Azorlosa and Martinelli (40,47), who worked with cellulosic and noncellulosic fibers, suggest that CMC and PVP might be blended to advantage when white-ness retention of cotton—synthetic fiber blends is the objective. Table 3 summarizes data on the efficiency of PVP for protecting nylon, Dacron*, Orlon*, and Dynel** when washed with an alkaline-built anionic in the presence of a heavy soil load, Aquablak B.

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Correlation of Detergency with Physicochemical Factors

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IN 1949, Foster D. Snell suggested that eventually it would be possible to calculate the soil-removing efficiency of surfactants for specific, soil-substrate, detergent applications by a formula whose parameters were selected physicochemical factors of the detergency mechanism (1). He visualized a hypothetical function (1) like this:

$$\text{Detergency} = 0.14\ X + 0.61\ Y + 0.21\ Z + 0.32\ W$$

In which,   X = wetting power
               Y = dispersing power
               Z = micellar solubilization
               W = contact angle

The units of these variables were not defined. This prediction, still unfulfilled, emphasized the complexity of detergency and implied the difficulty of its correlation with a single factor or action. Both points are demonstrated by the changing regard for Preston's well-known relationship (2) that the detergency of an ionic surfactant is proportional to its long-chain ion concentration. The relationship is probably more recognizable in its corollary form that maximum detergency occurs at or very near the critical micelle concentration (CMC). The unqualified validity of this concept, which was developed in a study of laundry detergency, has been seriously questioned of late. It has been shown that in hard surface detergency, maximum soil removal is attained at concen-trations considerably greater than the CMC (3,4,5). Preston's experiments were influenced by the cotton fabric substrate he used. In addition it is reasonable to assume that his launderometer data, while simulating practical laundering, was dependent to an appreciable degree on mechanical action, another variable of the detergency mechanism. It seems probable, therefore, that the higher surfactant concentrations necessary for attaining maximum hard surface detergency are due in part to the absence of such vigorous mechanical agitation.

Excellent reviews of the extensive field of detergency correlation are available, from the surveys of the older work by McBain (6) and by Fall (7) which include references to the almost forgotten factors of gold number, carbon number and dye number, to the recent treatise of Schwartz and his co-workers (8). It is safe to say that in common with Preston's relationship the principal characteristics of the proposed correlations is their limited applicability.

I hope the preceding remarks concerning some of the problems of detergency correlation will serve as a background for the description of the scope and status of its investigation at the U. S. Army Coating and Chemical Laboratory.

Our work on this subject has been in the fields of both applied and basic research. In applied research we have indicated the presence of detergency correlation in commercial soak alkaline cleaners of improved

TABLE I
Surfactants in Applied Research

Anionic:
   sodium dodecyl sulphate (USP grade)......................................SDS
   sodium keryl (C_{10}-C_{20} straight chain alkyl) benzene
     sulphonate, commercial, 40% active.....................................SKBS
   sodium oleate soap (purified grade)..Na oleate
Nonionic:
   ethylene oxide adducts of nonyl phenol—
     15 mole ratio adduct...NPPGE
     30 mole ratio adduct...NPTGE
     50 mole ratio adduct...NP50E
     100 mole ratio adduct...NP100E
   ethylene oxide adducts of
   2,4,7,9-tetramethyl-5-decyne-4,7-diol—
     10 mole ratio adduct...D-10
     15 mole ratio adduct...D-15
     30 mole ratio adduct...D-30
   polyoxyethylene-(9–10) of octylphenol.................................OPE9-10

