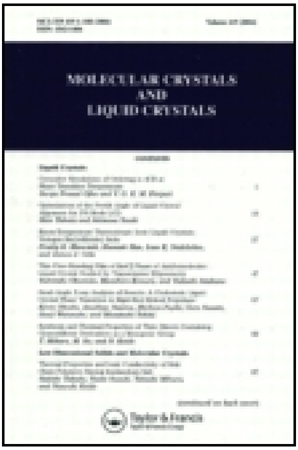

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Thermal Stability in Relation to Hydrolysis of Sodium Decylsulphate in a Solutoin with Nematic Lyotropic Properties

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Thermal Stability in Relation to Hydrolysis of Sodium Decylsulphate in a Solution with Nematic Lyotropic Properties

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We have studied the effect of temperature as a function of time on sodium decylsulphate in the ternary nematic solution first proposed by Radley and Reeves. The hydrolysis of the ester was followed by recording the pH-profile and by determining the liberated decanol. We found that the ester was subject to slow uncatalyzed hydrolysis in the beginning and to much faster acid catalyzed hydrolysis later on. The decylsulphate underwent insignificant cleavage over 48 hours up to at least 70°C with perfect retention of the nematic phase. The results showed that the chemical stability was as good as that of many thermotropic compounds.

INTRODUCTION

Nematic lyotropic solutions have raised much interest since their discovery by Lawson and Flautt[1] and their extension to a variety of compositions by Radley and Reeves.[2,3] These nematic solutions can be oriented in a magnetic field, a property widely used in NMR—studies of molecular order. They are interesting membrane models and we have used them in the laboratory to study the dichroism of incorporated dye molecules for the determination of the order parameter.[4]

At present we are mainly concerned with the particular ternary system, as described by Radley and Reeves,[3] of the following composition: sodium decylsulphate 35,9%, decanol 7,2% and deuterium oxide 56,9% giving the well known nematic type I phase between 28 and 45°C. Working with this solution, we raised the temperature well above ambient temperature, and the sample was maintained there for several hours. Texture examination at the end of the experiment sometimes showed modifications in comparison with the initial sample. This made us ask the question: to what extent can we rely upon the stability of the solution with respect to hydrolytic cleavage? The fact that care must be taken to avoid hydrolysis of the decylsulphate is often mentioned in the literature[5,6] and that deterioration to isotropic samples occurs,[2] although the solutions are found to be stable for years at room temperature.[7]

The synthesis of sodium decylsulphate and the preparation of its lyotropic phases have been extensively described in the literature.[3,5] The final ester was always found to contain small amounts of decanol even when satisfactory elemental analysis results were obtained. The alcohol was determined by gas chromatography. The phase was made up in the indicated proportions considering the decylsulphate as pure.

Hydrolysis of aqueous solutions of monoalkylsulphates and of sodium decylsulphate in particular at elevated temperatures has been the subject of various publications.[8,9,10] The effect of catalysts and of micellar aggregation have been discussed and the cleavage has been found to take place through various mechanisms leading to the overall reaction:

$$ROSO_3^- + H_2O \longrightarrow ROH + HSO_4^-$$

Some alkene formation through elimination was found to take place when the reaction was acid catalyzed, although this was of little importance in the cases of some long chain esters.

Hereafter we have studied the effect of time on the hydrolysis of the decylsulphate in the ternary solution at different temperatures. We have observed this in two ways: (1) by recording the change in pH; (2) by determining the decanol content.

EXPERIMENTAL

Sodium decylsulphate was prepared and purified as described.[3] Recrystallization from aqueous alcohol was found to favor hydrolysis. The quality of the product was improved by washing the final ester with cold acetone. Deuterium oxide, decanol and dodecanol (used in the gas chromatographic determination) were purchased from Merck and the alcohols were distilled before use. The phases were made up in the manner described by weighing the components into tightly stoppered Erlenmeyer flasks. Homogenization was achieved by alternative sonication and magnetic stirring at the temperature of the nematic I phase (about 35°C).

