# Effect of Cotton Substrate Characteristics upon Surfactant Adsorption

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It is shown that the reported differences in anionic surfactant adsorption on cotton can be largely attributed to the presence of variable amounts of natural wax on the fiber surface. High adsorption values with peaks near critical micelle concentration (cmc) result from surfactant adsorption on the wax surface. Wax-free surfaces fail either to show the same high maxima or the same relative magnitude of adsorption. At surfactant cmc the adsorption relationship for waxy cotton (millimoles/g. of cotton) cationic:nonionic:anionic was roughly 66 to 17 to 74. For dewaxed cotton, this became 40 to 10 to nil.

Confirming the findings of others, no adsorption by cotton of sodium tripolyphosphate occurs either with waxy or wax-free cotton. Also addition of tripolyphosphate decreased the adsorption of several anionic surfactants.

At concentrations greater than cmc and at sufficiently-high solution temperature, anionic surfactants can solubilize cotton wax, leaving a less waxy substrate upon which adsorption is then reduced.

CONSIDERABLE VARIATION in the adsorption of surfactants upon cotton has been noted in published data and ascribed to surfactant purity and adsorption technic (12). Sorption maxima and kink points in the adsorption isotherm were detected in the region of critical micelle concentration (cmc) by Evans (7), Meader and Fries (19), Fava and Eyring (9), and Sexsmith and White (22). Weatherburn and Bailey (27) found that sorption increased logarithmically to a constant value in the cmc range. In contrast, Jayson (14) and Boyd and Bernstein (3) failed to show the maxima at near cmc. The data of Perry and coworkers (21) point up the differences in magnitude of adsorption, which it is apparent are not explained simply by either surfactant purity (or sample) or adsorption technic.

Even though adsorption technics may vary, the marked differences in values were apparently to be found in another variable, the substrate. It is known that raw cotton varies widely in character, and it is likely that physical and chemical treatment of the fiber and fabric changes fiber characteristics still further.

In attempting clarification of the mechanism of action of sodium carboxymethyl cellulose (NaCMC), Nieuwenhuis and Tan (20) found that solvent-extracted unbleached cotton and bleached fiber varied considerably. The latter exhibited the protective action of NaCMC. Epton and Preston (6) demonstrated that the nitrogen content of raw cotton caused a variation in surfactant adsorption; this increased with increasing nitrogen content. Others, recognizing that the condition of cotton could affect their results materially, resorted to various types of preparatory procedure. Sookne and Harris (24) prepared standard cellulose by ethanol extraction, followed by a boil with 1% sodium hydroxide solution, providing dewaxed and depectinized fiber. Wahba (26) prepared "standard" cellulose by high pressure boiling of cotton linters in caustic soda solution, the fiber to be used for estimation of moisture adsorption.

This brief review demonstrates the variability of adsorption data, shows that attempts have been made to standardize fabrics and fibers prior to adsorption experiments, and suggests the possible variation in starting substrate. Pointed up is the need for more clearly defining the condition of the substrate used in adsorption experiments.

Variation in our own experiments necessitated a "standard" condition of cotton fabric, and data then developed help to explain certain characteristics of published surfactant adsorption results.

## Materials and Equipment

*Fabric.* Cotton pure finish, Indianhead plain weave, thread count 48 x 54, weight 5.0 oz./yd.$^2$ was used. This was desized by the following system: boiled with 1% NaOH solution and twice rinsed with water at the boil; bleached with 0.01% available chlorine solution; scoured at the boil with 0.075% soap chips, rinsed free of soap with hot distilled water; soured at 100°F. with 0.05% acetic acid solution; rinsed free of acid with hot water; dried.

The desized fabric was punched into $\frac{1}{2}$-in. disks for the sorption studies.

*Adsorption Apparatus.* The apparatus consists of six chain-driven spindles operated at 76 cycles/min. through a 370° arc, equipped with circulating water bath ($\pm 0.5$°C.).

Stainless steel stirrers with curved blades to fit 100-ml. Florence flasks were attached by rubber tube couplings; the shafts were machined to fit through 24/40 joint glass bearings. Matched sets of flasks were selected and calibrated at 25°C. for total volume (no air space, including bearing, blade, and cotton load) making corrections for buoyancy, temperature, etc.

