

TABLE II
Effect of Oils Containing Cyclopropene Fatty Acids on Gossypol Absorption and Toxicity

	% of administered gossypol which appeared in the feces				Toxicity LD-50 (g/kg body wt)
	Doses of gossypol given (g/kg body wt)				
	1.50	2.00	2.50	3.50	
Gossypol administered:					
In corn oil.....	4.27	6.56	9.67	9.88	2.57 ± 0.25
In cottonseed oil.....	3.20	4.10	7.30	4.90	2.27 ± 0.21
In corn oil with <i>S. foetida</i> oil (20 mg/dose).....	1.00	3.83	5.33	4.71	2.10 ± 0.21

was given to each of ten rats. None of these animals died.

Although there was a trend toward greater toxicity when gossypol was administered in cottonseed oil or in corn oil with *S. foetida* oil added, as compared to corn oil alone, the differences were relatively small, and in the case of corn oil and cottonseed oil the difference was not statistically significant. The difference between the toxicity of gossypol in corn oil and gossypol in corn oil with *Sterculia foetida* oil added was statistically significant at the 5% level of probability.

Analysis of the feces for total gossypol (Table II) showed that less gossypol remained in the feces when the test dose was administered in cottonseed oil or *S. foetida* oil. A possible explanation of this finding is that the cyclopropene fatty acids may increase the absorption of gossypol.

Acknowledgments

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A Kinetic Approach to Detergent Synergism

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Abstract

It is shown that kinetic theory can be applied to the removal of a heterogeneous soil by detergent solutions. By assuming first-order kinetics, constant permitting rate comparisons were calculated for the removal of baked P³² milk films from stainless steel test discs by NaOH, a nonionic surfactant, and combinations of the two. Values for E* were obtained from Arrhenius plots. The data indicate an abrupt change in the activity of the nonionic detergent occurred as it passed through the cloud point region. Synergism was demonstrated in solutions of NaOH-surfactant maintained below cloud point temps; at higher temps, this synergism was apparently lost. Possible explanations of synergism and detergency as affected by the cloud point phenomenon are discussed.

Introduction

THERE ARE PROBABLY a variety of forces involved in the binding of soils by substrates, and in most cases soil removal is reduced to the problem of decreasing these forces, and supplying sufficient ex-

cess energy to overcome an energy barrier and free the soil. The main function of the detergent is to minimize the binding forces, for lack of a more specific term, and to reduce the energy level of desorbed soil particles and thus discourage their redeposition.

The soil desorption undoubtedly involves a variety and series of steps and reactions, some chemical and others largely physical. Because the desorption step demands that the dissolved detergent molecule (or ion, or aggregate) contact the deposited soil or the substrate at the deposition site, the overall effect should be somewhat analogous to a bimolecular reaction which can, after collision, proceed in various directions to a variety of end products. Although there are theoretical objections to treating an undissolved and heterogeneous soil deposit as if it were a single molecular species, it has been demonstrated (1) that the removal of such films can be considered as a process first order with respect to soil (S) and first order with respect to detergent (D):

$$-dS/dt = K(D)(S)$$

It would be ideal to eliminate the effect of soil concentration on this expression by constructing linear plots of (S) as a function of t for various detergent concentrations. For a given value of (S), the tan-

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TABLE I
Statistical Derivation of K Values for Detergent Removal of Milk Soils