1) The pH-measurements were done with a Metrohm pH-meter E 515 equipped with a combined electrode 121 H for high temperatures. About 7 g of sample were needed. The electrode vessel was equipped with a reflux con-

denser. The samples were thermostated using an oil bath and runs were made at 50°C, 70°C, 80°C, and 90°C (within ±0,5°C). At each temperature the electrode was calibrated against standard buffer solutions. The pH was recorded as a function of time.

At the end of the runs on weighed samples, the acid content was determined by titration against standard 0,1 M sodium hydroxide solution.

2) In the gas chromatographic determination of the decanol content, a model phase was prepared replacing decanol by dodecanol in the same molar proportions as in the normal ternary solution. The dodecanol was used as an internal standard. The components were weighed into test tubes to form samples of about 250 mg. The tubes were sealed, homogenized and heated in a thermostated oil bath at 50°C, 70°C, 90°C, and 105°C (within ±0,5°C), removed and chilled at various time intervals. The content of each tube was then shaken with ether, and the extract was washed, dried over sodium sulphate, and filtered. The solution was then injected onto an Inox column of diameter 1/8″ and length 1,5 m filled with 3% 0 V 17 on Gaschrom Q 100–120 mesh and analyzed for decanol and dodecanol at 130°C using a Girdel P T 75 chromatograph in a flow of nitrogen at 1,5 Bar (17 ml/min) and with a flame detector. The response of the chromatograph to decanol-dodecanol mixtures and the validity of the extraction procedure were checked on test mixtures and the results were found to vary within ±2%.

For decanol determination in the sodium decylculphate, weighed mixtures of decylsulphate and dodecanol, in the proportions of about 7:3, were suspended in an excess of cold acetone, stirred for 15 min. and filtered. Such a solution was injected onto the chromatographic column under the above conditions. The reproducible results were higher than those for the initial decylsulphate after extraction from the aqueous ternary solution, probably due to slight retention of decanol by the micelles in the latter case.

RESULTS

The preparations of sodium decylsulphate were found to contain 1,0 ± 0,1% of decanol. A similar content was also found in compounds purchased from Merck.

The pH-value of the ternary solution with normal phase behavior was found to be 7,3 ± 0,3 checked on a great number of samples. With sometimes acidic solutions, probably due to poor ester quality, the expected textures and transitions were not observed.

1) Hydrolysis determination by pH.

The change of pH as a function of time at various temperatures is shown in Figure 1a, b, c, and d. The logarithmic pH-deviations from the end value are