TABLE II
Detergency vs. HLB

Nonionic		Anionic		Surfactant mixture		Mineral oil	Detergency asphalt (min for removal)
Symbol	HLB	Symbol	HLB	Mol %— nonionic	Net HLB		
D-10	13.21			27.6	27.45	good	5,6
OPE9-10	13.40			28.9	27.54	good	8
D-15	14.90	SDS	40.00	22.3	28.24	good	7,9
D-30	17.08			14.1	29.26	good	6,7
NPTGE	17.20			14.2	29.32	good	19
NP100E	19.05			5.2	30.19	good	21
OPE9-10	13.40			36.3	12.50	good	12
D-30	17.08	SKBS	11.70	18.7	14.22	good	9,9
NPTGE	17.20			18.8	14.28	good	16
NP100E	19.05			7.2	15.14	unsatisfactory	21
OPE9-10	13.40			30.1	15.80	good	21
NPPGE	15.00			23.4	16.60	good	10,13
D-30	17.08	Na Oleate	18.00	14.8	17.57	good	10,10
NPTGE	17.20			14.8	17.63	good	7,9
NP50E	18.18			10.0	18.09	unsatisfactory	10
NP100E	19.05			5.5	18.49	unsatisfactory	15,18

NOTES: All cleaners contain,
  $Na_2SiO_3 \cdot H_2O$ .... 34.5% Na_2SO_4 .... 8.9%
  $NaH_2PO_4 \cdot H_2O$ ...... 12.0%   nonionic 5.2%
  $Na_3PO_4 \cdot 12H_2O$ .... 33.5%   anionic (100% active) .. 5.9%
  All cleaning solution concentrations = 7.5%

detersiveness, cleaners containing synergistic mixtures of anionic and nonionic surfactants. In basic research we have attempted to develop detergency functions applicable to systems of several surfactants and a common soil, and to systems of several soils and a common surfactant.

Detergency Correlation in Applied Research

We have utilized the generalities and specificities established by our basic studies of surfactants (9,10, 11,12) for applied research in the field of alkaline cleaners. This research has led to the promulgation of Federal Specifications P-S-751, P-C-437, P-C-436a and TT-R-230, and Military Specifications MIL-C-11494 (Ord) and MIL-C-51052 (Ord). Two significant facts were uncovered early in this work (13). First, efficient hot soak tank alkaline cleaning did not require the conventional, highly caustic solutions of 13.0–13.4 pH, but could be obtained from moderately alkaline cleaners of 11.8–12.1 pH containing suitable synthetic detergents. Second, specific anionic-nonionic surfactant mixtures possessed synergistic detergent characteristics in alkaline solutions of 11.8–12.1 pH. To indicate synergism, a simple, rapid, asphalt detergency test was developed and is now incorporated in Federal Specification P-C-436a. The satisfactory passing of this test by an aqueous-based solution demonstrated, we believe, the existence of superior (or synergistic), surface-active properties of wetting power, penetrability, and peptizing power. After 15 years' experience with this test, no single surfactant, anionic or nonionic, has been found, which in medium pH alkaline solution can completely remove sticky, strongly adherent, asphalt soil. Recently we investigated the synergism exhibited in the asphalt detergency test by anionic-nonionic surfactant combinations of soak alkaline cleaners and attempted to establish any correlation between improved detersiveness and selected physicochemical factors.

Experimental

Detergency was determined as described in Federal Specification P-C-436a, using 1,600 cc of boiling, 7.5%, distilled water solutions of the test compounds contained in 2-liter beakers. Test panels of SAE 1010, 18–20 gage, cold rolled steel, 2½ by 2½ in. in size, were subjected to standardized polishing, cleaning, weighing, soiling of one face with 320 to 340 mg petroleum asphalt, aging, and cleaning for 21 min, or less if soil removal was complete before that time. Residual soil was determined by the gravimetric method, following water rinsing, drying, and cooling to room temp.

Surface tensions were determined by a du Nouy tensiometer at 25–26C with test solutions aged 1 hr. Harkins-Jordan correction factors were applied.

