REFERENCES

1. American Oil Chemists' Society, "Official and Tentative Methods of Analysis," 2nd ed., Cd 1–25, rev. to 1956, Chicago, 1946–56.
2. Brice, B. H., Swain, M. L., Herb, S. F., Nichols, P. L. Jr., and Riemenschneider, R. W., J. Am. Oil Chemists' Soc., *29*, 279–287 (1952).
3. Chapman, D., Crossley, A., and Davies, A. C., J. Chem. Soc., 1502–1509 (1957).
4. Craig, L. C., Hausman, W., Ahrens, E. H. Jr., and Harfenist, E. J., Anal. Chem., *23*, 1236–1244 (1951).
5. Dutton, H. J., and Cannon, J. A., J. Am. Oil Chemists' Soc., *33*, 46–49 (1956).
6. Dutton, H. J., Lancaster, C. R., and Brekke, O. L., J. Am. Oil Chemists' Soc., *27*, 25, 30 (1950).
7. Eckey, E. W., "Vegetable Fats and Oils," p. 676, Reinhold Publishing Corporation, New York, 1954.
8. Hilditch, T. P., and Stainsby, W. J., J. Soc. Chem. Ind., *55*, 95T (1936).
9. Hilditch, T. P., J. Am. Oil Chemists' Soc., *26*, 41–45 (1949).
10. Kartha, A. R. S., *Ibid.*, *30*, 326–329 (1953).
11. Lutton, E. S., *Ibid.*, *34*, 521–522 (1957).
12. Mattson, F. H., and Lutton, E. S., J. Biol. Chem., *233*, 868–871 (1958).
13. Meara, M. L., J. Chem. Soc., 2154–2157 (1949).
14. Nijkamp, H. J., Anal. Chem. Acta., *10*, 448–458 (1954).
15. Savary, P., Flanzy, J., and Desnuelle, P., Biochim. et Biophys. Acta., *24*, 414–423 (1957).
16. Scholfield, C. R., and Dutton, H. J., J. Am. Oil Chemists' Soc., *35*, 493–496 (1958).
17. Scholfield, C. R., and Hicks, Mary A., *Ibid.*, *34*, 77–80 (1957).
18. Vander Wal, R. J., J. Am. Oil Chemists' Soc., *35*, 483 (1958).

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Recovery of Gossypol from Cottonseed Gums[1]

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CONSIDERABLE attention has been given to methods for the isolation of gossypol from cottonseed (1). These procedures all involve a preliminary solvent extraction of gossypol from defatted meats, or isolated pigment glands, by use of solvents such as diethyl ether or acetone. While satisfactory for small-scale preparations, the excessive costs of solvent extraction systems for the removal of a constituent present to the extent of about 1% in the cottonseed kernel mitigate against large scale use of such systems.

Cottonseed gums, obtained as a by-product, on water-washing of crude cottonseed oil processed from the seed by direct extraction, contain considerable quantities of gossypol and phosphatides (2, 3, 4) and offer a practical source of gossypol. The relatively mild conditions employed in the commercial degumming process (2) should minimize the oxidative degradation of the gossypol in the gums. It has been estimated that at one solvent-extraction plant, these gums are presently produced at an annual rate of about 2,000 tons, representing a potential source of some 200,000 lbs. of gossypol. It has also been reported that considerable amounts of gossypol can be removed from conventional screw-pressed and prepressed oils by a degumming process similar to that employed for solvent-extracted crude oils (5).

The present investigation was undertaken with the view of developing a practical process for the isolation of gossypol from this by-product of cottonseed processing and to make available sufficient amounts of gossypol to explore potential uses of this unique and reactive compound.

Basic Investigations

The proximate composition of cottonseed gums as produced by a commercial degumming process (2) is recorded in Table I. Analysis of the acetone insoluble fraction disclosed that about 70% of the total gossypol in the gums is segregated in this fraction, from which it cannot be removed by repeated acetone extractions. This suggested that most of the gossypol in gums is present in a "bound" form, presumably in chemical combination with phoshatides. Other exploratory experiments indicated that it would be necessary to cleave this gossypol combination product and to separate gossypol from the considerable amounts of surface-active phosphatides prior to its isolation.