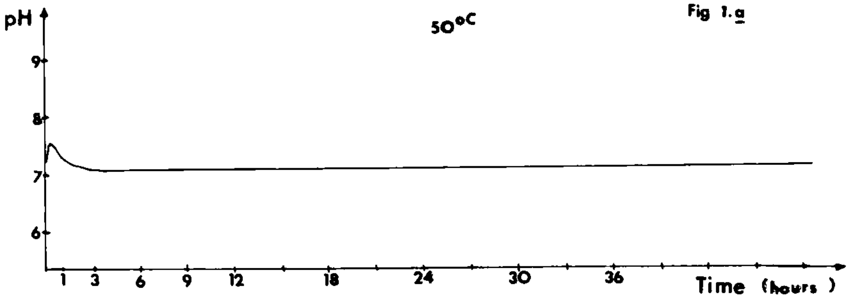
Fig 1.a

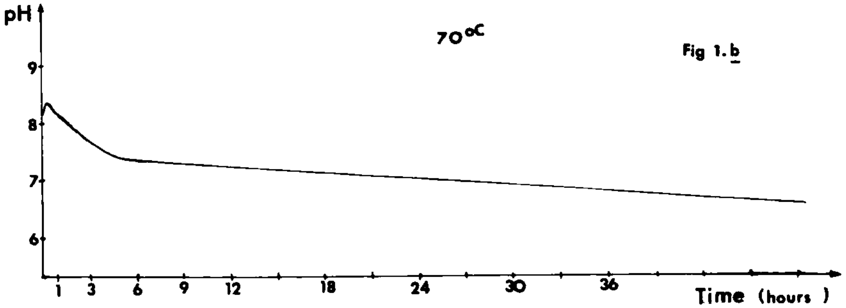
Fig 1.b

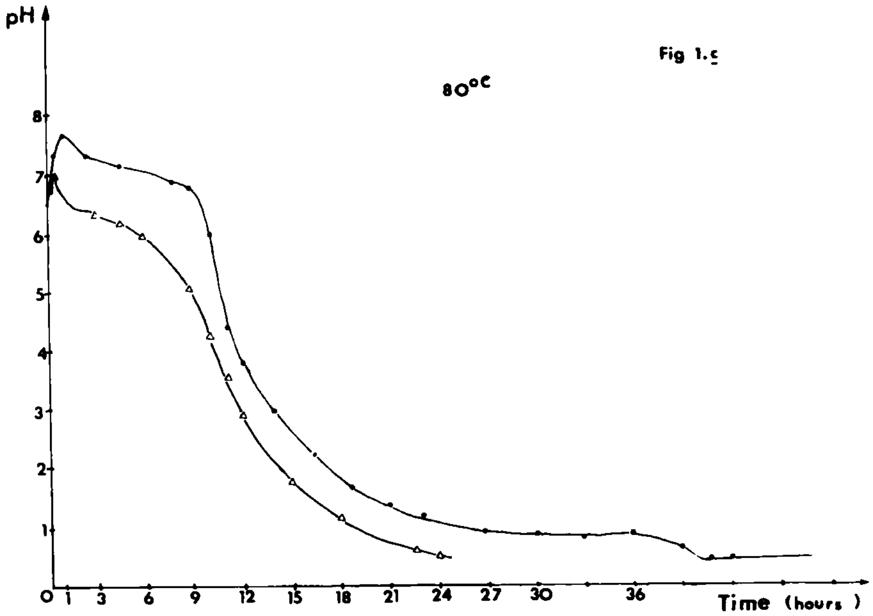
Fig 1.c

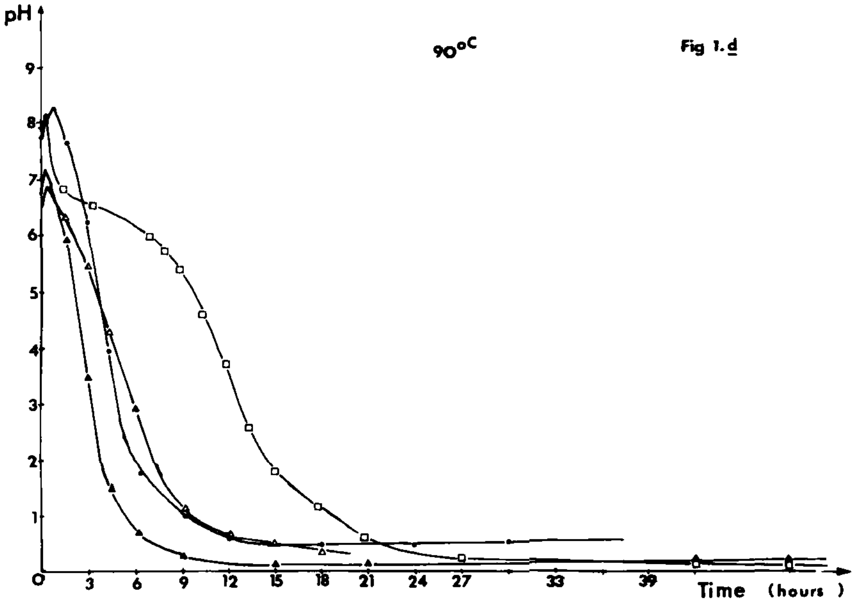

FIGURE 1 The pH-values plotted against time for the ternary solution—sodium decylsulphate 35,9%, decanol 7,2%, and deuterium oxyde 56,9%: a at 50°C, b at 70°C, c at 80°C (curves for two runs are shown), and d at 90°C (curves for four runs are shown).