All test compounds contained the same amounts of builders as the Standard Control Compound of Fed. Spec. P-C-436a; and, therefore, all formed solutions of approximately the same pH, 11.8–12.0 at 25–26C. On a dry basis, the builder percentages were as follows:

    sodium metasilicate pentahydrate............34.5%
    primary sodium phosphate monohydrate..12.0%
    trisodium phosphate dodecahydrate.........33.5%

Thus, 20% of the formulation consisted of surfactants plus sodium sulphate builder, divided into 5.2% nonionic, 5.9% anionic, and 8.9% sodium sulphate.

Three types of anionics were included in the study: an alcohol sulphate (SDS), a straight chain alkyl aryl sulphonate (SKBS), and a soap (Table I).

The nonionics were commercial products, homologous series of ethylene oxide condensates of nonylphenol and tetramethyldecynediol and also the 9–10 mole ratio adduct of octylphenol.

Results
Detergent Synergism vs. Hydrophile-Lipophile Balance (HLB)

Table II shows the effect of the HLB of the nonionic surfactant on the detergent efficiency of the previously described alkaline cleaners containing various anionic-nonionic mixtures. It is to be noted that since the three anionic syndets vary considerably in HLB, the effect of anionic HLB level is also indicated. The HLB values of the nonionic surfactants were calculated by Griffin's method for polyethenoxy adducts (14), and the values for the anionic detergents were taken from the literature (14). Mineral oil detergencies, using Fed Spec. P-C-436a procedure, are also given by Table II. Briefly, the mineral oil detergency method involves 3 min cleaning with no agitation of the 2½ by 2½ in. steel panels soiled with SAE 30, non-detergent mineral oil, rinsing in water at room temperature with no agitation, and evaluation by the water-break test confirmed by the "residue-pattern" test (15). "Good" mineral oil detergency in the table signifies confirmed freedom from water-breaks. It should be noted that cleaners containing the same percentages of builders as given in Table II, but containing only one surfactant—anionic or nonionic—gave poor incomplete asphalt removal; and all cleaners with one surfactant except the ones formulated with

TABLE III
Asphalt Detergency vs. Anionic Surfactant Properties

Anionic surfactant	Anionic surface tension, dynes/cm	Anionic CMC, molar	Nonionic agent, and asphalt detergency (min for removal)			
			OPE9-10 (HLB = 13.40)	D-30 (HLB = 17.08)	NPTGE (HLB = 17.20)	NP100E (HLB = 19.05)
Na oleate	27.0 (16)	.0007 (18)	21	10,10	7,9	15,18
SKBS	30.5 (17)	.0015 (19)	12	9,9	16	21
SDS	37.8 (16)	.0081 (20)	8	6,7	19	21

NOTES: Asphalt detergencies are those of the Table II cleaners containing the corresponding anionic-nonionic mixtures.
Surface tension and CMC values are for the pure (unbuilt) agents at 25C, the surface tensions are for concentrations of 0.44 g/100 ml (the Table II anionic surfactant concentrations). The CMC for SKBS is that of a 12-carbon straight chain alkyl benzene sodium sulphonate. Literature references are given.

sodium oleate soap clean mineral oil completely. It is seen from Table II that nonionic surfactants with HLB values of 13.21–17.08 imparted excellent asphalt detergency to solutions containing the alcohol sulphate (5–9 min removal), and they imparted good asphalt detergency to cleaners containing the alkyl aryl sulphonate (9–12 min removal). For both these anionic systems, there was no significant variation of asphalt detergency in this nonionic HLB range. In cleaning solutions containing sodium oleate soap as the anionic surfactant, asphalt detergency improved from fair (21 min removal) to excellent (7–10 min removal) in the 13.40–18.18 nonionic HLB range. With all three anionic surfactant systems, asphalt detergency then fell off with further increase in nonionic HLB value to 19.05. Table II also indicates that the anionic sodium dodecyl sulphate, with the highest HLB of 40.0, formed the most synergistic detergent mixtures with nonionic additives in the 13.21–17.08 HLB range. It is to be noted that the 17.08 nonionic HLB point is a characteristic one for systems with sulphonate or sulphate anionic syndets, and 18.18 is the analogous point for sodium oleate soap systems. Increase in the HLB of the nonionic agent beyond these points causes a decrease in surface-activity as judged by asphalt detergency. Finally Table II shows no general correlation between asphalt detergency and either nonionic mole fraction or net HLB of the surfactant mixture.