*Du Nouy Interfacial Tensiometer.* A jacketed dish was used for temperature control ($\pm 0.2$°C.). Ring corrections by the method of Zuidema and Waters (29) were applied.

*Soxhlet Extractors.* Large size for thimble 6 cm. in diameter and 18 cm. in length was used.

*Surfactants.* The sorbates measured and their characteristics are shown in Table I.

*Coleman Universal Spectrophotometer.* A model with $\frac{1}{2}$-in. rectangular cells was operated at 650 m$\mu$ for methylene blue for surfactant anions and at 625 m$\mu$ for molybdenum blue assay of $P_2O_5$.

## Adsorption Procedure

Cotton disks conditioned at 66% RH at 25°C. were weighed (6 g. to the nearest 0.01 g.) directly into the Florence flask, and the sorbate solution was added just to overflowing. The bearing and blade were introduced, eliminating air space. In general screening, the systems (at given temperature) were stirred 10 min. at a rate of 76 cycles/min. through an arc of ca. 370°. The flasks were removed after 10 min., and

TABLE I
List of Sorbates

| Compound | Source | Description | % Active | Formula weight | Dye solubilization cmc data | | Sorption assay methods [a] |
|---|---|---|---|---|---|---|---|
| | | | | | °C. | % Conc. | |
| **A. Anionics** | | | | | | | |
| Na Dodecylbenzenesulfonate (NaDDBS) | Monsanto | Desalted, deoiled. Alkylate boiling range = 540–610°F. (Atm.) | 97 | 348 | 25 / 35 / 60 | 0.115 / 0.13 / 0.14 | TPT / MBX |
| Na Tridecylbenzenesulfonate (NaTDBS) | Monsanto | Desalted, deoiled | 95 | 362 | 25 / 50 / 75 | 0.05 / 0.10 / 0.10 | TPT / MBX / ...... |
| Na Pentadecylbenzenesulfonate (NaPDBS) | Monsanto | Desalted, deoiled. Alkylate boiling range = 156–157°C., 2 mm. | 97 | 390 | 25 / 50 / 75 | 0.017 / 0.021 / 0.035 | TPT / ...... / ...... |
| Na n-Dodecyl sulfate (Na n-DDS) | Monsanto | From Eastman Kodak n-dodecanol (m.p. = 23–24°C.) | 99± | 288 | 25 / 60 | 0.229 / 0.225 | TPT / MBX |
| **B. Cationic** | | | | | | | |
| Hexadecyltrimethylammonium bromide (HDTAB) | Eastman Kodak (T-5650) | Technical | 90+ | 364 | 25 | 0.033 | MBX |
| **C. Nonionics** | | | | | | | |
| n-Dodecanol + 9.6 EO | Monsanto | Salt and PEG-free | Ess. 100 | 609 | 25 | 0.007 | ST |
| Tridecanol + 10.1 EO | Monsanto | Dry (neutralized and filtered) | 91 (9% PEG) | 646 | 25 / 50 / 75 | 0.0092 / 0.0078 / 0.00757 | ST / ...... / ...... |
| **D. Inorganic Builders (Salts)** | | | | | | | |
| Sodium tripolyphosphate (STP) | Monsanto | TR 10–16 | 90+ | 366 | .. .. | ...... | MB |

| Anionic | % Anionic by weight | % STP by weight | cmc Data | | | Sorption assay method |
|---|---|---|---|---|---|---|
| | | | °C. | Anionic % conc. | Total solids % conc. | |
| **E. Anionic/STP combinations (1:2 mole ratio)** | | | | | | |
| NaDDBS | 32.2 | 67.8 | 50 | 0.070 | 0.218 | TPT – Anionic |
| NaDDBS | 32.2 | 67.8 | 60 | 0.070 | 0.216 | MBX – Anionic / MB – STP |
| NaTDBS | 33.1 | 66.9 | 50 | 0.031 | 0.094 | TPT – Anionic |
| NaPDBS | 34.7 | 65.3 | 50 | 0.01 | 0.028 | TPT – Anionic |
| Na n-DDS | 28.2 | 71.8 | 60 | 0.122 | 0.432 | TPT – Anionic |

[a] TPT—two-phase titration; MBX—methylene blue extraction; ST—surface tension; MB—molybdenum blue.

the bulk of the liquid was decanted through coarse fritted glass filters. Unexposed solutions were similarly filtered for control data. Total exposure time was ca. 12 min.

