U. S. Department of Commerce National Bureau of Standards

RESEARCH PAPER RP801

Part of Journal of Research of the National Bureau of Standards, Volume 14, June 1935

SELECTIVE ADSORPTION FROM SOAP SOLUTIONS

By Harvey A. Neville[1] and Milton Harris[2]

ABSTRACT

Soap is adsorbed from aqueous solution at all types of interfaces, but the ratio of fatty acid to alkali in the adsorbed portion varies with the nature of the interface.

Soap foam, continuously removed from an aqueous solution by CO_2-free air, was found to be less alkaline than the original solution, while the latter became progressively more alkaline. The addition of alkalies to the soap solution decreased the selective effect and modified the character of the foam.

When carbon black, paraffin oil, and pure olive oil were brought in contact with soap solutions, the aqueous medium became more alkaline and acid soap was adsorbed at the interface.

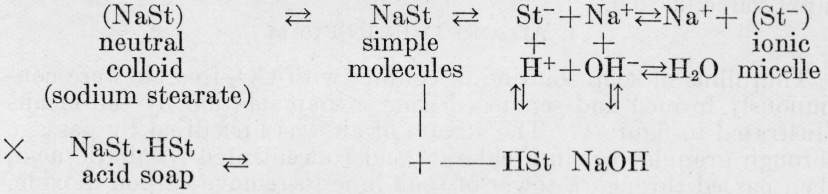
Fuller's earth, olive oil containing free fatty acid, wool, and silk, in soap solutions adsorbed soap and alkali at the interface and the aqueous medium became more acid. Cotton showed no selective adsorption and adsorbed a relatively small amount of soap.

The results of these experiments are consistent with the theory of the existence of an acid soap, resulting from the hydrolysis of soap in dilute solution.

CONTENTS

I. INTRODUCTION

The existence of an acid soap resulting from the hydrolysis of soap in dilute aqueous solution has been suggested by different investigators. Its formation has been represented by Williams (1)[3] as follows:



$$\begin{array}{ccccc}
\text{(NaSt)} & \rightleftarrows & \text{NaSt} & \rightleftarrows & \text{St}^- + \text{Na}^+ \rightleftarrows \text{Na}^+ + (\text{St}^-) \\
\text{neutral} & & \text{simple} & & + \quad + \qquad\qquad \text{ionic} \\
\text{colloid} & & \text{molecules} & & \text{H}^+ + \text{OH}^- \rightleftarrows \text{H}_2\text{O} \;\; \text{micelle} \\
\text{(sodium stearate)} & & | & & \updownarrows \qquad \downuparrows \\
 & & | & & \\
\times \;\; \text{NaSt}\cdot\text{HSt} & \rightleftarrows & + & \text{------} & \text{HSt} \quad \text{NaOH} \\
\text{acid soap} & & & &
\end{array}$$

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[1] Associate Professor of Chemistry, Lehigh University.

[2] Research Associate at the National Bureau of Standards representing the American Association of Textile Chemists and Colorists.

[3] Figures in parentheses here and throughout the text refer to the references given at the end of this paper.

The acid soap is probably also ionized as a colloidal micelle.

The addition of alkali to the soap solution obviously represses this hydrolysis. It is also apparent that the hydrolytic equilibrium will be disturbed by contact with any material which preferentially adsorbs fatty acid, acid soap, or alkali. There is considerable evidence (1) to show that the principal surface-active constituent of a soap solution, to which is attributed its efficiency as a lubricant, detergent, and emulsifying agent, is the acid soap. This view is consistent with the fact that the addition of alkali to a neutral soap solution raises the surface tension and decreases the effectiveness of the soap in the processes mentioned, while the addition of fatty acid often improves the emulsifying and lubricating ability of the soap solution.

If the acid soap is the surface-active agent in the solution, it will concentrate at interfaces and the aqueous medium will become more alkaline in contact with chemically neutral or inert materials. However, when the material forming an interface with the soap solution is acidic in nature or strongly adsorbs OH^- ions, the aqueous solution may become more acidic, since the selective adsorption of OH^- ions may exceed the opposing effect due to the removal of acid soap.

TABLE 1.—*Selective adsorption at various types of interfaces in 0.25-percent soap solution*

Material in contact with soap solution	Aqueous medium becomes more—	Adsorbed at interface
Air (foam)	Alkaline	Acid soap.
Carbon (lampblack)	do	Do.
Fuller's earth	Acid	Soap and OH^-.
Paraffin oil (medicinal)	Alkaline	Acid soap.
Olive oil [1]	do	Do.
Do.[2]	Acid	Soap and OH^-.
Wool	do	Do.
Silk	do	Do.
Cotton	No change	Soap.