Detergent Synergism vs. Anionic Surfactant Properties

In Table III it is seen that the increasing detergent synergism (or asphalt detergency) of the Table II cleaners is related to increasing surface tension and increasing CMC of their unbuilt anionic surfactants when the HLB of the nonionic constituent does not exceed 17.08. The order of increasing synergism is that of soap, alkyl aryl sulphonate, and alcohol sulphate. With nonionics of greater HLB, this order is reversed.

Harkins postulated the formation of mixed micelles in solutions containing anionic and nonionic sufactants thru the solubilization of the nonionic molecules by anionic micelles (18). He showed that this interaction was accompanied by a lowering of the anionic CMC (18). Nonionic surfactants in general have low CMC values; for example, the CMC of NPTGE is 2.75×10^{-4} M (21). Now, since the CMC of an anionic-nonionic mixture lies between the values of the individual surfactants (22), it seems that the greatest CMC lowering by a nonionic agent would occur with the anionic having the largest CMC. It is probable, therefore, that the increasing order of detergent synergism, when the nonionic HLB does not exceed 17.08, is also the order of increasing anionic CMC lowering.

TABLE IV
Detergent Synergism vs. Nonionic HLB and Surface Tension

Nonionic surfactant	Surface tension, dynes/cm	Temperature °C.	HLB
OPE9-10	30.0	25.8	13.40
D-10	30.5	25.8	13.21
NPPGE	35.3	25.6	15.00
D-15	33.6	25.3	14.90
D-30	36.1	25.4	17.08
NPTGE	42.4	25.6	17.20
NP50E	45.1	25.5	18.18
NP100E	45.0	25.8	19.05

NOTES: Concentration of all surfactants = 0.39% (their concentration in the Table II cleaners).

Detergent Synergism vs. Nonionic HLB and Surface Tension

Table IV shows that increasing HLB of the nonionic agents correlates approximately with increasing surface tension of their 0.39% solutions, which is their concentration in the cleaners of Table II. Therefore, nonionic additives with surface tensions of 30–36 dynes per cm impart detergent synergism to alkaline cleaning solutions of about pH 12 containing a sulphate or sulphonate anionic syndet. This trend reverses at higher nonionic surface tensions.

Summary of Detergency Correlation in Commercial Cleaning Solutions

The results of this study of detergency correlation in commercial alkaline cleaners may be summarized as follows:

First, in alkaline cleaning solutions of about pH 12 containing a primary alcohol sulphate or a straight chain alkyl aryl sulphonate anionic syndet, detergent efficiency is increased considerably by the addition of nonionic surfactants in the HLB range of 13.21–17.08, with surface tensions in the 30–36 dynes per cm range; further increase of nonionic HLB and surface tension to 19.05 and 45.0, respectively, causes a decrease in detergency. When sodium oleate soap is the anionic syndet in similar alkaline cleaning solutions, detergent efficiency is increased by nonionic additives with 13.40–18.18 HLB values; further increase of nonionic HLB to 19.05 also produces lowered detergency.

Second, in alkaline cleaning solutions of about pH 12 containing anionic-nonionic surfactant mixtures in which the HLB of the nonionic agent is in the 13.21–17.08 range, the anionic with the highest HLB produces the most detergent synergism.

Third, in alkaline cleaning solutions of about pH 12 containing anionic-nonionic surfactant mixtures in which the HLB of the nonionic agent is in the 13.21–17.08 range, increasing detergency is directly related to increasing surface tension and critical micelle concentration of the unbuilt anionic surfactant. The relationships are reversed at higher nonionic HLB values.