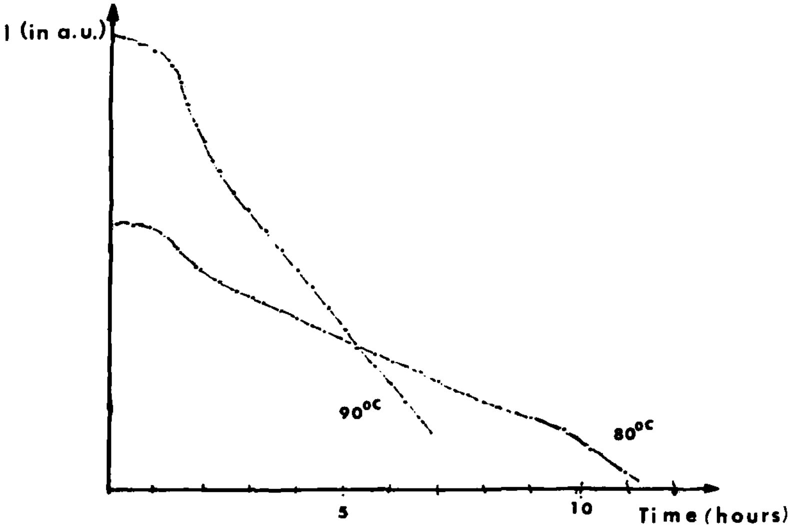

FIGURE 2 The values of $I = \log(pH - pH_c)$ plotted against time taken from the curve —●—●— at 80°C and from the curve —▲—▲— at 90°C. pH_c — the constant end value of the pH (see Figure 1).

plotted against time in Figure 2. All the runs seemed to have a short apparent stabilization period.

At 50°C there was no significant change in the pH over 48 hours and even longer periods. At 70°C there was a slight fall in slope of the pH-curve. Microscopic examination showed the expected transitions after these runs. The textures were even better developed than in the initial samples.[4]

At 80°C there was a slight fall in the curve and then a change to a much steeper slope after 6–9 hours. Curves are shown for runs on two samples. A constant value of the pH was reached in about 24 hours. Titration of the acid then formed in the sample indicated a hydrolysis yield of only a few per cent. When a sample was maintained in the thermostat for a long time, two phases separated. The acidimetric titration after 72 hours corresponded to 96% hydrolysis of the decylsulphate.

At 90°C the change to a steeper slope was reached after only 2–3 hours, and the constant value of pH in less than 12 hours, when phase separation occurred. The experimental curves for four samples are shown. Titration at this point indicated 95% hydrolysis of the sample.

2) Hydrolysis determination by gas chromatography.

The yields of hydrolysis as determined by the decanol content through quantitative gas chromatographic analysis are shown in Table I. A few values obtained through acidimetric titration are inserted for comparison purposes.

At 50 and 70°C, no hydrolysis took place and the trace amounts of decanol found were due to the presence of decanol in the decylsulphate.

At 90°C, the onset of hydrolysis apparently occurred after 31–34 hours and the reaction was nearly complete after 37 hours. At 105°C the reaction started after about 6 hours and was then quickly completed as seen from quite a number of separate samples.