*Sorption Assay Methods.* Solutions before and after adsorption were assayed to give $\Delta\%$ concentration, then sorption was calculated:

$$\frac{\text{mg. sorbed}}{\text{g. cotton}} = \frac{\Delta\% \text{ conc.} \times \text{flask solution vol.} \times 1000}{\text{g. cotton} \times \text{cotton \% solids}}$$

(Cotton solids at 66% RH at 25°C. were 93–94%)

$$\frac{\text{millimoles sorbed}}{\text{g. cotton}} = \frac{\text{mg. sorbed/g. cotton}}{\text{sorbate formula weight}}$$

Surfactant anions were determined by the two-phase, cationic titration with cetyltrimethylammonium bromide and methylene blue indicator (1,5). The methylene blue extraction method of Fairing and Short (8) was used for surfactant cations by optical density measurements at 650 m$\mu$.

Tripolyphosphate was analyzed by conversion to orthophosphate (11), then as molybdenum blue by spectrophotometric measurement at 625 m$\mu$, for total $P_2O_5$.

## Experimental and Discussion

*Fiber Swelling.* Evans (7) correlated the adsorption of surfactants with the transverse swelling of cotton and other fibers. In dilute solutions little change occurred, but at maximum adsorption a decrease in swelling was found. Attempts were made to verify these findings at 970 magnification with fibers from the desized disks. Using sodium dodecylbenzene sulfonate in a concentration range of from 0.02 to 0.40%, and at critical micelle concentration (0.12%), the results were so variable as to have little significance. Averages of 2.2% to 5.5% for the range of values were found, but the replicates varied so widely as to negate statistical treatment. With this variability, attempts to correlate fiber swelling with surfactant concentration and sorption were unsuccessful, and fiber swelling was considered a minor factor in adsorption.

*Moisture Effect Upon Adsorption.* Sookne and Harris (24) in some very precise work with cotton fibers found that fiber moisture content markedly affected their results, and a correction factor was developed. However Weatherburn and his coworkers (28) investigated the effect of water hydration of fibers and found that this correction was considerably less than the probable error of sorption experiments. It was found that a correction factor for the moisture content of the conditioned fiber quite adequately covered this variable. Determination with our fiber of the effect of moisture content showed that conditioning at 66% RH at 25°C. was a suitable system: only vacuum-dried cotton sorbed water to a preferential degree. Table II presents these data.

Bikerman (2) pointed out that cellulose can preferentially sorb water or solvent molecules and lead to spurious sorption results. However the results of Table II show that identical sorption values for a n-dodecanol-9.6 EO adduct were obtained with the proper correction. In agreement with Magne and his coworkers (18) it appeared that, at 6–7% moisture content, primary sorption of water on free hydroxyl

TABLE II

Sorption of n-Dodecanol + 9.6 EO[a] by Cotton Having Various Moisture Contents

| Conditioning relative humidity 25°C. | % Water in cotton | mg. Sorbed/g. cotton (dry basis) |
|---|---|---|
| 0 | 0.9 | 0.919 ± 0.009[b] |
| 30 | 1.8 | 0.989 ± 0.027 |
| 66 | 5.6 | 0.997 ± 0.020 |
| 100 | 15.4 | 0.989 ± 0.007 |

[a] Measured at cmc, 0.007% conc.
[b] Average deviation.

sites had already occurred, minimizing the probability of preferential solvent sorption. Consequently the disks used were conditioned at 66% RH at 25°C., and proper correction was made for contributed moisture content.

*Adsorption Time.* In the dynamic detergent operation an exposure time of 30 min. is relatively long; many washing operations are completed in 15 min. or less. In very precise work, equilibrium values over long periods of time may be required, but for our purposes, shorter periods were used.

In addition, two samples of cotton were used, one the desized disks, and the other chopped fiber from the same source; both were simply desized. Table III shows that the adsorption of NaDDBS is essentially complete (at cmc) after a 5-min. exposure.