Discussion

Detergency Correlation of Table II Cleaners

It is suggested that the change in surface activity indicated by the asphalt detergency test, and occurring a) in cleaners containing the sulphonate or sulfate anionics when the nonionic HLB exceeds 17.08, and b) in cleaners containing sodium oleate soap when the nonionic HLB is greater than 18.18, is due to the following reason:

The longer ethylene oxide chains of nonionic agents with HLB values exceeding 17.08 or 18.18 as just described cause a change, or partial change, in the type of their solubilization by the anionic surfactant. This change may be from the oriented polar-nonpolar type of solubilization in which the hydrocarbon chains of
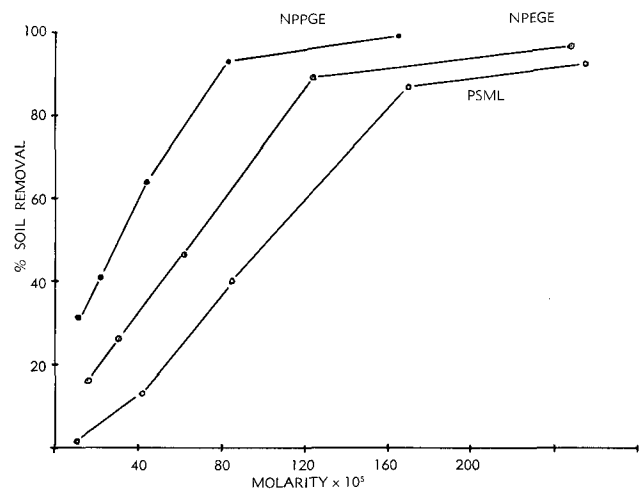
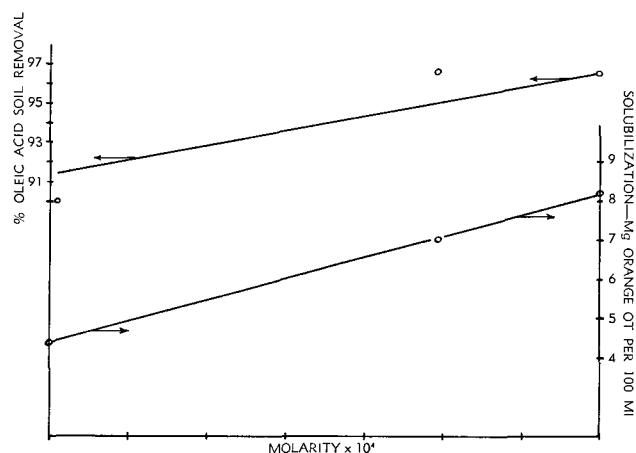FIG. 1. Detergency-concentration curves, triolein.

FIG. 2. Detergency and solubilization Isotherms for NPEGE

$$D = K_1 S + K_2$$

where,

D = % soil removal
S = mg Orange OT/100 ml
K_1 and K_2 = constants

hence,

$$D = 1.31 S + 85.75$$

the nonionic penetrate between those of the anionic molecules in the outer micellar layers to adsorption type solubilization in which there is no penetration of the anionic micelle by the nonionic surfactant (18). Such variation in micellar interaction could influence the size, shape, and charge density of the mixed micelle, and consequently the colloidal behavior of its solutions.

The marked inter-relationship of the parameters involved in this study of anionic-nonionic surfactant mixtures is considered significant. Connection of composite surface-activity to a single parameter would appear to be inadequate, an oversimplification. Our basic studies of detergency correlation have been guided by this working hypothesis. As will be shown, we have developed a linear detergency function with micellar solubilization as the variable (23). But the linearity constants of the function have been related to the physicochemical factors of soil dipole moment, surfactant HLB, and soil-surfactant interfacial energy.