TABLE I

Proximate Composition of Cottonseed Gums

Constituent	Range (4 samples)
	%
Moisture (6)	41.0 –44.9
Neutral oil (6)	12.4 –16.4
Total phosphorus (7)	1.16– 1.26
Phosphatides (P × 25)	29.0 –31.5
Acetone solubles (6)	17.2 –20.9
Acetone insolubles (6)	37.1 –40.3
Total gossypol (8)	4.33– 5.46

By use of mild acid hydrolysis in methyl ethyl ketone (MEK), in which both water and phosphatides have limited solubility, a fairly simple procedure was devised for cleaving the gossypol and separating it from phosphatides. In the process the gums are refluxed with MEK that contained either oxalic or phosphoric acids, using a gums-to-solvent ratio of about 1:1. Upon cooling, the mixture separates into a supernatant MEK phase which contains most of the gossypol and a lower phosphatide-water phase. The lower phase is then washed with MEK to remove practically all of the gossypol. After concentration of the combined MEK decantate and washings by distillation, addition of glacial acetic acid to the concentrate allows isolation of gossypol as the crystalline acetic-acid addition compound. The crude gossypol acetic acid is purified by two recrystallizations. Relatively pure crystalline gossypol is obtained from the pure gossypol-acetic acid complex by dispersing the complex in dilute aqueous sodium carbonate, then acidifying with a mineral acid.

Processing Variables. Optimum conditions of time and acid concentration for hydrolysis and for precipitation and purification of gossypol were established. Cottonseed gums, 500 g., were refluxed with 500 ml. of MEK containing the desired acid concentration and cooled to 50°F. After removal of the MEK supernatant the lower phase was washed by vigorous mixing with four successive 100-ml. portions of solvent. Combined decantates and washings, usually 800 ml., were concentrated by distillation to about 300 ml., and gossypol-acetic acid was isolated

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by addition of glacial acetic acid. Crude products were filtered, washed thoroughly with hexane, and vacuum-dried at 50°C.

The use of 0.2 molar oxalic acid or 0.4 molar phosphoric acid for the hydrolysis step resulted in the highest yields and purities of crude gossypol acetic acid (Table II). Increase in hydrolysis time beyond

Table II

Effect of Acidic Conditions and Hydrolysis Time on Recovery of Gossypol from Cottonseed Gums

Hydrolysis[a]		Precipitation		Crude gossypol acetic acid		Recovery of gossypol from gums[c]
Acidic conditions—MEK solution	Time	Acetic acid: concentrate	Time	Dry wt.	Purity[b]	
	hr.		*hr.*	*g.*	%	%
None	2.0	1:2	48	12.7	88.1	36.3
0.4 M—acetic	2.0	1:2	48	4.7	78.7	12.1
0.2 M—oxalic	0.5	1:3	16	15.8	93.1	37.8
0.2 M—oxalic	1.0	1:3	16	17.7	94.4	54.6
0.2 M—oxalic	2.0	1:3	16	17.7	95.7	55.1
0.2 M—oxalic	4.0	1:3	16	17.5	92.2	52.5
0.2 M—H_3PO_4	0.5	1:3	16	11.7	95.0	36.2
0.2 M—H_3PO_4	1.0	1:3	16	12.6	95.1	39.2
0.2 M—H_3PO_4	2.0	1:3	16	16.1	95.6	50.2
0.4 M—H_3PO_4	2.0	1:3	16	17.7	95.4	55.1
0.4 M—H_3PO_4	4.0	1:3	16	15.7	94.1	48.1

[a] 500 g. of gums containing 5.5% gossypol refluxed with 500 ml. of MEK-acid solution (73.5°C.).

