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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 $\text{Na}_4\text{P}_2\text{O}_7$ 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 dimethyl-aminoazobenzene 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 $m\mu$ (maximum absorption) in a 1/2-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.

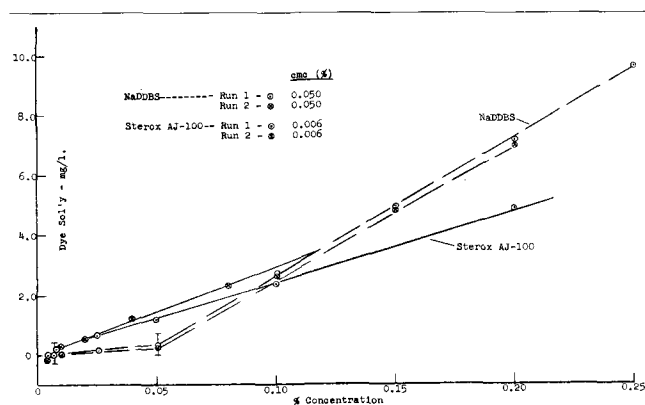


FIG. 1. Solubilization curves.

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 $\pm 4.9\%$ for Orange No.

4 and $\pm 6.2\%$ for DMAB for cmc values ($\times 10^3 M$) of 26.4 and 26.0, respectively.

The preferred solubilization procedure for dodecyl (tetraisopropyl) benzene sodium sulfonate showed good correlation between the solubilization and surface tension methods, and poorer agreement for conductivity and photometric spectral dye (2) methods. For a commercial nonionic surfactant [Sterox AJ-100, tridecyl alcohol-ethylene oxide (EO) condensate] relatively good agreement was also found between the dye solubilization and surface tension methods.

Inorganic Builder Effect

Relative Sensitivity of Actives to Builder Addition. Differences in sensitivity of various surfactants to electrolyte addition have been demonstrated (11, 12, 13, 14). As a preliminary to more extensive investigation, the effect on cmc was determined for various molar ratios of NaDDBS and a nonionic surfactant to tetrasodium pyrophosphate. Table I shows that

TABLE I
Sensitivity to Builder Addition

Surfactant	Mole ratio surfactant: Na ₄ P ₂ O ₇	cmc		% cmc reduction
		M $\times 10^3$	%	
NaDDBS.....	0	4.8	0.17
NaDDBS.....	1:1	3.46	0.12	29.0
NaDDBS.....	1:4	2.14	0.075	56.0
Tridecyl alcohol-10.14 EO....	0	0.155	0.009
Tridecyl alcohol-10.14 EO....	1:4	0.155	0.009	0

the anionic surfactant is sensitive to such addition while the nonionic is not, confirming the findings of others. Further tests of nonionic surfactants at higher EO ratios were not pursued in view of the findings of Hsiao *et al.* (9) that nonylphenol adducts of from 10 to 30 EO molar content showed the same relative decreases in cmc when measured in a NaCl solution of constant concentration.

Builder Effect on NaDDBS in Distilled Water. The influence of builders on critical concentration has received considerable attention by several investigators; most work has been done with anionic surfactants (9, 11, 14, 15). These findings may be summarized. Addition of inorganic salts to surfactants decreases the cmc and increases the solubilizing activity. Anionic surfactants are enhanced more by inorganic salts than are nonionics. The enhancement of activity by builders (inorganic salts) appeared to be a decreasing linear function of the log of cmc plotted against the log of the total concentration of ions opposite in charge to that of the micelles.

The cmc lowering is attributed to an increase in concentration of gegenions (or counter ions) in the vicinity of the micelle. This would decrease the degree of ionization of the surfactant molecule, rendering it more lipophilic and consequently enhancing micelle stability.

While cmc lowering by builders offered a potential means of screening builders as detergent adjuncts, the latter point above indicated that builder cations rather than anions were believed the controlling factor. This means that for builders compared on an equal weight percentage basis in a given formulation, sodium chloride or sulfate should be more effective than sodium pyrophosphate or tripolyphosphate since the former supply more sodium ions per unit weight than do the latter. Builder influences were investi-

gated for simple and complex inorganic salts to test the validity of these findings.