Detergency Guidelines

Detergency testing in our basic research program was conducted essentially as described earlier in this paper (5,15). A residual soil level of approximately 1–10% was maintained in these studies. This permitted the use of the gravimetric method of cleanliness evaluation (5). A typical statistical analysis for a series of ten replicates, using palmitic acid soil and a 0.26% solution of sodium dodecyl benzene sulphonate, showed that the 95% confidence interval in this residual soil range was 92.0–95.4% soil removal.

Now, in determining the relative cleaning abilities of detergents the comparison is desired at or very close to 100% soil removal. Our work has indicated the danger of projecting low level soil removal to complete removal because of considerable differences in detergency-surfactant concentration rates of change (5). Initial studies of hard surface detergency at this laboratory revealed the existence of a characteristic high level soil removal range in most detergency-surfactant concentration isotherms (5). If was found that for soils such as fatty acids, alcohols, esters, and amines, and with many types of syndets, soil removal was low at the CMC, but then increased sharply with increasing concentration until approximately 90% detergency was reached, at which point soil removal began to level off and approach 100% at a much lower rate. Figure 1 shows characteristic detergency-concentration curves for three surfactants with triolein soil. NPPGE is the 15-mole ratio ethylene oxide

adduct of nonylphenol; NPEGE is the 20-mole ratio adduct. PSML is the 23-mole ratio ethylene oxide adduct of sorbitan monolaurate. We called the concentration at 90% detergency the CC-1 point. It is a concentration below which a surfactant is unable to effect soil removal at what we consider a practical level. The upper limit of our detergency correlation range, the CC-2 point, was arbitrarily set at twice the CC-1 concentration. It is extremely interesting that J. C. Harris independently and at the same time selected the 90% soil removal point as an arbitrary level for a proposed detergency equation (25).

Development of Detergency Function

Figure 2 shows typical detergency and micellar solubilization isotherms for the nonionic syndet, NPEGE, the 20-mole ratio ethylene oxide adduct of nonyl phenol, and oleic acid soil, in the CC-1 to CC-2 range. The deviations of the linear detergency plot from actual soil removal values are within the precision of the gravimetric method. Micellar solubilization, which was determined by a dynamic, Orange OT, technique (5) is linear with respect to cencentration in this range. It is believed that the dynamic solubilizations obtained here by 25 min interactions at 180F are more compatible with the dynamic detergencies used in our work than thermodynamic, or saturation, solubilizations. Now, since both detergency and solubilization in the CC-1 to CC-2 range are linear with respect to concentration, each with a positive slope, it follows mathematically that the detergency-solubilization function is also linear; that is,

$$D = K_1 S + K_2$$

Where, D = detergency, in % soil removal, at 180F.
S = micellar solubilization, in mg Orange OT per 100 ml, at 180F.
K_1 and K_2 = constants

Taking numerical values from the detergency and solubilization isotherms, the detergency equation for this soil-surfactant system in this practical, soil removal range, becomes:

$$D = 1.31 S + 85.75$$

Similar equations can be derived for all soil-surfactant systems except those not possessing CC-1 and

TABLE V

Detergency Correlation of Polyoxyethylene Nonyl Phenols and Octadecylamine Soil

Surfactant	Ethylene oxide mole ratio	Concentration, molarity		% Soil removal	Solubilization, S, mg orange OT/100 ml	Calculated function, D = $K_1 S + K_2$
NPEGE	20	.00636,	CC-1	92.6	14.1	D = 0.36 S + 89.58
		.00954		99.0	21.5	
		.0127,	CC-2	99.3	27.3	
NPTGE	30	.000455,	CC-1	91.4	1.10	D = 4.16 S + 88.82
		.000682		98.1	1.75	
		.000909,	CC-2	99.0	2.45	
NPTTGE	40	.000505,	CC-1	90.0	1.04	D = 3.87 S + 88.38
		.000758		97.1	1.65	
		.00101,	CC-2	97.2	2.28	
NP50E	50	.000788,	CC-1	88.5	1.96	D = 4.25 S + 80.76
		.00118		93.4	2.83	
		.00158,	CC-2	96.8	3.77	

CC-2 points. A relatively few systems have detergency isotherms in which soil removal rises sharply to a maximum of less than 100% and then falls off with increasing concentration (5). The potassium laurate-oleic acid soil system is an example of this type. A few systems do not attain 90% soil removal; for example, NPIOOE and octadecylamine soil have a maximum detergency of only 55%.