TABLE III

Effect of Time on Dodecylbenzenesulfonate[a] Sorption

| Time | mg. Sorbed/g. cotton |
|---|---|
| A. Cotton Fabric (water-washed, desized) | |
| 5 min. | 2.2 |
| 15 min. | 2.1 |
| 30 min. | 2.1 |
| B. Chopped cotton fibers (water-washed, desized)[b] | |
| 30 min. | 2.8 |
| 6 hrs. | 2.4 |
| 24 hrs. | 1.8 |

[a] Measured from a 0.12% solution, i.e., at cmc.
[b] Wax-containing. Note that sorptions were nil for DDBS ions at all times tested when dewaxed cotton was employed.

*Cotton Purification.* Table IV presents some pertinent data concerning the characteristics of water-desized and solvent (1:1 methanol/benzene) extracted fabric. Methods (4,15) for investigating wax removal by Soxhlet organic solvent-extraction have successfully removed the wax. The pertinent factor seems to be the presence of solvent-extractable wax, which remains even after the rather stringent desizing treatment given. The waxy material appears to be largely
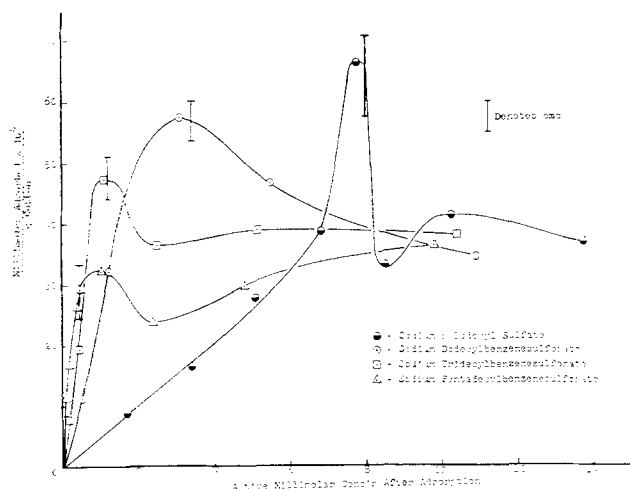


FIG. 1. Adsorption isotherms for various anionic surfactants at 25°C.

aliphatic in nature and is probably the natural wax found by others (17).

The cotton surface-area values were determined by the nitrogen BET procedure, showing the marked differences between the two states (disk or chopped). Titratable acidity differences after dewaxing were negligible, showing that carboxy groupings had little effect upon adsorption differences.

The five washes with detergent solution suggest gradual wax removal so that, after a finite usage period, garments approach the solvent-dewaxed state. That differences between new and used cotton fabrics exist was demonstrated by Lambert (16), who ascribed radiocalcium adsorption differences to degradation of the used cotton fabric. It has available considerably greater numbers of ion-exchangeable carboxyl groups. Since the degradation period of five washes is low (Lambert used 6-year-old fabric) and because titratable acidity differences are very slight, variation between the present fabrics is ascribed to wax removal rather than other phenomena.

### Surfactant Adsorption Data

*Wax-Containing Desized Cotton.* The several isotherms for a homologous series of sodium alkylbenzene sulfonates and sodium n-dodecyl sulfate of Figure 1 show the following: well defined sorption maxima near the cmc; sorptions at the cmc increased with

TABLE IV

Analytical Data for Cotton Fabric Samples and the Solvent[a] Extract from Cotton

| State | Desized Indianhead cotton sample | % H₂O after drying (Karl Fisher) | % Nitrogen | % Carbon[b] | Surface area[c] (m²/g.) | % Solvent extract (wax) | Titratable acidity (Milli-equivalents ×10⁴/g.) |
|---|---|---|---|---|---|---|---|
| ½-in. disks | Without further washing | 0.52 | 0.009 | 44.29 | | 0.59, 0.53 | 5.5 |
| ½-in. disks | Water-Washed | 0.89 | 0.008 | 43.09 | 0.52 | 0.48, 0.68 | |
| ½-in. disks | 5 washings in detergent solution[d] | | | | | 0.31 | |
| ½-in. disks | Solvent and water-washed[a] (dewaxed) | 0.80 | 0.010 | 43.79 | 0.62 | Nil | 6.5 |
| Chopped fiber | Without further washing | | | | | 0.38 | |
| Chopped fiber | Solvent and water-washed[a] | | | | 3.0 | Nil | |
| Solvent extract | | | 1.10 | 71.52 | | | |
| Additional properties: dark brown wax having little water solubility at room temperature. Tested negatively for protein (along with unwashed cotton) by biuret and xanthoproteic tests. IR Spectroscopy: highly aliphatic with many CH₂ groups; alcohol and ester groups present. UV Spectroscopy: unsaturation indicated, but not aromatic. | | | | | | | |