A comparison was made of the effects of various builders on dye solubilization and cmc for mixtures of 1:1 and 1:4 molar ratios of NaDDBS to builder. Differences observed stem either from the number of sodium ions (equivalents) supplied by the builder or from qualitative effects of builder anions. Table II is a condensation of the considerable volume of data developed. The data of Figure 2 indicate, for 1:1 mole ratios of various builders to active, that

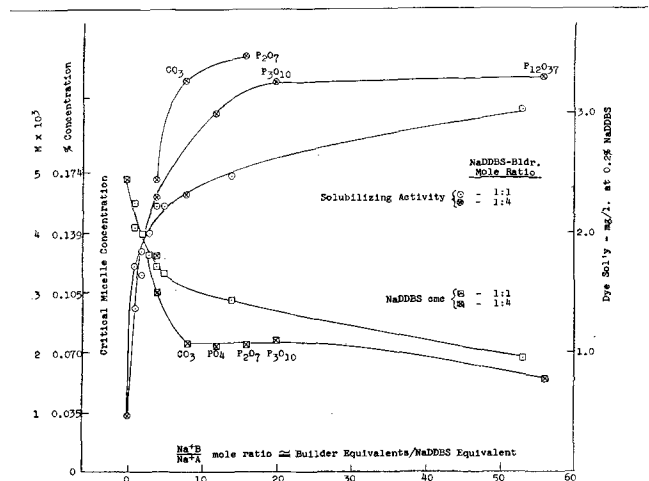


Fig. 2. Effect of builders on NaDDBS solubilizing activity and cmc.

both cmc and solubilizing activity are logarithmic functions of the number of sodium ions contributed by the builder. As the sodium or gegenion concentration is increased, solubilizing activity increases at first very rapidly, then levels off. The cmc variation is similar in nature but is of course in the opposite direction, *i.e.*, a progressively smaller decrease in cmc is observed with increasing builder equivalents. Since smooth curves were obtained, even though different anions were involved, these data strongly indicate that builders indeed influence cmc of anionic surfactant primarily through a common or sodium ion effect, confirming the findings of others (1, 15) for different compounds.

Consideration of data at 1:4 NaDDBS-builder mole ratios however shows that increasing the number of builder anions as well as sodium ions can influence the result (Figure 2) and displace points off the two main curves for 1:1 mole ratios. Points for carbonate, orthophosphate, pyrophosphate, and tripolyphosphate are considerably displaced, indicating that these anions were particularly effective. These anion influences prevent a truly quantitative treatment of builder activity based on sodium ion contribution alone. However such a treatment is given since the sodium ion contribution remains as the most important and generally applicable influence of the builders on the cmc of NaDDBS.

Equation for the Builder Sodium Ion Effect on NaDDBS. As shown above, the cmc values appeared to be logarithmically related to the number of sodium ions supplied by the various builders. Plotting cmc against

$$\log \frac{Na^+_{\text{Builder}}}{Na^+_{\text{Active}} (\text{NaDDBS})}$$

TABLE II
Effect of Builders on the cmc and Solubilizing Power of NaDDBS

Builder	Data for active-builder mole ratios of									
	1:1				1:4					
	Bldr.	cmc			Dye sol'y (mg./l.) at 0.2% active	Bldr.	cmc			Dye sol'y (mg./l.) at 0.2% active
	Conc.	M×10 ³	Red'n		Conc.	M×10 ³	Red'n			
	%	%	%	%	%	%	%	%	%	
None (NaDDBS alone).....	0	0.17	4.90	0.48 ^a	0	0.17	4.90	0.48 ^a
NaCl (chloride).....	14.3	0.16	4.50	8.2	1.38	40.2	0.13	3.63	25.9	2.30
NaOH (hydroxide).....	10.3	0.14	4.10	16.3	1.72	39.5	0.10	3.00	38.8	2.44
Na ₂ SiO ₃ (metasilicate).....	26.0	0.14	4.00	18.4	1.66	58.4	0.075	2.16	56.0	2.32
Na ₂ CO ₃ (carbonate).....	23.4	0.14	4.00	18.4	1.85	55.0	0.075	2.15	56.3	3.28
Na ₃ PO ₄ (orthophosphate).....	32.1	0.13	3.65	26.6	2.00	65.4	0.074	2.12	56.6	3.00
Na ₄ P ₂ O ₇ (pyrophosphate).....	43.4	0.12	3.46	29.4	2.22	75.5	0.075	2.14	56.4	3.48
Na ₅ P ₃ O ₁₀ (tripolyphosphate).....	51.2	0.12	3.33	33.9	2.22	80.9	0.076	2.20	55.2	3.26
Na ₁₄ P ₁₂ O ₃₇ (polyphosphate).....	78.2	0.10	2.88	41.2	2.48	93.6	0.054	1.55	72.5	3.33
Na ₅₃ P ₅₀ O ₁₅₄ (polyphosphate).....	93.7	0.066	1.90	61.2	3.03

