Surface Areas of Sulfated Detergents

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The following report is concerned with surface films of some organic salts of lauryl sulfate. Apart from surface films of insoluble materials, relatively few data are available on the spread monolayers of soluble detergents. These soluble materials can not be spread under ordinary conditions, but by using a sufficiently high concentration of salts in the substrate, they can be expected to spread at the air-water interface. As for surface films of sodium lauryl sulfate (SLS), very useful studies(1-3) have been made since the early works of Bull(4) and Brady(5). The present writer attemps here to investigate the spread surface films of morphorin, triethanolamine and pyridine salts of lauryl sulfate.

These three specimens are synthesized from lauryl alcohol and obviously they differ from one another only in end group attached to the same dodecyl sulfate portion of the molecule. It is therefore expected that the dodecyl sulfate portion with these heavy organic groups at the end would exhibit effects different from SLS, but it is found experimentally that they occupy the identical surface area with SLS.

Experimental

Materials.—A general synthetic method is as follows; thirty seven grams of lauryl alcohol distilled at 142∼144°C/15 mmHg is sulfated in

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1) B. A. Petheica, *Trans. Faraday Soc.*, **50**, 413 (1954).
2) J. T. Davis, *J. Colloid. Sci.*, **11**, 377 (1956).
3) G. Nilsson, *J. Phys. Chem.*, **61**, 1135 (1957).
4) H. B. Bull, *J. Am. Chem. Soc.*, **67**, 10 (1945).
5) A. P. Brady, *J. Colloid Sci.*, 4, 417 (1949).

hexane with 33 g. of pure chlorosulfonic acid at around 0°C over the period of 4 hours. After the completion of the reaction, the product is poured dropwise into 200 cc. of 10% aquous morpholin solution with stirring at the temperature below 5°C. The whole material is then shaken twice with petroleum ether to remove unreacted alcohol. The water portion is dried over the hot water bath and finally in a vacuum desiccator. The product is recrystalized repeatedly from ethylacetate or ethanol.

The chemical structure and nitrogen analysis are shown in Table I.

TABLE I
ANALYSIS OF LAURYL SULFATE

	N calcd.	Analysis found %
Morpholin	3.97	3.90
Triethanolamine	3.37	3.50
Pyridine	4.05	4.08

Measurements.—Surface pressure (F) is measured with a surface balance of Wilhelmy type. The detergent is spread from its *iso*-propanol (40% by volume)—water solution over the substrate containing 25% ammonium sulfate. After 10 minutes, the film is compressed to a desired area for the measurements.

Results.—Fig. 1 shows surface pressure changes of morpholin, triethanolamine and pyridine salt of lauryl sulfate on 25% ammonium sulfate at 18°C, respectively.

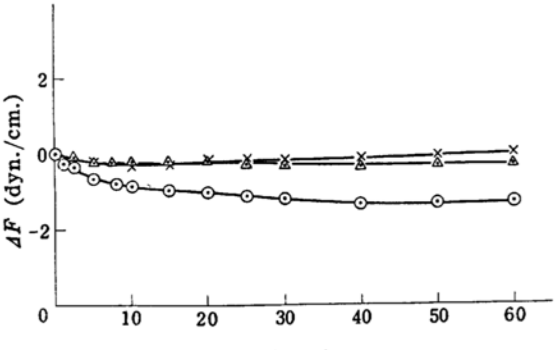

Fig. 1. Surface pressure changes with time (Substrate 25% $(NH_4)_2SO_4$)
Const. area

⊙	Morpholin	50.1 Å²/mol.
△	triethanolamine	50.7
×	pyridine	47.7

These $F-t$ curves indicate[6] that F does not decrease considerably and they make fairly stable monolayers inspite of heavy soluble organic group attached. Fig. 2 represents $F-A$ diagrams of these sulfated detergents on the same substrate. It appears that $F-A$ curves of these three specimens are approximately identical.

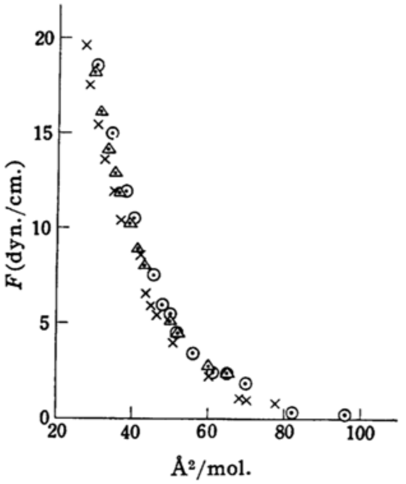

Fig. 2. Surface pressure-area diagrams (Substrate 25% $(NH_4)_2SO_4$)

⊙ Morpholin
△ triethanolamine
× pyridine

Discussion

It is known that spread and adsorbed monolayers of SLS are of the same character[1]. Although added salt condenses the monolayer as would be expected[7], Petheica has shown that all the monolayers obey the relation $F(A-A_0)=nkT$ where A_0 is a coarea term for an uncohering film, T the absolute temperature, k Boltzmann constant and n a constant.

The whole part of curves in Fig. 2 is slightly more expanded than SLS[1], but it obeys the above equation within graphical and experimental error. A_0 is thus calculated to be about 34 Å²/mol. between areas of 40 Å²/mol. and 70 Å²/mol. for all organic salts, and 40 Å²/mol., A_0 decreases to about 18 Å²/mol., which corresponds to the cross sectional area of hydrocarbon chain of the detergent molecule. It is interesting to note that these values of A_0 are in good agreement with surface areas of SLS calculated from the above equation of state or by other methods[1-3].

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