[a] Desized Indianhead cotton was thoroughly water-washed or solvent-extracted (by Soxhlet with methanol/benzene, 1:1) and water-washed, then dried. The solvent-extracted material was accumulated by successive extractions of 100-g. cotton batches; each batch extracted a minimum of 24 hrs.
[b] Values adjusted to anhydrous basis.
[c] By BET nitrogen absorption method.
[d] Washed in rotating tumbler with 0.2% solution of 15% nonionic surfactant, 65% tetrasodium pyrophosphate, 20% soda ash.

increasing cmc values (decreasing hydrophobe chain length); and below cmc increase of sorption most rapidly for long-chain hydrophobes while above cmc more decrease of sorption for shorter-chain hydrophobes.

Explanations for these peak adsorptions at cmc with subsequent lowering of adsorption above this point have been various. Meader and Fries (19) inclined toward the explanation that single ion (or monomer) activity beyond maximum adsorption decreased, lowering adsorption. Data of Fava and Eyring (9) show the same drop in adsorption, but explanation for this effect was avoided by pointing out that at these higher concentrations "liquid hold-up" of this adsorption scheme sharply reduced the accuracy of the determination. Jayson (13) performed his experiments with radiotagged NaDDBS somewhat below the cmc hence did not show the peak adsorptions of Fava and Eyring, or Meader and Fries. Though the substrates are different (carbon instead of cotton), Vold and Sivaramakrishnan (25) showed these same peak adsorptions in the region of cmc with subsequent reductions at higher adsorption concentrations. In explanation they postulated that, when the ionic strength of the solution so compressed the surface double-layer that electrical repulsion between adsorbed ions became less than the van der Waals attraction of their paraffin chains, surface micelles were formed. Desorption of both simple monomer ions and surface micelles then was believed to occur upon collision of micelles in solution with the adsorbing surface.

The data of Figure 1, for the desized but wax-containing cotton, show the same type of adsorption maxima as do those of both Fava and Eyring, and Meader and Fries. In these cases the fabric treatment was such as to leave the natural wax in the cotton.
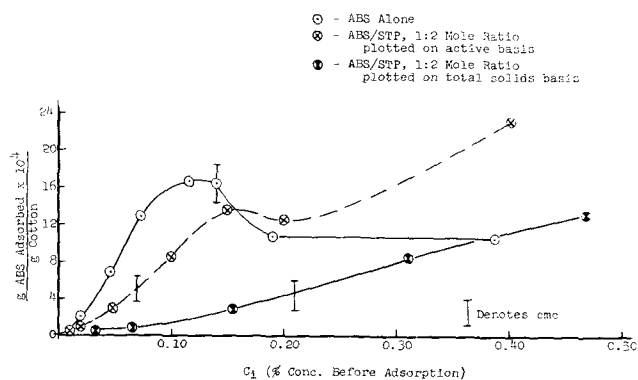


FIG. 2. Adsorption isotherms for sodium dodecylbenzene sulfonate with and without STP builder.

Figure 2 is representative of the adsorption curves for the homologous series of alkylbenzene sulfonates with and without added sodium tripolyphosphate (STP) builder. A 1:2 molar ratio of NaDDBS to STP was used. Previous work (10) had shown this as an effective combination. Several conclusions were apparent from these experiments. Addition of STP had no effect on the relative sorption tendencies of the several alkylbenzene sulfonates. Addition of STP decreased sorption of anionics. The sorption relation to cmc was not apparent with STP present, and sorption levelled off or increased above cmc.

Jayson (14) showed that tetrasodium pyrophosphate, though not adsorbed by cotton, increased the adsorption of NaDDBS on the substrate, as did Perry and coworkers (21) for sodium myristyl sulfate. Contrary to this and in keeping with our findings, both Meader and Fries (19) and Boyd and Bernstein (3) found that the presence of polyphosphates decreased surfactant adsorption. Several theoretical explanations for these differences have been given, but, along with Jayson, we attribute these conflicting views to cloth treatment as shown by further experiments.

