10	0.050	0.086	9.90	9.9	68
4.0	0.05	0.0125	0.028	5.11	10.2	63
4.0	0.10	0.0250	0.049	9.90	9.9	67

R =  $c/c_g$   
 where c = ester concentration  
 $c_g$  = solubility of ester in sodium lauryl sulphate.

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lives  $t_{\frac{1}{2}}$ , and initial rate constants  $K$ , calculated by dividing the initial rate by the ester concentration. The results at various saturation ratios are given in Tables 1 and 2.

### Discussion

From the initial rate constants,  $K$  and half lives,  $t_{\frac{1}{2}}$ , given in Tables 1 and 2, it would appear that the hydrolysis of propyl benzoate in aqueous solutions of cetrimide and sodium lauryl sulphate depends on the saturation ratio as defined in equation (1). A similar relation between hydrolysis rate and saturation ratio has been shown previously for the hydrolysis of propyl benzoate in cetomacrogol (Mitchell, 1963). This dependence of reaction rate on saturation ratio provides a basis for comparing the effects of different surface-active agents on rates of hydrolysis.

When  $R > 1.0$ , both the true aqueous "phase" and the micelles are fully saturated with ester. Ester in excess of its solubility is present as emulsion droplets stabilised by an adsorbed film of surface-active agent. The effect of an increase in the amount of surface-active agent, and thereby the number of micelles, is to transfer ester from the emulsion droplets to the micelles. The enlargement of the interfacial area of dispersed ester may be expected to facilitate both hydroxyl ion attack and diffusion of ester from the micelles into the true aqueous "phase". In sodium lauryl sulphate and cetomacrogol however the initial rate constant for emulsions is independent of the nature and amount of surface-active agent and therefore the rate of reaction is not controlled by the interfacial area of dispersed ester (Fig. 3). On the other hand, in cetrimide the initial hydrolysis rate of emulsified ester increases with cetrimide concentration, reaching a maximum when sufficient is present to solubilise the ester, i.e. when  $R = 1.0$  (Fig. 2, curve 3). The increase in rate constant is probably due to attraction of hydroxyl ions to the enlarged interface presented by the positively charged cationic micelles.

Addition of each surface-active agent in excess of that needed for solubilisation so that  $R < 1.0$ , is accompanied by a decrease in rate of hydrolysis. It has been suggested previously (Mitchell, 1962, 1963) that the additional surface-active agent reduces the amount of ester in the true aqueous "phase" relative to that in the micelles. Ester in the micelles is less accessible to hydrolytic attack and the rate of reaction falls.

Rates of hydrolysis as indicated by the half life, depend on the nature of the surface-active agent. At the same saturation ratio the rates of reaction are in the order cetrimide  $>$  cetomacrogol  $>$  sodium lauryl sulphate. As suggested above, it is likely that the rate of reaction is controlled partly by the charge on the micelle. Thus hydroxyl ions will be attracted to cationic micelles, repelled by anionic micelles and should be unaffected by non-ionic micelles. Half lives in cetomacrogol therefore should be intermediate between those in cetrimide and sodium lauryl sulphate. These suggestions are supported by the results in Tables 1 and 2 and previous work (Mitchell, 1963).

The present paper and others in this series have shown that the hydrolysis of esters and the oxidation of aldehydes dispersed in aqueous solutions of surface-active agents depends, with the exception of oxidation of aldehydes in charged surface-active agents, on the saturation ratio. The saturation ratio can be altered by varying either the concentration of surface-active agent or the concentration of reactant. In the solubilised state a decrease in saturation ratio is accompanied by a decrease in the rate of hydrolysis and oxidation. From a consideration of the nature of these reactions it is probable that the explanation is different in each case. In the case of hydrolysis it has been considered reasonable to assume that ester dispersed in the true aqueous "phase" will be more readily hydrolysed than ester within the micelles. In contrast, oxidation of aldehydes proceeds by a chain reaction (Bäckström, 1927; Cooper & Melville, 1951) and is therefore more likely to be favoured by the local concentrations of aldehyde associated with the micelles. In both cases, however, the addition of surface-active agent in excess of that needed for solubilisation leads to a decrease in reaction rate. Solubilisation can be regarded as a distribution phenomenon in which the water-insoluble material is distributed between the micellar "phase" and the true aqueous "phase" (McBain & Hutchinson, 1955). Since the solute is preferentially soluble in the micelles an increase in the concentration of surface-active agent will increase the amount of solute in the micellar "phase" at the expense of that in true solution. With ester it has been suggested that this is responsible for the observed decrease in the rate of hydrolysis. At the same time, however, an increase in the number of micelles will lead to a reduction in the number of reactant molecules per micelle. This will not affect the rate of a hydrolytic reaction but in the oxidation of aldehydes where a chain mechanism is operating, a decrease in reaction rate is not unexpected.

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