Solution composition		Temp C	Best-fit line ($y=bx+ax$)		N	r	K(D) $\times 10^3$	K $\times 10^2$
(NaOH) $\times 10^2$	(Surfactant) $\times 10^3$		a	b, $\times 10^3$				
5	0	51.7	2.09	6.50	120	.940	2.81	5.62
5	0	60.0	2.05	8.10	279	.978	3.52	7.04
5	0	68.3	2.04	9.30	160	.973	4.25	8.50
5	0	76.7	1.99	13.6	238	.965	5.90	11.8
0	0.2	37.8 ^a	1.96	1.09	118	.924	.473	237.0
0	0.2	43.3 ^a	1.94	1.11	120	.922	.482	241.0
0	0.2	51.7 ^a	1.96	1.80	239	.936	.782	391.0
0	0.2	60.0 ^b	1.93	1.34	200	.965	.582	291.0
0	0.2	68.3 ^b	1.91	1.53	200	.922	.664	332.0
0	0.2	76.7 ^b	1.90	2.07	120	.948	.899	499.0
0	0.6	37.8 ^a	1.98	1.10	119	.972	.478	79.6
0	0.6	43.3 ^a	1.97	1.65	120	.937	.716	119.0
0	0.6	51.7 ^a	1.97	2.38	120	.987	1.02	171.0
0	0.6	60.0 ^b	1.95	1.41	120	.963	.612	102.0
0	0.6	68.3 ^b	1.95	1.73	120	.954	.751	125.0
0	0.6	76.7 ^b	1.95	2.42	120	.946	1.05	175.0
5	0.6	37.8 ^a	1.98	1.13	120	.951	.491	.982
5	0.6	43.3 ^a	1.95	2.06	120	.944	.894	1.79
5	0.6	51.7 ^a	2.04	7.44	118	.940	3.23	6.46
5	0.6	60.0 ^b	1.97	6.93	160	.935	3.01	6.02
5	0.6	68.3 ^b	2.02	11.9	119	.953	5.17	10.3
5	0.6	76.7 ^b	2.00	14.8	120	.926	6.43	12.9
5	1.8	37.8 ^a	2.00	2.34	118	.956	1.02	2.40
5	1.8	43.3 ^a	2.07	7.05	117	.942	3.06	6.12
5	1.8	51.7 ^a	2.08	9.76	120	.950	4.24	8.48
5	1.8	60.0 ^b	2.00	10.0	120	.962	4.35	8.61
5	1.8	68.3 ^b	2.04	13.7	120	.937	5.95	11.9
5	1.8	76.7 ^b	2.03	18.0	120	.942	7.82	15.6

^a Below cloud point
^b Above cloud point

gents of such curves would equal K (D). Unfortunately, values for (S) at given values of t vary over a range and do not yield single precise points. Even when identical soiled test discs are subjected to the same cleaning treatments, the amount of soil removed shows some variation from disc to disc. Consequently, it would be quite difficult to determine the actual position of the curve at a given value of t. But because this is a repetitive operation, it should be possible to construct a satisfactory mathematical model by assuming first order kinetics, and calculating best-fit lines for semilog plots. The highly significant coefficients of correlation, evidencing valid predictability, would seem ample justification for using this approach.

Experimental Methods

Preparation of Soil Films. Sufficient (one to two drops) P³² phosphate solution was added to 100 ml of homogenized pasteurized milk to give 8,000 to 20,000 counts/min (cpm)/ml. A steam manifold arrangement was used to dry 0.5 ml aliquots of this labeled milk on stainless steel test discs as previously reported (2). The resulting film was a reproducible heterogeneous soil containing fat, protein, and mineral deposits.

Soil Removal. Soiled test discs were fastened, 40 at a time (2), to a supporting strip that was then inserted in a 4 ft length of 1½ in. glass pipe. Solutions of detergent chemicals in distilled water were circulated through the test area under closely con-

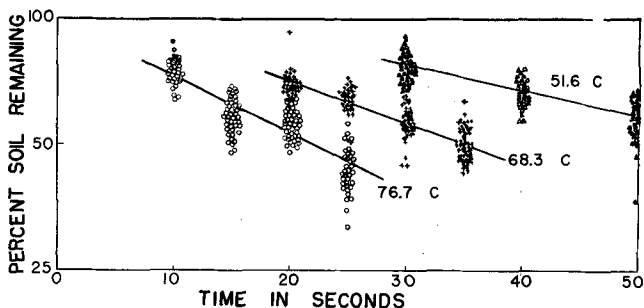


FIG. 1. Removal of a heterogeneous soil from stainless steel by .05 M NaOH, as a function of time.

trolled conditions of time, turbulence, and air content (2,3,4). To avoid entrained air, the line returning solution to the reservoir was extended to discharge below the solution surface. Large diameter lever-actuated valves at either end of the test section permitted this to be drained promptly and with minimum turbulence at the end of each run.

Measurement of Soil Removal. Radioactivities were determined with a thin-window (1.4 mg/cm²) Geiger tube in a Tracerlab SC-9E shielded manual sample changer. Counts were recorded on a Tracerlab SC-1000 scaler. All discs were counted for one min periods. Percent soil removal was taken as

$$100 \times \frac{(\text{net cpm, soiled disc}) - (\text{net cpm, cleaned disc})}{\text{net cpm, soiled disc}}$$

It has been demonstrated (5) that this correlates quite well with the actual wt of soil removed. These counting rates are sufficiently low that coincidence losses are negligible. The greatest errors would have been expected in the low-count discs, and in these the ratio of total counting rate to background counting rate was never less than 200. Accordingly, the probable error (6) for these lower count discs is of the order of 1.5% and less for the majority of samples which possessed higher counts.