[b] Purity determined by colorimetric analysis (8) for percentage of gossypol and by ratio of extinction coefficient of crude product to that of purified gossypol acetic acid at 365 mμ in benzene.

[c] Recovery $= \frac{\text{wt. gossypol acetic acid} \times \text{purity} \times 0.896}{\text{wt. gums} \times \% \text{ gossypol}}$.

1 hr. for oxalic acid or 2 hrs. for phosphoric acid had no effect on yields. The highest recovery of gossypol from the gums was about 55% of the gossypol present. Attempts to improve recovery beyond this amount were unsuccessful.

A methyl ethyl ketone concentrate from a larger-scale experiment, in which 40 lbs. of gums were processed, was employed in order to study the effect of variations in acetic-acid concentration, precipitation time, and temperature on the yield of gossypol acetic acid. From results summarized in Table III

TABLE III

Effect of Precipitation Conditions on Yield of Gossypol Acetic Acid from MEK Concentrate

Precipitation conditions[a]			Crude gossypol acetic acid		
Ratio, acetic acid: concentrate	Time	Temp.	Dry wt.	Purity[b]	Yield[c]
	hr.	*°C.*	*g.*	%	%
1:10	16	25	10.2	94.0	25.7
1:5	1	25	15.1	94.0	38.0
1:5	16	25	20.8	95.1	53.0
1:3	0.5	25	19.3	94.0	48.4
1:3	1	25	20.3	95.3	51.8
1:3	16	25	20.6	95.7	52.5
1:2	1	25	22.3	94.3	56.1
1:2	16	25	21.4	95.3	54.3
1:5	16	4	16.5	94.0	41.5
1:3	16	4	20.0	94.0	50.1
1:2	16	4	21.5	94.0	53.9

[a] 500 ml. of MEK concentrate containing 33.57 g. of gossypol plus stated volume ratios of glacial acetic acid.

[b] See Table II.

[c] Yield $= \frac{\text{wt. gossypol acetic acid} \times \text{purity} \times 0.896}{33.57}$.

it is apparent that the quantity of complex isolated is limited by an equilibrium involving acetic acid concentration, reaction time, and probably gossypol concentration. Using a volume ratio of acetic acid to concentrate of 1:3 and a precipitation time of 1 hr. at 25°C., the yields obtained, 52%, did not differ appreciably from those found when higher acid concentrations or longer time were employed. Attempts to increase gossypol content by further concentration of the MEK phase prior to the addition of acetic acid resulted in extremely viscous and oily solutions, from which it was difficult to isolate gossypol acetic acid. Neutral oil and other unknown impurities present in the MEK concentrate contributed to this effect.

Crude gossypol acetic acid of about 92% purity can be upgraded to 98% purity by a single recrystallization from MEK as gossypol acetic acid with an 86% yield (Table IV). Two recrystallizations with

TABLE IV

Yield Data—Purification of Crude Gossypol Acetic Acid

Purity of crude gossypol acetic acid	Solvent	Recrystallization			Purified gossypol acetic acid	
		Ratio of crude product to MEK	Ratio of acetic acid to MEK	Number of purifications	Purity	Yield[b]
%		*W/V*[c]	*V/V*[d]		%	%
92.0	MEK	1:6	1:3	1	98.0	86.5
92.0	MEK	1:6	1:3	2	98.6	76.8
92.0	MEK	1:6	1:3	4	100.0	63.4
92.0	MEK[a]	1:6	1:3	1	98.0	84.3
92.0	MEK[a]	1:6	1:3	2	99.1	77.0
92.0	MEK[a]	1:6	1:3	4	100.0	64.0

[a] 20% carbon.

[b] Average data from 5 experiments.

[c] Weight to volume (g./ml.).

[d] Volume to volume.

an over-all yield of 77% resulted in a product of 99% purity. Because of the high purity of the crude gossypol acetic acid, 92–94%, concentrated solution can be employed, and yields on recrystallizations are considerably higher than the recovery values found for isolation of gossypol acetic acid from gums.