[1] Contained 0.33 percent of free fatty acid.
[2] Contained 7.90 percent of free fatty acid.

II. RESULTS AND DISCUSSION

The qualitative effects obtained with various types of interfaces in dilute soap solution are shown in table 1.

The soap used in all experiments was a neutral pure olive-oil soap, which showed equivalent amounts of alkali and fatty acid upon analysis. The soap solutions were prepared with freshly boiled distilled water. The concentration used was 0.25 percent and gave a pH value of 10.0.

1. ADSORPTION IN FOAM

Thin films of soap solution in contact with CO_2-free air were continuously formed and separated from a soap solution by the means illustrated in figure 1. The stream of air was first dried by passage through granular calcium chloride and concentrated sulphuric acid, then passed through a tower of soda lime to remove carbon dioxide, and finally rehumidified to avoid evaporation of the soap solution. Two liters of soap solution was placed in the first aspirator bottle, and with this amount of solution, a foam-height of 20 cm was required before the foam passed into the collecting bottle. The rate of the air stream was regulated to maintain a slow, steady delivery of foam permitting good drainage of the films so that a "dry" foam was obtained. The delivery tube had an internal diameter of 8 millimeters, and the foam extruded from this built up into a very stiff mass in the collecting bottle, and remained unbroken for several hours. When the delivery end of this tube was constricted to 1 millimeter in diameter, the foam broke to a spray in the collecting bottle and samples of the resulting liquid could be taken at once. Some results obtained by this method are shown in table 2.

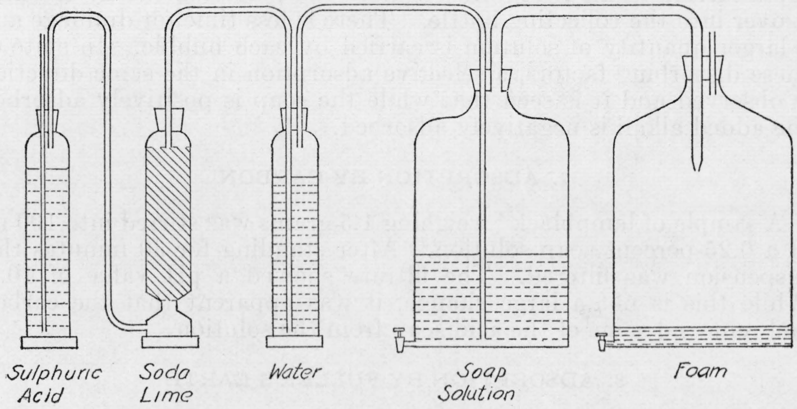

FIGURE 1.—*Apparatus for preparation of foam.*

TABLE 2.—pH *values and the soap and sodium-carbonate concentrations of solutions and of the foams formed by bubbling* CO_2*-free air through the solutions*

Description of solution	Concentration, percent	pH value
Original soap solution	0.25 soap	10.0
First 40 ml of broken foam	1.13 soap	9.6
Sample of 25 ml of broken foam after total of 250 ml removed	1.12 soap	9.6
Remainder of original solution	0.08 soap	10.5
Original solution of soap and soda ash	0.25 soap 0.50 soda ash	11.0
First 25 ml of broken foam	0.98 soap 0.45 soda ash	10.8

It is apparent from these data that the films of bubbles formed from a dilute soap solution contain a higher concentration of a solute which is less alkaline than the original soap, and the residual soap solution becomes progressively less concentrated and more alkaline as the foam is removed. In other words, the solute which is adsorbed at the air-solution interface is a product of the hydrolysis of soap, which does not carry equivalent amounts of sodium hydroxide and fatty acid. The solution resulting from the broken foam exhibits a marked turbidity which clears upon the addition of alkali.

The direction of this selective adsorption is the opposite of that reported by Zacharias (2), who found that the residual soap solution became progressively more acid as successive increments of foam were produced and removed—the final solution had a pH value of 6.5 and would no longer lather. He apparently did not test the foam itself and mentioned no precautions against contamination by carbon dioxide.

It may be noted in table 2 that the composition of the foam is approximately constant, changing very little in soap concentration and not measurably in pH value, while the original soap solution decreases to one-third its original strength and becomes more alkaline. This constancy of composition may be taken as evidence of a saturated film of the surface-active constituent of the soap solution.

When soda ash is added to the soap solution, the hydrolysis is repressed and a much less stable foam results. In this case a more rapid stream of air is required to raise the foam sufficiently to carry it over into the collecting bottle. There is less time for drainage and a larger quantity of solution is carried by each bubble. In spite of these disturbing factors, a selective adsorption in the same direction is observed and it is seen that while the soap is positively adsorbed the added alkali is negatively adsorbed.