Detergent Chemicals. A. R. sodium hydroxide and Igepal CO-630 (Antara Chemical Co., New York) were used in these studies. The surfactant, obtained as 100% active ingredient, is a nonylphenoxypoly(ethyleneoxy) ethanol. This nonionic liquid surfactant is widely used for detergency, emulsification, and wetting. It has a critical micelle concentration (cmc) of approximately .0001 M. All detergent solutions were made up in distilled water, and protected from air by covering the reservoir with plastic sheeting.

Results and Discussion

Figure 1 shows semi-log plots of the removal of soil as a function of time for 0.05 M NaOH at several temps. The best-fit lines were calculated by the method of least squares. The coefficients of correlation are shown in Table I; each is highly significant. Values for K were calculated from the relationship $K = \text{slope}/2.303 (D)$. Values so derived for the surfactant appear to be considerably too large. Close observations indicated that NaOH was probably slightly more efficient than the surfactant at removing this type of soil. While the K(D) values are comparable, the values of K for .0006 M surfactant are approximately ½ those for .0002 M surfactant. This indicates that even though one series has three times the concentration of the other, the concentration of active surfactant is of the same order in both cases. This anomalous behavior is very probably due to the micellar phenomenon, or to the fact that even at the lower concentration, sufficient surfactant is available to saturate these surfaces.

Examination of the data in the K(D) and K columns of Table I indicates that Arrhenius plots for these data could be compared only if they were based on log K(D) rather than log K. Accordingly, this procedure was followed. Lines from either method would exhibit the same slope, so this would have no effect on subsequent calculation of activation energies.

Detergent blends have long been advocated, in the belief that a synergism or complementary interaction makes such a blend more effective than the simple sum of their individual efficiencies. Figure 3 shows plots of the rate of soil removal as a function of temp

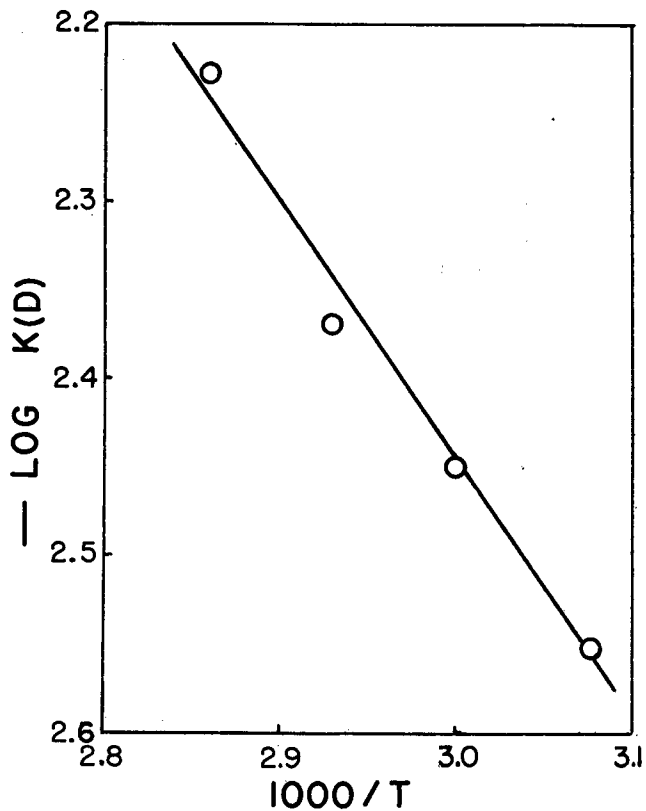


FIG. 2. Removal of a heterogeneous soil from stainless steel by .05 M NaOH.

for 0.05 M sodium hydroxide solutions containing .0006 and .0018 M/L, respectively, of Antara CO-630 nonionic surfactant. The discs were subjected to the same conditions as those of the above experiments. At least 118 test discs were run at 37.7, 43.3, 51.6, 59.9, 68.3, and 76.7C at each of three periods of time for each concentration. The statistical results are summarized in Table I. Both sets of data show scatter,