Purified gossypol acetic acid can be converted to gossypol by solution in diethyl ether and evaporation over water to remove the ether and acetic acid (1). This dissociation does not result in any further purification (Table V). Both dissociation and purification can be effected by solution of crude gossypol acetic acid in sodium hydroxide, followed by acidification, extraction with ether, and recrystallization from an ether-xylene mixture (10). A single purification of crude gossypol acetic acid by this technique produced gossypol of 99.5% purity with a 67% yield (Table V). Both of these procedures, while effective for the purpose, require the use of one or more organic solvents. It was found that gossypol acetic acid can be conveniently dissociated by solution in dilute sodium carbonate, under anaerobic conditions, and

TABLE V

Conversion of Gossypol Acetic Acid to Gossypol

Purity of gossypol acetic acid	Conversion method	Gossypol	
		Purity[a]	Yield
%		%	%
96.0	NaOH—ether-xylene (10)	99.5	67.4
100.0	Ether soln. evaporated over water (1)	99.7	.....[b]
99.7	Ether soln. evaporated over water (1)	99.7	.....[b]
98.7	Ether soln. evaporated over water (1)	98.2	.....[b]
97.6	Ether soln. evaporated over water (1)	97.6	.....[b]
100.0	Na_2CO_3 solution acidification	98.0	.....[b]
98.7	Na_2CO_3 solution acidification	97.0	.....[b]

[a] See Table II.

[b] Quantitative yield, gossypol-insoluble in water or dilute acid solution.

that relatively pure gossypol can be precipitated by acidification of this alkaline solution with mineral acid. About 10 ml. of 0.2 molar carbonate solution are used per gram of purified gossypol acetic acid. Sodium hydrosulfite, 0.1%, was added to the carbonate solution to insure reduction of gossypol products (1). A thin layer of hexane was floated on the surface of the carbonate solution, prior to acidification, to minimize further atmospheric oxidation. The gossypol produced in this manner was filtered and water-washed to remove adsorbed salts. The vacuum-dried product was almost equivalent in purity to the gossypol acetic acid used (Table V).

Isolation as Dianilinogossypol. Since dianilinogossypol is relatively insoluble in most of the common solvents, some experiments were performed on the isolation of gossypol from gums as this derivative. Gums were dispersed in hexane, then warmed to promote separation of excess water. The hexane phase was treated with aniline. About 60% of the gossypol present was recovered as dianilinogossypol (89% purity). Crude products were difficult to filter and were contaminated with phosphatides. Addition of aniline to MEK concentrates obtained from the acid hydrolysis of gums, as previously described, resulted in the separation of crude dianilinogossypol of 84% purity. The product was essentially free from phosphatides and represented about 57% of the gossypol in the gums. Recovery of gossypol from dianilinogossypol, by the best available procedure (10), is reported to be of the order of 63%. By use of this conversion yield and the value of 57% for the recovery of gossypol from gums as dianilinogossypol, the calculated over-all yield of gossypol by this process would be of the order of 36%. This is almost equivalent to over-all yields obtained by the gossypol acetic-acid isolation. Since conversion of dianilinogossypol to gossypol is at present more difficult and costly than simple dissociation of gossypol acetic acid, the dianilinogossypol process was not examined extensively.

Pilot-Plant Processing

Based on the results of the laboratory experiments, a pilot-plant-scale process was developed for the batch-wise treatment of 40-lb. lots of gums. Essential details of the process are given in the flowsheet (Figure 1).