^a Corrected for distilled water blank, all others uncorrected since dye solubility in electrolyte solutions is essentially zero.

yielded a dispersion of points about a straight line having the equation,

$$cmc = 0.00425 - 0.00156 \log (Na^+_B / Na^+_A).$$

The line of Figure 3 was obtained by least squares data-fitting.

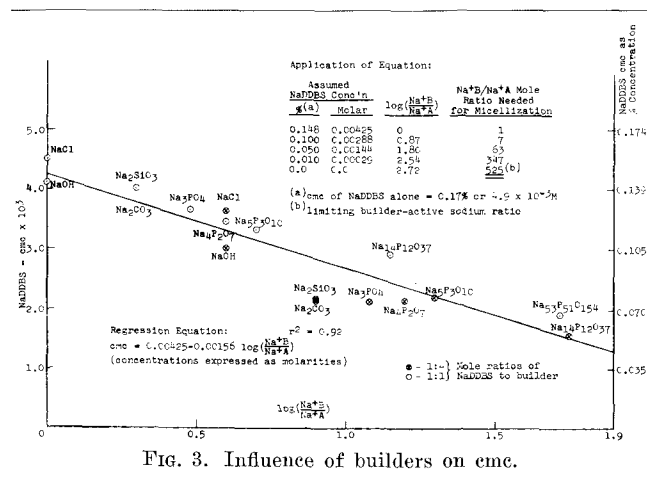


Fig. 3. Influence of builders on cmc.

This equation was set up with a builder/active component to permit calculating the ratio needed to obtain a desired cmc. For example, suppose that NaDDBS is to be formulated in a built detergent composition and it is estimated that the composition will be used by the consumer at levels of active as low as 0.10% concentration. Therefore it will be desirable to have sufficiently high builder-active ratio of the active to be micellized at 0.10% or $2.88 \times 10^{-3}M$. Substituting in the equation or from the curve it is found that:

$$\log (Na^+_B / Na^+_A) = \frac{0.00288 - 0.00425}{-0.00156} = 0.878$$

$\therefore Na^+_B / Na^+_A = 7.55 =$ builder-active sodium ion mole ratio or equivalents builder/active equivalent. Any builder desired can be used to supply the needed equivalents, e.g.:

Builder	Equiv'ts bldr./ active equiv.	Bldr. equiv. wt.	Builder-NaDDBS wt. ratio	Composition	
				Bldr.	Active
Na ₂ CO ₃	7.55	53.0	(7.55×53)/348=1.15	52.5	47.5
Na ₄ P ₂ O ₇	7.55	66.5	(7.55×66.5)/348=1.44	59.0	41.0
Na ₅ P ₃ O ₁₀	7.55	73.2	(7.55×73.2)/348=1.59	61.3	38.7
Na ₂ SO ₄	7.55	71.0	(7.55×71.0)/348=1.54	60.6	39.4

Combinations of builders may be used if, for example, it is desirable to have 30% polyphosphate in the composition for calcium sequestration. Then only the remaining amount of given builder needed may be calculated.

Another application of the builder equation is given in Figure 3. If the cmc is set at zero, the builder-active ratio calculated represents the limiting ratio, which reflects sensitivity of a given active to improvement by builder: the lower the ratio the greater the sensitivity. To estimate this limiting value for a given active, it is necessary to determine the cmc's of several builder-active combinations and to extrapolate to zero cmc from a plot of cmc vs. $\log (Na^+_B / Na^+_A)$.