*Desized, Dewaxed Cotton.* The adsorption of tridecylbenzene sodium sulfonate ions by wax-containing and dewaxed cotton disks is shown in Table V. It is apparent that adsorption on the dewaxed cotton is essentially negligible.

TABLE V

Sorption of Tridecylbenzenesulfonate Ions by Cotton

| Surfactant concentration | mg. Sorbed g. Cotton | |
| --- | --- | --- |
| | Wax-containing desized cotton | Dewaxed cotton |
| 0.02 | 0.6 | Nil |
| 0.05 (cmc) | 1.7 | 0.2 |
| 0.10 | 1.5 | 0.3 |

With different surfactants and tripolyphosphate, Table VI shows that the cationic surfactant is

TABLE VI

pH Effects for Sorptions on Dewaxed Cotton
(25°C.)

| Sorbate | Initial % conc. | pH | | Radical measured for sorption | Millimoles sorbed × $10^4$ per g. cotton |
| --- | --- | --- | --- | --- | --- |
| | | Initial adjusted | After exposure | | |
| HDTAB [a] | 0.033 (cmc) | 9.42 | 7.81 | Cation | 55.6 |
| | | 7.81 | 7.29 | Cation | 40.5 |
| TDA + 10.1 EO [b] | 0.009 (cmc) | 10.65 | 10.60 | Entire mol. | 8.4 |
| | | 7.86 | 7.42 | Entire mol. | 9.9 |
| STP | 0.009 | 9.56 | 6.56 | Anion | Nil |

[a] Hexadecyltrimethylammonium bromide.
[b] Tridecyl alcohol—10 EO adduct.

adsorbed rather highly. Cation exchange causes a marked decrease in the more highly adjusted pH level, indicating release of hydrogen ions from the dewaxed cotton substrate. The nonionic surfactant showed slight adsorption. No STP anion was adsorbed even though a change in pH occurred upon exposure. Consistent with the findings of Jayson, and Boyd and Bernstein, no adsorption of tripolyphosphate was found. These data suggest the cation exchange mechanism of adsorption with the cationic surfactant, and consistent with only slight pH change, hydrogen bonding is suggested for the nonionic surfactant (nonionic surfactants are however very mildly cationic in character).

Comparison of the two fabrics is given in Table VII, showing that, dependent upon the character of the fabric treatment, negligible-to-considerable sorption of surfactant can be expected.

Since Evans' (7) fiber swelling theory appeared inapplicable according to our experiments and as adsorption was not attributable to nitrogen content (Table IV), as suggested by Epton and Preston (6), another mechanism must be operative. In explanation of the relatively high adsorption of anionic surfactant on waxed desized fabric, the following mechanism may exist. The presence of hydrophobic wax may be the reason for anionic adsorption. The

TABLE VII
Comparative Sorption Data for Waxy and Dewaxed Cotton Fabric

| Sorbate or System | % Conc. | Radical measured | Waxy Desized Cotton | | Dewaxed Cotton | |
|---|---|---|---|---|---|---|
| | | | $\Delta\%$ Conc. | Millimoles sorbed$\times 10^4$ g. of cotton | $\Delta\%$ Conc. | Millimoles sorbed$\times 10^4$ g. of cotton |
| Hexadecyltrimethylammonium bromide | 0.033 (cmc) | Cation | 0.0106 | 66 | 0.0065 | 40 |
| Tridecanol + 10 EO | 0.009 (cmc) | Entire molecule | 0.0049 | 17 | 0.0028 | 10 |
| Sod. dodecylbenzenesulfonate (NaDDBS) | 0.12 (cmc) | Anion | 0.0115 | 74 | Nil | Nil |
| NaDDBS/STP (1:2 mole ratio) | 0.177 (cmc) | DDBS anion | Ess. nil | Ess. nil | Nil | Nil |
| | | TP anion | Nil | Nil | Nil | Nil |
| STP | 0.12 | Anion | Nil | Nil | Nil | Nil |