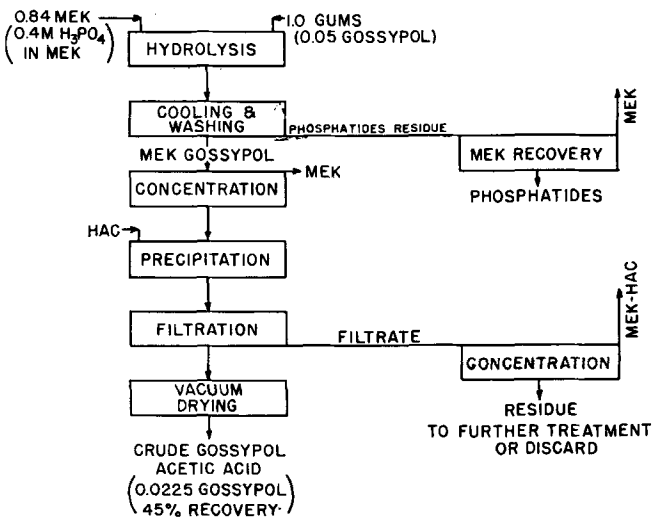

FIG. 1. Flowsheet for recovery of gossypol as crude gossypol acetic acid.

Hydrolysis. Cotton gums, 40 lb.; MEK-water azeotrope, 5 gals.; and phosphoric acid, 873 g., were mixed in a corrosion-resistant, steam-heated reaction vessel equipped with a stirrer and reflux condenser. The mixture was heated at the reflux temperature (167° F.) for 2 hrs., then cooled to 100°F.

Washing. The cooled mixture was transferred to a cone-shaped, corrosion-resistant vessel equipped with a cooling coil and stirrer and cooled to 50°F. The supernatant MEK layer was returned to the reaction vessel. The lower phosphatide-water phase was washed successively with four 1-gal. portions of MEK-water azeotrope. The MEK layer was decanted each time after the two phases had separated.

Concentration. The combined decantate and washings, 8 gals., were concentrated to 3 gals. by distillation. The distillate, MEK-water azeotrope, was reserved for subsequent reuse.

Precipitation. The MEK concentrate, 3 gals., and glacial acetic acid, 1 gal., were mixed in a corrosion-resistant vessel, stirred until crystallization began (10 min.), then allowed to stand 1 hr. at about 75–80°F.

Filtration. The supernatant MEK-acid layer was decanted, and the crude gossypol acetic-acid slurry was filtered on coarse filter paper under reduced pressure. The product was washed with hexane (0.25 gal.) or a 1:1 mixture of MEK and glacial acetic acid until the washings were colorless. The crude product can be air-dried if it is protected from light or preferably vacuum-dried for 4 hrs. at 50°C. For 40 lbs. of gums containing 5% gossypol (2 lbs. gossypol), the yield of crude gossypol acetic acid was 1.1–1.2 lbs. with a purity of 92–93% and represented about 48% recovery of gossypol.

Purification. Crude gossypol actic acid, 1.1–1.2 lbs., was dissolved in 0.75 gal. of MEK-water azeotrope with stirring at room temperature and was filtered to remove traces of phosphatides and other impurities. Glacial acetic acid, 0.25 gal., was added. The solution was stirred until crystallization began, then allowed to stand 1 hr. at 70–75°F. The product was filtered and washed as previously described, then vacuum-dried at 50°C. for 4 hrs. Yield of purified gossypol acetic acid was 0.94–0.96 lb. (87%) with a purity of 97–98%. If further purification is desired, the product can be recrystallized as outlined above. After two purifications the yield was 0.85–0.92 lb. (77%) with a purity of 98.5–99%.

Conversion to Gossypol. Purified gossypol acetic acid, 1.0 lb., was dissolved with slow stirring in 1.20 gals. of 0.2 molar sodium carbonate solution containing 0.1% sodium hydrosulfite. To insure against air oxidation a thin layer of hexane was floated on the surface of the carbonate solution before addition of the gossypol acetic acid. Sulfuric acid, 4%, was added with stirring until the evolution of carbon dioxide ceased and the solution became acidic. The hexane layer was decanted, and the precipitated gossypol was filtered under reduced pressure by using a coarse paper. It was washed free of acid with hot water and then vacuum-dried at 50°C. (16 hrs.). The yield of gossypol was quantitative, amounting to a recovery of 89.6% by weight of the gossypol acetic acid used.