When a mole ratio of 1:4 was used, the increasing number of both builder anions and cations affects results and displaces points off the two main curves for 1:1 mole ratios. This deviation from the norm in which only the sodium ion had been indicated as the effective factor may help partially to explain why the specific compounds are, in fact, superior surfactant builders.

It is believed that the use of the applied equation to permit calculation of the ratio of surfactant to builder to obtain a desired cmc value is unique to the builder technology. It offers a mathematical approach to the problem of surfactant building which may prove a valuable tool.

For good reasons, cmc values have been measured in distilled water, or water of even greater purity. However, for practical purposes, it would be desirable to measure cmc values under conditions simulating practical usage. Since one of the primary functions of builders is to protect actives against water hardness (and perhaps to prevent hardness from promoting soil redeposition during laundering), it remained to determine the influence of builders on cmc with hardness present.

Builder Effect on NaDDBS in Hard Water. Solubilizing activities were determined for Sterox AJ-100, sodium oleate, and NaDDBS in waters of various hardnesses (as ppm CaCO₃ from CaCl₂). As in the case of added builder, the nonionic Sterox AJ-100 was relatively insensitive to hardness. Sodium oleate, as expected, was uniformly reduced in solubilizing power as the water hardness was increased (Table III).

The most unusual response was obtained from NaDDBS (Figure 4), which gave erratic curves in graphs of mg./l. dye solubility vs. NaDDBS concentration at various hardnesses. (These data did not allow extrapolation to the cmc.) It is apparent that

TABLE III
Solubilizing Activity of Sodium Oleate in Solutions of Various Hardnesses

% Concentration	Mg./l. dye sol'y at hardnesses		
	0 ppm ^a	50 ppm ^a	150 ppm ^a
0.10.....	7.22	5.00	1.09
0.08.....	5.11	3.22	0.73
0.06.....	3.11	1.78	0.44
0.04.....	1.58	0.67	0.13
0.02.....	0.89	0.40	0.11
0.014.....	0.56	0.22
0.01.....	0.20	0.02
0.006.....	0.42	0.11

^a As ppm CaCO₃ from CaCl₂

addition of hardness to NaDDBS first increases solubilization (though the response varies with Na DDBS concentration), then at extreme hardness levels (1,000 ppm) solubilizing activity is reduced almost to zero. Figure 5 shows that the response depends on whether

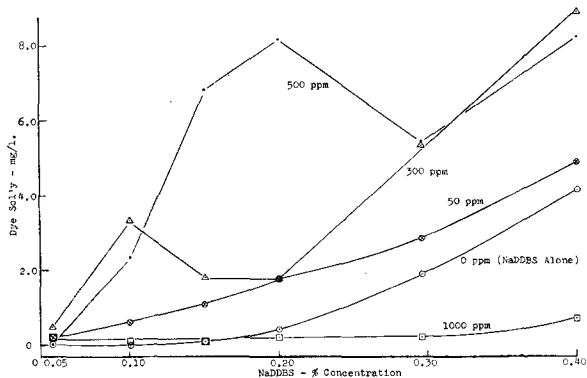


FIG. 4. Solubilizing activity of NaDDBS in solutions of various hardnesses (ppm CaCO₃ from CaCl₂).

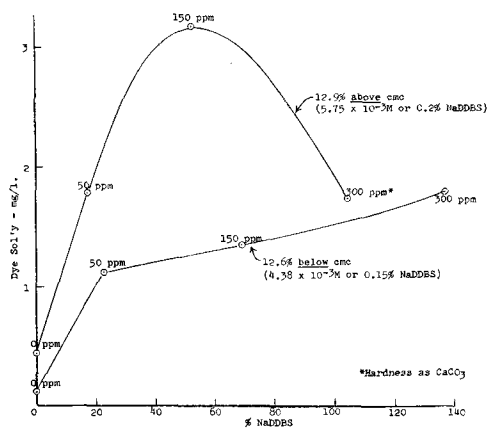


FIG. 5. Effect of hardness from CaCl₂ on the solubilizing activity of NaDDBS.