However, the derivation of a great number of one-parameter, detergency functions, each applicable to one surfactant-soil system, would be of limited value. It was felt that to be of real significance the detergency function should indicate dependence on both surfactant and soil. For example, it seemed that in a series of related soil-surfactant systems, in which the soil was common, that detergency should show dependence on some property of the surfactants. Similarly in a series of systems in which the surfactant was common, it was reasonable to expect detergency to be connected to some soil factor. The results of attempts to achieve this broader and more general type of detergency correlation are promising. Analysis of selected series of soil-surfactant systems, consisting of as many as five surfactants with a common soil, or four soils with a common surfactant, have indicated that the linearity constants K_1 and K_2 of the detergency-solubilization equation (D = $K_1 S + K_2$) have more than mathematical significance (23). It was found, first, that the K_2 values (mathematically, the ordinate intercepts at zero solubilization) of both multi-surfactant and multi-soil series of systems could be related to Antonow's interfacial tension; second, the K_1 values (the slope constants) of multi-surfactant systems could be related to surfactant HLB; and third, the K_1 values of multi-soil systems could be connected to soil dipole moment. It is to be noted that

TABLE VI

Polyoxyethylene Nonyl Phenols with Octadecylamine Soil, Continued

Ethylene oxide mole ratio	K_1	K_2	HLB	Tensions at CC-1 points, dynes/cm	
				Surface tension	Antonow's tension, A
20	0.36	89.58	16.00	35.8	14.1
30	4.16	88.82	17.20	39.6	17.9
40	3.87	88.38	17.78	41.3	19.6
50	4.25	80.76	18.18	43.3	21.6

Therefore, $K_1 = -402.76 + 45.93 (HLB) - 1.296 (HLB)^2$
$K_2 = 25.74 + 8.25 A - 0.264 (A)^2$

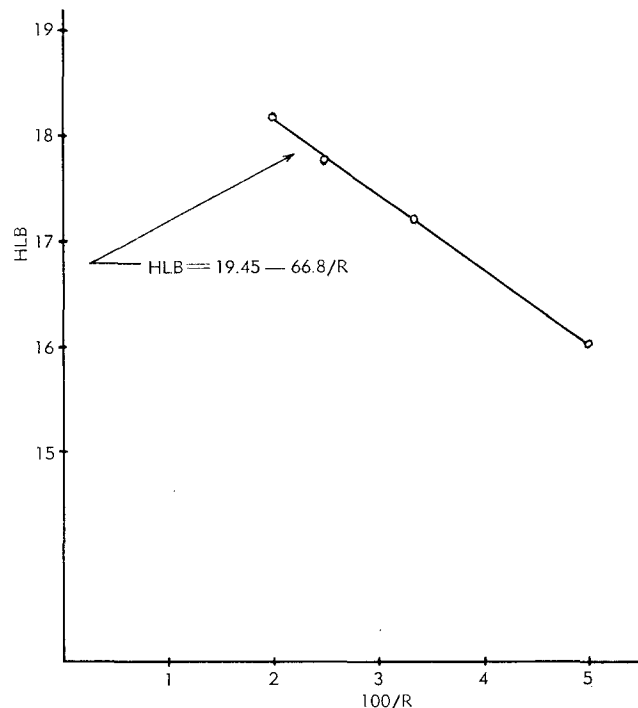| Ethylene oxide mole ratio	K_1		K_2	
	Experimental	Calculated	Experimental	Calculated
20	0.36	0.34	89.58	89.58
30	4.16	3.83	88.82	88.82
40	3.87	4.18	88.38	86.02
50	4.25	3.91	80.76	80.77