Results. A summary of yield data from 12 pilot-plant experiments, utilizing the batch process, is given in Table VI. Isolation of gossypol from the gums ranged from about 40 to 53% of the gossypol present,

TABLE VI

Pilot-Plant Recovery of Gossypol Acetic Acid from Cottonseed Gums

Cottonseed gums		Hydrolysis			Crude gossypol acetic acid		Recovery of gossypol from gums[e]
Sample	Weight used	Acidic conditions	Time	Gossypol removed from gums[c]	Dry wt.	Purity[d]	
	lb.		*hr.*	*%*	*g.*	*%*	*%*
A[a]	41.2	0.2 M—oxalic	2	84.0	542	95.0	48.9
A[a]	42.6	0.2 M—oxalic	1	.....	549	93.2	47.5
B[b]	40.0	0.2 M—oxalic	2	91.4	496	93.8	49.9
B[b]	40.0	0.2 M—oxalic	2	93.3	462	92.6	45.9
B[b]	40.0	0.4 M—H_3PO_4	2	92.3	499	91.8	49.1
A[a]	40.8	0.4 M—H_3PO_4	2	94.3	606	92.0	52.9
A[a]	41.1	0.4 M—H_3PO_4	2	96.0	545	92.2	48.0

[a] Gums containing 5.0% gossypol.

[b] Gums containing 4.6% gossypol.

[c] Based on colorimetric analysis of MEK concentrate for gossypol.

[d] See Table II.

[e] Recovery $= \frac{\text{wt. gossypol acetic acid} \times \text{purity} \times 0.896}{\text{wt. gums} \times \% \text{ gossypol}}$.

with an average yield of 47%. By calculations based on the average recovery value, 47%, and the purification data recorded in Tables IV and V, the results indicate that gossypol of 98% purity can be produced with an over-all product yield of 41% and a product of 99% purity with a yield of 36%.

Pilot-plant experiments were conducted with both oxalic and phosphoric acids as hydrolyzing agents to verify laboratory results. For any contemplated large-scale use the phosphatide residue remaining after separation of gossypol could be stripped of solvent and added back to the meal. For such uses phosphoric acid has obvious advantages and would be used in preference to oxalic acid.

Continuous Processing. The batchwise process was developed to establish and study the principles involved in the separation and isolation of gossypol from gums. For large-scale operations a continuous process would be desirable. Several pilot-plant experiments were conducted in which a mixture of gums, MEK, and either phosphoric or oxalic acid was pumped through a stainless-steel, steam-jacketed heat exchanger; pressure was controlled by a spring type of back pressure valve. The experiments indicated that the hydrolysis step can be accomplished in 4–5 min. at 310°F. under a pressure of 175 psi. Yields and purities of crude gossypol acetic acid were equivalent to those obtained in the batchwise process. It was also established that the hydrolyzate from the pressure hydrolysis could be easily countercurrently washed with MEK to remove all of the hydrolyzed gossypol. These results indicated that the process can be made continuous or semi-continuous. It may be desirable to conduct the precipitation batchwise. Using data from several pilot-plant experiments, the amount of products that could be obtained were calculated and are shown in Table VII. For each 100 lbs. of gums processed (5% gossypol) some 23 lbs. of gums solids containing 4.5 lbs. of gossypol would be concentrated in the MEK phase. Assuming a 50% recovery value, about 2.25 lbs. of gossypol would be recovered as crude gossypol acetic acid. The dry solids in the washed phosphatide residue, 36 lbs., represents 65% of the original gums solids and contain 97% of the phosphatides in the gums. The original gums contain about 54% phosphatides (P × 25) on a dry basis while the dry phosphatide residue would contain some 84% phosphatides. This represents a concentration and purification of phosphatides since neutral oil, gossypol, and other constituents have been removed in the MEK phase. If the phosphatide residue is stripped only to remove MEK, the product would contain some 40% moisture and about 50% phosphatides. Thus each 100 lbs. of gums processed would yield 2.25 lbs. of crude gossypol acetic acid and 63 lbs. of a phosphatide concentrate.