the NaDDBS concentration is above or below the cmc as follows: above the cmc, addition of hardness enhances solubilization by NaDDBS up to the point of half conversion to the calcium salt. Greatest solubilizing activity is obtained for the mixed sodium, calcium salt of NaDDBS. Continued addition of hardness results in a lowering of solubilization. Extrapolation to complete conversion to the calcium salt, in an atmosphere of excess calcium ion, would result in precipitation and loss of solubilizing activity. At an NaDDBS concentration 12.6% below the cmc, addition of calcium ion results in an increase in solubilization to a

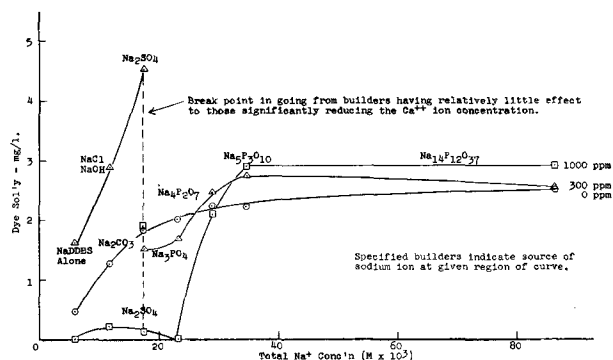


FIG. 6. Sodium ion effect at various hardnesses (equal bldr. anion conc'n).

point well beyond the apparent conversion to the full calcium DDBS. No maximum in solubilization is apparent in the curve, but if sufficient hardness in the form of calcium were added, the curve would drop to zero solubilization. An explanation for the differences in these curves may be sought in the equilibria attained in complex systems of sodium and calcium ions and in partially soluble sodium-calcium or calcium DDBS salts.

However whether tests were made above or below cmc had considerable effect on solubilization, and Figure 5 shows that the mixed sodium, calcium salt of NaDDBS has a maximum solubilizing power as compared with sodium compound. This conforms to improvement in lather, detergency, and other surfactant properties when conversion to the partial calcium, magnesium, or other polyvalent cation salt is accomplished (4).

Measurement of solubilization by NaDDBS combined with various builders (each $5.75 \times 10^{-3}M$), and subsequent graphing against the sodium ion concentration, did not yield smooth curves for hard-water systems as was obtained for distilled water measurements (Figure 6). Therefore builder effects in hard water systems are not simply related to the sodium ions contributed but depend on other factors as well:

- the effect of hardness alone on the surfactancy of the active: effectiveness in promoting micellization increases with the valence of the metallic ion;
- the influence of builder on the calcium salt of the active;
- the calcium sequestering or precipitating ability of the builder;
- the quantity of hardness present relative to active and builder components.

The results for the polyphosphates are similar in 0, 300, and 1,000 ppm waters. This is expected since, assuming that each mole of polyphosphate sequesters at least two moles of calcium, there was sufficient builder to sequester 1,000 ppm CaCO₃:

NaDDBS conc'n:	$5.75 \times 10^{-3}M$ (constant) or 0.2%
Builder conc'n:	$5.75 \times 10^{-3}M$ (constant)
Hardness or Ca ⁺⁺ conc'n:	$\frac{300 \text{ ppm } 1,000 \text{ ppm}}{3 \times 10^{-3}M \ 10 \times 10^{-3}M}$

Figure 6 shows, for 300 ppm water, that as simple builders, such as sodium chloride, hydroxide, and sulfate, are added to NaDDBS, solubilization increases rapidly. These salts are relatively weak as precipitants for calcium ion and have no calcium-sequestering activity. The solubilities of calcium chloride,

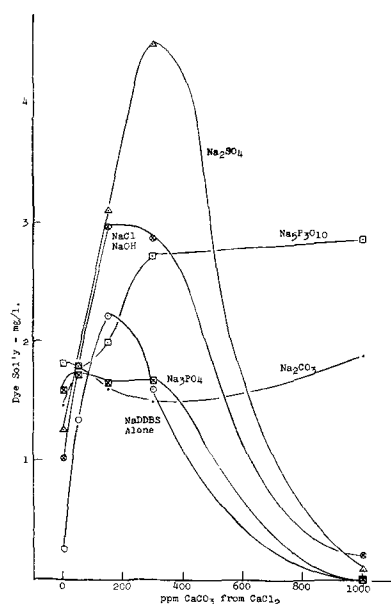


FIG. 7. Effect of hardness on solubilizing activity of NaDDBS-builder combinations (each at $5.75 \times 10^{-3}M$ —equal anion conc.).