rapid increase up to cmc may be attributed to monomer sorption on the wax surface. In the absence of micelles the wax remains unsolubilized and offers a surface for sorption. Immediately above cmc, solubilization can occur, and a portion of the wax may be removed to the solution phase (at a sufficiently high temperature). Wax removal leaves the relatively inactive wax-free cotton surface, resulting in adsorption decrease. In the presence of a 1:2 molar ratio of sodium tridecylbenzene sulfonate and STP, it is shown in Figure 3 that at 50°C. the cmc after
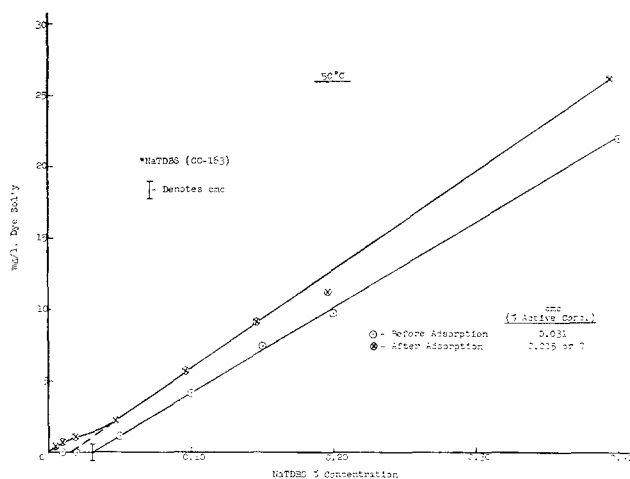


FIG. 3. Effect of adsorption by cotton on the solubilizing activity and cmc of a sodium tridecylbenzenesulfonate-STP (1:2 mole ratio) combination.

adsorption on the desized waxy cotton was lowered from 0.031% to 0.015% or less. This indicates that the dye used for the solubilization determination (External D & C Orange No. 4; 1-o-tolylazo-2-naphthol) (10) was solubilized by the mixed wax-surfactant micelles. Control experiments made with dewaxed cotton showed no such change in surfactant solution activity.

In view of the cotton wax influence with waxy cotton, in which low sorption values indicate greater effectiveness in wax removal, the several anionic compounds in order of increasing sorption and lowered wax removal are:

$$C_{15}\emptyset SO_3^- : C_{13}\emptyset SO_3^- : C_{12}\emptyset SO_3^- : nC_{12}OSO_3^-$$
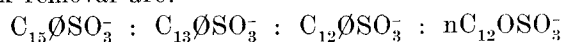
This also helps to explain why, with STP present, lower amounts of surfactant were sorbed. More wax was solubilized, and less surface for adsorption remained. It is suspected that lowered adsorption at higher temperatures may be partially explained by the same mechanism.

The data of Table V show that adsorption on dewaxed cotton was not at a maximum at cmc as it was

for waxy cotton, helping additionally to explain the importance of cotton condition in adsorption studies. These facts also help to explain why, in the presence of builders, some investigators have found an increase in surfactant adsorption, why the magnitudes of adsorption vary, and why still other investigators have shown quite low adsorption values.

Adsorption studies with dewaxed cotton, as a more controllable standard fabric condition, continue.

## Summary

Dependent upon the presence or absence of a natural waxy coating on cotton, the adsorption of surfactants, particularly the anionics, can vary from appreciable to negligible. It appears that the adsorption occurs on the waxy surface rather than the pure cotton substrate when wax has not been fully removed. At concentrations above cmc and at sufficiently high temperatures it was shown that the wax was solubilized, appearing in the micelles. These findings explain why some investigators have shown appreciable maxima at cmc while others were unable to reproduce these findings with their fabric. It is possible by controlling wax content to achieve either result, or others intermediate between them.

For waxy cotton with alkylbenzene sulfonates or alkyl sulfate, well-defined sorption maxima occurred near cmc. The adsorption of these same compounds at cmc with dewaxed cotton was negligible. Radiotagged surfactants will be used for estimation at these low-adsorption levels.

The addition of STP to alkylbenzene sulfonate solutions had no effect on their relative sorption values (waxy cotton), but total sorption was decreased. The sorption relation to cmc was not apparent with STP in the surfactant solution. No sorption of STP by either type of cotton was evident.