TABLE VII

Distribution of Gums Constituents in Processing

Fraction and constituent	Distribution (average of two experiments)	
	Lbs. per 100 lbs. of gums processed	As % of the constituent in original gums
	lbs.	*%*
Gums		
Total solids	58.6	100.0
Gossypol	4.81	100.0
Phosphatides (P × 25)	31.2	100.0
Neutral oil	13.3	100.0
MEK concentrate		
Total solids	22.3	38.1
Gossypol	4.36	90.7
Phosphatides (P × 25)	0.22	0.7
Neutral oil	13.3	100.0
Phosphatide residue		
Total solids	36.9	63.0
Gossypol	0.3	6.5
Phosphatides (P × 25)	30.7	98.4

Summary

A process has been developed for the isolation of pure gossypol from the gums obtained by water-washings of crude hexane-extracted cottonseed oil. Gums are heated with methyl ethyl ketone containing phosphoric acid to cleave gossypol-phosphatide reaction products and are cooled to separate a ketone phase containing the gossypol from a phosphatide-water phase. After concentration by distillation, gossypol is isolated from the methyl ethyl ketone concentrate by addition of glacial acetic acid to form the acetic acid addition compound of 92–94% purity. Two recrystallizations as the acetic-acid complex produce gossypol acetic acid of 99% purity. The purified product can be dissociated by solution in dilute sodium carbonate, from which pure gossypol is recovered by acidification with mineral acid.

Yield data from pilot-plant experiments indicated that about 47% of the gossypol in gums is recovered as crude gossypol acetic acid. Depending on the degree of purification of the crude product, the over-all yield of purified gossypol from gums will range from 41% for a product of 98% purity to 36% for a gossypol of 99% purity.

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REFERENCES

1. Boatner, C. H., in "Cottonseed and Cottonseed Products," ed. by A. E. Bailey, pp. 215–219, Interscience Publishers, New York, 1948.
2. Whittecar, W. C., J. Am. Oil Chemists' Soc., *32*, 564–565 (1955).
3. Sikes, J. K., J. Am. Oil Chemists' Soc., *34*, 72–75 (1957).
4. Sikes, J. K., J. Am. Oil Chemists' Soc., *35*, 445–448 (1958).
5. Deacon, B. J., and Wamble, A. C., Oil Mill Gaz., *59*, No. 11, 45–48 (1955).
6. American Oil Chemists' Society, "Official and Tentative Methods of Analysis," Ed. 2, Rev. to 1958, Chicago, 1946–1958.

7. Pons, W. A. Jr., Stansbury, M. F., and Hoffpauir, C. L., J. Assoc. Offic. Agr. Chemists, *36*, 492–504 (1953).
8. Pons, W. A. Jr., Hoffpauir, C. L., J. Am. Oil Chemists' Soc., *35*, 93–97 (1958).
9. Pons, W. A. Jr., Murray, M. D., O'Connor, R. T., and Guthrie, J. D., J. Am. Oil Chemists' Soc., *25*, 308–313 (1948).
10. King, W. H., and Thurber, F. H., J. Am. Oil Chemists' Soc., *30*, 70–74 (1953).
11. King, W. H., and Thurber, F. H., J. Am. Oil Chemists' Soc., *33*, 169–171 (1956).

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Detergent Builder Effect on the Critical Micelle Concentration of Surface-Active Agents

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NO ENTIRELY satisfactory explanation of why electrolytes are effective in improving detergency has been advanced. Suspending action (5), particle mobility (6), adsorption (8), solubilization (12), water softening (18), and other effects fail individually or collectively to explain satisfactorily their synergistic action.