The transition temperatures and textures of the initial ternary solution were in agreement with results from previous studies[4] and also with the capillary flow behavior.[11]

Crystalline Sample	$\xrightarrow{18^\circ C}$	Homeotropic texture with some ribbons. Nematic phase type II	$\xrightarrow{27^\circ C}$	Homogeneous or threaded texture. Nematic phase type I	$\xrightarrow{45^\circ C}$	Angular fan texture Middle phase	$\xrightarrow{\simeq 80^\circ C}$	Isotropic sample

The textures and transitions were maintained by the samples after removal from the thermostated bath and until hydrolysis started as determined above. In partly hydrolyzed samples, the transition at 27°C was less pronounced and occurred a few degrees higher. The fan texture at 45°C failed to appear. Some nematic droplets could still be observed just before the sample separated into two isotropic phases towards the end of hydrolysis. This was due to micellar destruction and separation of decanol and an aqueous solution. The upper organic layer contained decanol only as could be seen from the IR spectrum and from the gas chromatographic analysis. There was thus no alkene formation during hydrolysis.

TABLE I

Per cent sodium decylsulphate converted through hydrolysis at various times and temperatures as determined through the decanol formed in the solutions. The values in brackets are those found through titration of the liberated acid in the samples.

	50°C	70°C	80°C	90°C	105°C
1 h	0,4	0,3		0,4	
3 h	0,5	0,6		0,6	
4 h					0,3
5 h	0,5				0,2, 0,3
5 h 15					0,3
5 h 30					0,2
5 h 45					0,4
6 h		0,3	[<1]	0,5	89, 95
6 h 50					83
7 h					85, 94
8 h					94
11 h				0,3	
17 h				0,6	98
18 h	0,5				
19 h				0,2	
20 h		0,6			
24 h			[6]	0,2	
25 h				0,2	
29 h				0,2	
31 h				82	
34 h				1,3	
37 h				97	
45 h	0,4				
48 h		0,4		93, 95, [95]	
52 h				93	
72 h			[96]		

DISCUSSION

Different mechanisms have been shown to occur during hydrolysis of alkysulphates. These depend on the catalytic state of the solution and have been discussed in the literature.[9,10] In the work of Kurz, various rate constants were determined at 90°C. He found that the rate of hydrolysis of sodium decylsulphate was about four orders of magnitude greater in acidic solutions than in uncatalyzed buffered solutions. The acid catalyzed hydrolysis was about 10 times greater than for non-micellar esters and the rate depended somewhat on the acid concentration. The decylsulphate concentration was 0,04 to 0,4 M. No initiation period was mentioned for the onset of hydrolysis.

There were several differences in the state of the sodium decylsulphate in the ternary solution we have studied compared with the solutions studied by Kurz. The concentration was higher (1,4 M) probably leading to different micellar aggregation, and also the acidity changed throughout the hydrolysis as the system was unbuffered.

Nevertheless, our results can be explained from what has been already found. During the apparent initiation period, as seen from the decanol determination, slow uncatalyzed hydrolysis must take place in agreement with the neutral values of the pH. The fact that a fall in the pH value takes place prior to the important hydrolysis, as seen from the two techniques of measurement, is in agreement with what can be calculated from approximate formulae. It was shown experimentally that the yield of hydrolysis was less than 1% by the time that a pH value of 2,7 had been reached.

The main mechanism of hydrolysis is probably of the acid catalyzed type, and this begins when a certain hydrogen ion concentration is reached in the unbuffered solution.

The reaction rates of the various mechanisms are strongly enhanced when the temperature is raised to 80°C and above. The slow period becomes shorter, and the rate of the main hydrolysis reaction becomes faster.

The logarithmic plots of Figure 2 show quite evidently that the situation in the initial reaction period must be complex, while the straight lines in the last period are in agreement with a first order mechanism.

The main importance of these results is that the ternary solution undergoes no significant destruction through hydrolytic cleavage throughout its nematic domain up to about 45°C and even above this temperature during periods of at least 48 hours. The stability of such a nematic solution is thus as good as that of many thermotropic compounds when it is heated moderately and as long as no evaporation takes place. The results for the particular ternary system here studied are thought to be representative for the behavior of sodium decylsulphate in concentrated aqueous solutions of varying compositions.

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