hydroxide, and sulfate are well above the quantities actually present in solution so both the calcium and sodium ions promote micellization and increase solubilizing activity. Greatest improvement in 300 ppm water was obtained with sodium sulfate, which contributes two equivalents per mole. Use of sodium carbonate results in virtually all the calcium being precipitated as the carbonate, assuming that $CaCO_3$ is less soluble than Ca dodecylbenzene sulfonate. Since the sodium ion concentration is unchanged and the calcium ion is removed, solubilization remains at about the same level as was found for Na_2CO_3 in distilled water. The same result was obtained with sodium orthophosphate for similar reasons.

It is evident from the data that, for nonsequestering or nonprecipitating builders in 1,000 ppm water, there is present more than three times the number of calcium ions needed to convert the NaDDBS to the calcium salt. (One calcium ion reacts with two dodecylbenzene sulfonate ions.) This excess of calcium ions precipitated the NaDDBS and accounts for the poor solubilization by the NaCl-, NaOH-, and Na_2SO_4 -NaDDBS combinations in 1,000 ppm water. The results for carbonate and polyphosphate are similar at 1,000 ppm to those obtained at 300 ppm water hardness since enough builder was present to precipitate or sequester the $CaCO_3$ ($10 \times 10^{-3}M Ca^{++}$). The sodium orthophosphate behaved anomalously, yielding zero solubilization even though enough was present to precipitate the hardness.

As discussed above, unless the hardness level is extreme, sodium sulfate appears superior to, while sodium chloride and hydroxide are at least equal to the polyphosphates in promoting solubilization by NaDDBS. Figure 7, in which solubilizing activity is plotted as a function of water hardness for the various builders, supports this conclusion, which agrees with distilled-water results.

The main conclusion to be drawn from this work is that cmc or solubilization measurements and common ion effect fail to provide complete explanations for the effectiveness of builder compounds: other explanations must be sought.

Summary

In distilled water systems:

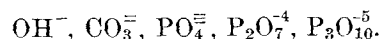
NaDDBS (sodium dodecylbenzene sulfonate) was shown to be more sensitive to builder effects on solubilization and cmc than nonionic Sterox AJ-100, suggesting the greater sensitivity of anionics to builder electrolyte addition than nonionics.

Addition of builder to a surfactant enhances activity by increasing solubilization while lowering the cmc. The enhancement varies logarithmically, at first rapidly, then progressively slower with the builder sodium ion contribution.

Builders promote the formation of micelles largely through a sodium or common ion effect. This effect for NaDDBS is described by the derived equation:

$$cmc = 0.00425 - 0.00156 \log \left(\frac{Na^+_{Builder}}{Na^+_{Active}} \right), \text{ (moles/l.)}$$

Builder anions also influence NaDDBS surfactancy (cmc and solubilization). Most effective anions for NaDDBS improvement were



In hard water systems:

Solubilization measurements again reflected the sensitivity of anionics and relative insensitivity of nonionics to water hardness. NaDDBS has a complex response to water hardness (Ca^{++} ion), increasing in activity to a maximum at about half molar conversion to the calcium salt, then reducing to zero in severe hardness (as the surfactant activity is reduced).

Builders forming simple soluble salts with calcium at use concentrations enhance solubilization in waters of moderate hardness (0–300 ppm $CaCO_3$). In severe hardness (1,000 ppm) NaDDBS solubilization was sharply depressed with these salts present.

Calcium precipitating (except orthophosphate) and sequestering builders, in removing the hardness-producing ions, yielded solubilization values similar to those of the NaDDBS-builder combinations in distilled water.

The results for the various actives tested show that, in studies of builder effects, each active type must be treated individually since each has a characteristic response to hardness. Consequently no simple mathematical treatment is possible for general behavior.

Solubilization and cmc measurement and common ion effect fail to account for the demonstrated superiority of certain electrolytes whose anions also influence surfactant action, and other explanations of their mechanism must be sought.