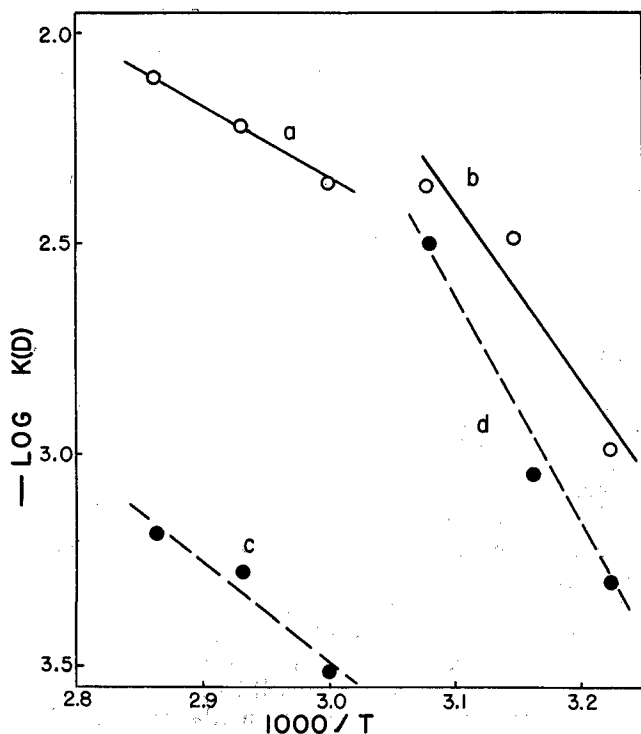


FIG. 3. Removal of a heterogeneous soil from stainless steel by NaOH plus a nonionic surfactant. a and b: (OH⁻) = .05 M, (surfactant) = .0018 M; c and d: (OH⁻) = .05 M, (surfactant) = .0006 M; b and d are below cloud point.

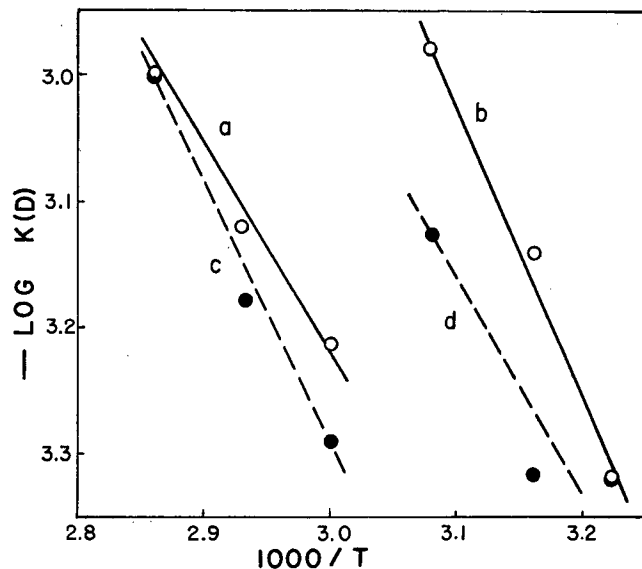


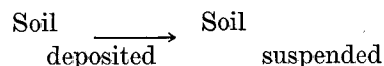
FIG. 4. Removal of a heterogeneous soil from stainless steel by a nonionic surfactant. a and b: (surfactant) = .0006 M; c and d: (surfactant) = .0002 M; b and d are below cloud point, a and c are above cloud point.

and in each instance, the scatter is maximal in the vicinity of 50–60C, which under these conditions is the cloud point region of the surfactant.

Figure 4 shows results for test discs cleaned with solutions .0002 and .0006 M in surfactant, respectively. Note the change in ordinate scale, to magnify any discontinuity. Again, both sets of data show max scatter at the cloud point. Close inspection indicates that the data in each of the experimental series shown in Figures 3 and 4 would be best satisfied with two straight lines that exhibit a sharp discontinuity at the cloud point.

Study of Figure 4 indicates that the higher surfactant concentrations exhibit less of a decrease in rate as a result of the cloud point phenomenon. Evidently some of the surfactant is rendered less active at the cloud point, and in the more dilute solution the amount of surfactant remaining active is comparatively small. At higher surfactant concentration, the demands of the cloud point phenomenon can be realized without too great a drain on surfactant activity.

From Table II, it can be seen that the values obtained for the energy of activation (E*) for the reaction



averages about 8–9 kcal when the detergent is NaOH or surfactant. Combinations of NaOH and surfactant achieve much higher values (20–27 kcal) when the solution is below cloud point temp. Above the cloud point temp, the surfactant is rendered largely inactive, and E* returns to values of 8–9 kcal.