Preston (16) demonstrated that a relationship existed between critical micelle concentration (cmc) and detergency and that the latter was at a near maximum coinciding with cmc. Specifically mentioned are alkaline salts in their effect on shifting the steep slope of the detergency curve for soap to concentrations below cmc without affecting the horizontal portion of the curve. Both McBain (14) and Kolthoff (11) described the effect of electrolytes in reducing cmc of surfactant solutions. Goette (3) indicated that different salts had different effects on Preston's critical washing concentration and, though $Na_4P_2O_7$ and Na_2SO_4 affected cmc about equally, the former had much greater effect in improving detergency (reducing the critical washing concentration). He pointed out that though the sodium ion shifted the detergency curve (toward equal effectiveness at lower solution concentration) and might be predominant in reducing cmc, the alkalinity and nature of the individual salt anions also influence detergency.

It is the purpose of this paper to explore the possible effect of such builders on critical micelle concentration as this factor seems to have a major correlation with detergency.

Preliminary and Experimental Work

Since both anionic and nonionic surfactants were to be examined in this study, a method for determination of cmc was required which was applicable to both types, eliminating as possibilities those procedures dependent upon ionic character of the compound. Chosen was a dye solubilization technique (10, 11, 12, 14, 15, 17). Preliminary evaluation indicated, as others had found (17), that 1-o-tolylazo-2-naphthol (External Orange No. 4, originally Orange OT) was less soluble in these systems than dimethylaminoazobenzene and additionally that slightly better reproducibility was attainable with it.

Procedure. External D & C Orange No. 4 was purified by recrystallization (20 g. from 1,800 ml. of ethanol followed by vacuum drying at 50°C.). Calibration curves of concentration *versus* optical densities were prepared by replicated measurement at 500 mμ (maximum absorption) in a ½-in. test tube in a Spectronic 20 (Bausch and Lomb) spectrophotometer.

Dye in 25-mg. quantities was transferred to 25 × 95-mm. vials fitted with foil-lined (tin or silver, 10-mil thickness) screw caps. Stock solution of surfactant was pipetted to the vials, and distilled water was added to provide proper dilution, covering a range of concentrations. The vials were rotated 16 hrs. at 25°C. Following the rotation period, the samples were stored upright for 24 hrs. at 25°C. Three-ml. samples of the supernatant liquid were filtered through small plugs of absorbent cotton, then transferred to photometer test tubes and diluted with 3-ml. of absolute alcohol. Optical density was measured against a 1:1 ethanol-water solvent blank for zero absorbency. Additional measurements were made after further aging to insure that dye solubilities were equilibrium values. The dye solubility was then plotted *vs.* surfactant concentration, and the cmc was derived by suitable extrapolation from above and below the region where greatest change in slope occurred, as indicated in Figure 1.

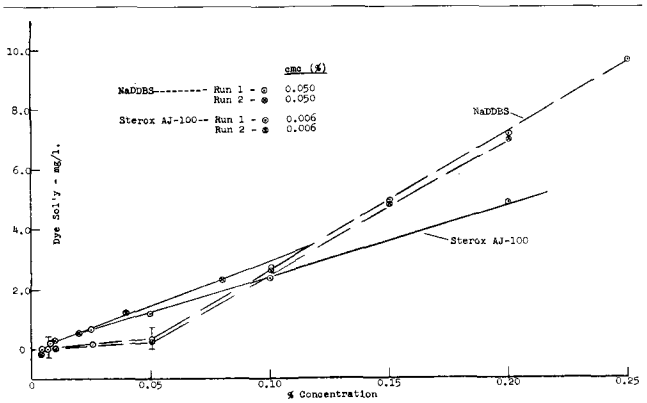

FIG. 1. Solubilization curves.

Materials Tested. The surfactants used were especially purified to remove salts or unsulfonated materials resulting from preparation. The electrolytes were chemically pure reagent materials except for the polyphosphates, which were commercial products. All were used on the anhydrous basis.

Comparison with Literature Values. Using repurified sodium laurate, the cmc values were determined by the solubilization method. The data were in good agreement with literature values (7, 17). Reproducibility was of the order of ±4.9% for Orange No.