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Kinetic Study of Gossypol Fixation in Cottonseed Oil¹

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THE DEVELOPMENT of red alkali-fast color bodies on the storage of certain crude cottonseed oils has been attributed to gossypol present in the oil (1, 2, 3). When gossypol is removed from the oil immediately on its removal from the seed, either by processing (1, 4) or by chemical treatment (5), color fixation does not occur on storage of the oil. While the evidence from the investigations cited is that reactions of gossypol with constituents of cottonseed oil are responsible for the development of color bodies in the oil, little is known of the chemistry involved.

Recent studies (6) show that fixation of gossypol occurs when gossypol is added to purified triglycerides, ethyl acetate, and crude cottonseed oil. An ester exchange reaction of gossypol and the glyceride esters of the oil has been suggested as a possible first step in a sequence of reactions that lead to the production of alkali-fast color bodies (7) although there is little evidence to support the suggestion.

The investigation reported herewith, which is concerned with the kinetics of the initial reaction in the development of orange and red alkali-fast color bodies in refined and bleached cottonseed oil when gossypol is added, was initiated in the hope that more information on the chemistry of color fixation might be obtained.

Experimental

Stock solutions containing 4 g./l. of gossypol were prepared by dissolving purified gossypol in refined, bleached, and deodorized cottonseed oil at 25°C. They were held at -18°C. until used. Aliquots of the stock solutions (*ca.* 10 ml.) were sealed in glass vials under nitrogen and brought up to temperatures for storage in the dark at 40°, 60°, and 80°C. The vials were removed from each storage at predetermined intervals. A portion of each vial was used for the determination of absorbance at 365 m μ with a Beckman Model B spectrophotometer, using cyclohexane as the dilution and reference solvent. Another portion was dissolved in 30 ml. of peroxide-free diethyl ether, and the unreacted gossypol was removed from solution by four successive extractions with 25-ml. portions of 4% aqueous sodium carbonate, which contained 0.1% sodium hydrosulfite as an antioxidant. The oil-ether solution was washed with distilled water, then dried over anhydrous sodium sulfate. The ether was removed by gently heating under a stream of nitrogen. The absorbance of the gossypol-free oil was determined at 365 m μ , as described above. The same procedure

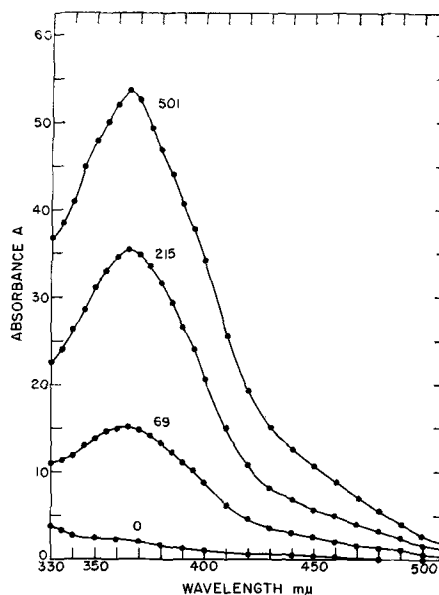


FIG. 1. Absorption spectra of carbonate insoluble gossypol reaction product for reaction times varying from 0 to 501 hrs. at 60°C.

was applied to the original stock solution to determine the initial absorbances at the time of preparing the vials for storage (zero time).

The absorptivity of gossypol in cottonseed oil was determined experimentally to be 37.5 at 365 m μ ; the concentration of gossypol was expressed as g./l. of oil. This factor was used in all calculations. The initial concentration of gossypol in the stock solution (C_0), g./l., was determined from the relationship:

$$C_0 = (A_1 - A_2)/37.5,$$

where A_1 and A_2 are the absorbances of the stock solution before and after alkali extraction. The concentration of the unreacted gossypol in the stored aliquots (C_1) was calculated similarly:

$$C_1 = (A_3 - A_4)/37.5,$$

where A_3 and A_4 are the absorbances of the stored oil before and after alkali extraction. The concentration of the reaction product in the oil is $C_0 - C_1$.

The absorptivity (a) of the reaction product of gossypol was calculated in terms of gossypol equivalents by use of the expression:

$$a = (A_4 - A_2)/(b \times c),$$

where b is the cell length in cm. and c the concentration of the reacted gossypol in g./l. of oil ($C_0 - C_1$).

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