TABLE II
Analysis of Arrhenius Plots

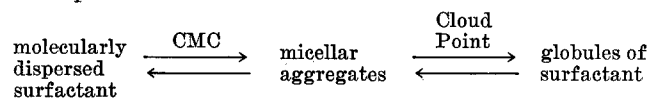
Solution composition		Best-fit line (log K(D) = a+b/T)		E*
(NaOH) ×10 ²	(Surfactant) ×10 ³	a	-b	
0	0.2 ^a	1.969	1655	7550
0	0.2 ^b	2.955	2084	9500
0	0.6 ^a	4.378	2388	11000
0	0.6 ^b	1.690	1636	7500
5	0	1.847	1431	6500
5	0.6 ^a	16.00	6006	25500
5	0.6 ^b	3.442	2311	10600
5	1.8 ^a	10.94	4302	19700
5	1.8 ^b	2.991	1782	8200

^a Below cloud point
^b Above cloud point

Several explanations could be offered for the synergism exhibited by NaOH and surfactant in solutions maintained below the cloud point. These include lowering of the surface tension, so permitting the solution to make closer contact with the soil, and the probability that hydroxide ion and surfactant remove various soil fractions at different rates. Harris and Satanek (10) found that surfactants were more effective in removing fatty soils than protein deposits. It is probable that the surfactant and hydroxide ion alternate at being the more effective detergent at any one site of the deposit, depending on the nature of the soil exposed to the solution.

The apparently anomalous behavior of the surfactant with relation to cloud point might be explained if the active form consisted of micelles distributed through the continuous phase. Ionic surfactants form micelles when the energy released by aggregation of the hydrophobic hydrocarbon chains balances the electrical repulsion of the ionic groups and the decrease in entropy resulting from the more highly organized state of the detergent. Nonionic surfactants generally have a lower cmc, probably because the energy from aggregation must balance only the entropy decrease. The resulting uncharged micelles could form loose clumps, separated by a network of water bound to the exposed hydrophilic groups. Reich (7) indicated that nonionic micelles were spherical, and the individual hydrocarbon chains were tightly coiled within the micelle. At cloud point temps, the increased thermal agitation of the molecules may be sufficient to break the individual micelles within a clump, and form free globules of surfactant that account for the turbidity. Surfactant confined to the interior of these globules would contribute little or nothing to detergent. This would explain the following observations:

a) the detergent efficiency of the nonionic decreases as the solution transcends the cloud point temp, b) the magnitude of this decrease is lower for more concentrated solutions, c) very dilute solutions do not exhibit the cloud point phenomenon (8), d) the temp of the cloud point varies inversely with surfactant concentrations (8), e) cloud points are exhibited only by nonionics—ionic surfactants produce micelles that would resist clumping. Cloud formation, then might be represented as



This would explain not only the results obtained in this study, but the observations of Ginn et al. (9) that solubilization of a fatty soil by a nonionic surfactant was maximal at cloud point temps, and decreased at higher temps.

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Study of Kettle Wax in the Sodium Palmitate-Water-Electrolyte System at 90C

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Abstract

An X-ray diffraction study has been carried out on kettle wax occurring at 90C for the ternary system sodium palmitate-water-sodium chloride.

It was found that kettle wax is not a simple phase, according to Gibb's phase rule, but a mixture of curd, neat and lye.

Introduction

A GREAT DEAL of the work carried out by McBain and coworkers (1,2,3) concerns the study of the phases present in the ternary systems soap-water-electrolyte at high temp. Several experimental techniques were employed including visual observation, thermal analysis and vapor pressure measurements. The existence of kettle wax amongst the phases identified was noted only when electrolyte was present, the other phases (curd, neat soap, middle soap) being also present in the binary soap-water systems.

The structure of all the liquid-crystalline phases existing in the soap-water systems has been thoroughly investigated in Strasbourg recently (4,5). We describe here very briefly the structure of middle and

neat soap, which are the most important phases occurring in soap-water systems. Middle soap is formed by a set of indefinitely long cylinders, arranged in a regular two-dimensional hexagonal array, and separated from one another by water. The polar groups of the soap molecules lie at the surface of these cylinders and the hydrocarbon chains are in a liquid state filling the interior of the cylinders. The neat soap consists of a set of plane parallel equidistant sheets, each formed of a double layer of soap molecules, and separated from each other by a layer of water. The hydrocarbon chains are in the "liquid" state and the polar groups lie at the surface of the sheets.

As an extension to this work it was decided to complete these results by determining the structure of kettle wax.

To this end, a study was undertaken of both the sodium palmitate-water-sodium chloride and sodium laurate-water-sodium chloride systems at 90C. Only the results of the first system will be presented in this note, the two systems being very similar to each other.

Attention was not paid as to an accurate definition of the phase diagram boundaries nor as to the structure of phases other than kettle wax.

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