2. ADSORPTION BY CARBON

A sample of lampblack[4] weighing 1.5 grams was stirred into 100 ml of a 0.25-percent soap solution. After standing for 30 minutes this suspension was filtered. The filtrate showed a pH value of 10.1. While this is not a large change, it was apparent that the carbon had removed some of the acid soap from the solution.

3. ADSORPTION BY FULLER'S EARTH

When a sample of fuller's earth was mixed with distilled water (pH = 5.9) and filtered, the filtrate showed no change in hydrogen-ion concentration. When 5 g of fuller's earth was stirred into 100 ml of the 0.25-percent soap solution (pH = 10.0) and filtered, the filtrate had a pH value of 9.2. The selective adsorption of alkali by fuller's earth is well known, for when a solution of sodium chloride is filtered through it, sodium hydroxide formed by hydrolysis is removed and the filtrate becomes acid.

4. ADSORPTION BY OIL DROPLETS

An emulsion was prepared from equal volumes of pure paraffin oil (medicinal) and the 0.25-percent soap solution. This was permitted to stand in a separatory funnel until it had creamed but had not broken. The lower aqueous layer was drawn off and it was found to have increased in alkalinity to a pH value of 10.4.

This experiment was repeated using a pure olive oil in place of the paraffin oil. The olive oil was found to contain 0.33 percent of free fatty acid. After creaming the aqueous layer had a pH value of 10.3.

A commercial olive oil which contained 7.90 percent of free fatty acid was emulsified in the same manner as the other oils. It formed a much more stable emulsion, and the aqueous layer after creaming had decreased in alkalinity to a pH value of 5.8. The above results indicate a selective adsorption of the acid products of the hydrolysis of soap or a negative adsorption of hydroxyl ions by oil droplets, except when the oil contains a considerable amount of free fatty acid.

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[4] Grade J. from L. Martin Co., Philadelphia, Pa.

5. ADSORPTION BY WOOL, SILK, AND COTTON

Two-gram specimens of purified[5] wool, silk, and cotton were soaked in 100-ml portions of the 0.25-percent soap solution. At intervals of time, the pH value of each solution was determined with the glass electrode. The results are recorded in table 3.

A similar set of experiments was made, except that aliquots were taken from each solution at stated intervals and analyzed for total alkali and fatty acid content. Only one aliquot was taken from each solution. The total alkali was determined by direct titration with standard acid, using methyl orange as the indicator. The total fatty acid was obtained by the procedure described by Levitt (5). The values in table 4 are given in millimoles per gram of conditioned fiber and each is the average of three determinations.

The results in tables 3 and 4 show that both wool and silk exhibit a pronounced selective adsorption of alkali, while cotton adsorbs equal but relatively small quantities of both alkali and fatty acid. Silk adsorbs the greatest amount of alkali. This is to be expected since its low isoelectric point (pH 2.5) (3) shows it to be one of the most acid proteins known. It is of interest to note that the soap solutions became turbid almost immediately after coming in contact with the wool and silk, while the solution in contact with cotton remained practically clear for 24 hours.

TABLE 3.—pH *values of 0.25-percent soap solutions in contact with wool, silk, and cotton for various lengths of time*

Time	pH of soap solutions in contact with—		
	Wool	Silk	Cotton
0	10.0	10.0	10.00
1 min	9.98	9.94	10.00
5 min	9.94	9.90	9.97
10 min	9.94	9.80	----------
15 min	9.90	9.75	9.92
30 min	9.81	9.59	9.93
1 hr	9.66	9.36	----------
17 hr	9.08	8.91	9.90

TABLE 4.—*Adsorption of alkali and fatty acid by wool, silk, and cotton in 0.25-percent soap solution*

[The values given are millimoles per gram of fiber weighed in equilibrium with an atmosphere of 65-percent relative humidity at 70° F.]

Time	Wool		Silk		Cotton	
	NaOH	Oleic acid	NaOH	Oleic acid	NaOH	Oleic acid
	Millimoles	*Millimoles*	*Millimoles*	*Millimoles*	*Millimoles*	*Millimoles*
5 min	0.035	0.009	0.072	0 066	0 010	0.013
15 min	.058	.014	.159	.079	.012	.014
30 min	.063	.018	.161	.084	.013	.011
1 hr	.073	.028	.165	.098	.012	.013
2 hr	.085	.032	.168	.103	.012	.012
24 hr	.107	.040	.178	.114	.015	.011

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[5] White worsted yarn, prepared from raw wool which had been solvent-extracted and washed with water, was used in this work. The yarn was extracted with alcohol and ether for six hours each, then washed with water, and conditioned at 65-percent relative humidity and 70° F. The preparation of the purified silk (3) and (4) has been described elsewhere.

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