At cmc with waxy cotton, the rough adsorption relationship (millimoles sorbed/g. cotton) for cationic, nonionic, and the anionic surfactants was of the order of 66:17:74. For dewaxed cotton this was 40:10:nil.

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# A New Industrial Process for Cottonseed[1]

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Described are the main principles of a new industrial process that permits the processing of cottonseed, producing a meal virtually free of free gossypol and of bound gossypol both and considerably improving the oil-refining yields.

A descriptive summary is given of the plant required and of the work cycle followed in the industrial establishment already in production for many years in Italy.

IN THE LAST 20 years two problems have received special attention in the field of cottonseed processing technology. The first was to eliminate the toxicity of cottonseed meal and the second was to improve the refining yields of the crude oil obtained by the crushing of cottonseed.

Regarding the first problem, it is known that the major source of the difficulties encountered in the use of cottonseed meal as a feed-stuff lies in the presence of a toxic pigment called gossypol. Almost all commercial meals and cakes contain only a small amount of free gossypol because, before crushing, the ground seed is subjected to a prolonged treatment with directly applied steam, which inactivates the gossypol insofar as it favors the combination of this product with the seed protein.

By this means the "cooking" of the seed solves to a partial extent the problem of the employment of cottonseed meal but at the cost of the nutritional value because the protein-gossypol compounds formed cannot be assimilated. Therefore important parts of the proteins present are not available. It has, in fact, been shown that the more prolonged and drastic the cooking, the less the nutritional value of the meal (1).

It is clear that the ideal solution would be to eliminate completely all the gossypol present in the seed, prior to cooking, so as to eliminate not only the "free" gossypol content but also the gossypol "bound" to the proteins. In a study made in collaboration by the Texas Agricultural Experiment Station and other institutes of the United States the conclusion was reached that "this would suggest that, if a suitable manufacturing method can be developed to produce meals containing only small amounts of both total and free gossypol, these would probably be meals of exceptionally high nutritional value, provided that the solubility of the protein remained high" (2).

In theory the total elimination of the gossypol is possible by the use of a solvent, such as butanone or acetone. Research has yielded satisfactory results. Meal directly purified of gossypol by extraction by solvents (butanone) have shown a nutritional value higher than that of soya meal (3,4). However the employment of such solvents has not been adopted in practice because they extract not only the gossypol but also the oil, which would be so impure as to be, in practice, unrefinable by ordinary means.

Another system, proposed recently by the Experimental Engineering Station of Texas, consists in the employment of n-octylamine, which would dissolve the gossypol. This method however is still being studied.

The second problem of major importance in the technology of the processing of cottonseed is that of refining loss and oil color. Because of the impurities contained in such oil (gossypol, phosphatides, etc.) ordinary methods of refining result in high refining losses.

Therefore, in the case of oils of medium acidity, the full loss of oil reaches values treble or more the acidity of the initial oil. More accurately to value these losses, reference must be made either to the "Wesson Loss" or, better still, to the "chromatographic loss," showing in the case of each oil the amount of the fatty acids and impurities. The loss factor is expressed by the ratio of the loss, practically checked in the refining process, to the chromatographic loss. For the batch-refining kettle process this loss factor rises between values of 2 and 2.5 for it is affected both by the acidity of the oil and its content of impurities.

Such high values, tolerable only with oil of low acidity and high purity, become serious whenever very acid oils from badly stored seeds must be processed. If such is the case, the real loss of oil in the refining process may reach 10% or even more of the oil treated.

Various ways of reducing these losses were studied. The simplest consists of centrifuging the soap stock to recover part of its neutral oil content. A better result is obtained by using two refining stages. First, slightly more than the theoretical amount of caustic soda suitable for the oil acidity is used. Thus complete neutralization results, with the oil unbleached. Then the whole mass is centrifuged to recover the most oil-impoverished soap stock, and the dark neutral oil is given a second treatment with caustic soda to attack the remaining gossypol and other impurities. This is followed by a second centrifuging, from which a neutral oil of good color results.

Later some continuous processes were studied in which the refining was carried out continuously with an exactly-measured amount of caustic soda. These plants normally use centrifugals and proceed by a number of stages. The oil is degummed, then undergoes two successive neutralizations, and is finally washed. Each stage is followed by centrifuging. There