FIG. 3. Polyoxyethlated Nonyl Phenols. R = ethylene oxide mole ratio. Hsiao, et al., J. Phys. Chem., 60, 657 (1956): ln CMC = 0.056R + 3.87, hence, $\log$ CMC = $\dfrac{1.68(20.42-HLB)}{19.45-HLB}$. CMC in micromolar units.

all the K_1 and K_2 relationships that we have derived are probably physical and not random, since they contain in every case fewer constants than the number of points or systems used in their derivations.

Detergency Correlation in a Multi-Surfactant, Common Soil, Series of Systems

Table V contains detergency and micellar solubilization data and calculated detergency functions, obtained as just described from the corresponding linear detergency and solubilization plots in the CC-1 to CC-2 range, for a series of systems consisting of the 20,30,40 and 50-mole ratio ethylene oxide adducts of nonyl phenol with octadecylamine soil. Details of the standardized octadecylamine soiling procedure have been reported (26), and involve brushing the molten amine on one face of the steel test panel, followed by draining at 105C in a vertical position. In Table VI, the K_1 and K_2 constants for this series of systems are listed with the HLB values of the adducts, and the surface and Antonow tensions at the CC-1 points. The listed Antonow tensions are differences between surfactant and octadecylamine surface tensions at about 28C. Strictly, these values are not Antonow inter-

TABLE VII

Multi-Soil, Common Surfactant (PSML), Detergency Correlation

Soil	Concentration, molarity		% Soil removal	Solubilization, S, mg orange OT/100 ml	Calculated function, D = $K_1 S + K_2$
Triolein	.00255,	CC-1	92.6	6.8	D = 0.91 S + 86.44
	.00383			9.3	
	.00510,	CC-2	97.4	12.1	
Oleic acid	.00131,	CC-1	91.5	1.9 at .00085M	D = 1.33 S + 89.01
	.00170		96.8	4.5	
	.00261,	CC-2	98.3	6.8 at .00255M	
Lauryl alcohol	.000424,	CC-1	88.8	1.0 at .000425M	D = 8.14 S + 82.60
	.000571		95.5		
	.000848,	CC-2	97.9	1.9 at .00085M	
Octadecyl-amine	.0106,	CC-1	92.9	22.5	D = 0.13 S + 92.10
	.0159		99.5		
	.0212,	CC-2	99.6	56.3	

TABLE VIII
Multi-Soil and PSML Correlation, Continued

| Soil | K_1 | K_2 | Soil | | At CC-1 Concentration | |
			Dipole moment debyes	Surface tension dynes/cm	Surface tension dynes/cm	Antonow's tension, A
Triolein	0.91	86.44	3.08	31.6	34.1	2.5
Oleic acid	1.33	89.01	1.009	31.5	34.1	2.6
Lauryl alcohol	8.14	82.60	1.7	28.3	33.9	5.6
Octadecyl-amine	0.13	92.10	1.3	21.7	33.8	12.1

Therefore, $K_1 = 2.9 - 3.0 \sin (6.283 \, DM)$, where DM = debyes
$K_2 = 98.73 - 5.24 \, A + 0.379A^2$

| Soil | K_1 | | K_2 | |
	Calculated	Experimental	Calculated	Experimental
Triolein	1.45	0.91	88.00	86.44
Oleic acid	2.73	1.33	87.67	89.01
Lauryl alcohol	5.75	8.14	81.28	82.60
Octadecylamine	0.05	0.13	90.82	92.10

facial tensions, because the two materials are not mutually saturated, but they are specific factors. The surface tension of octadecylamine has been estimated as 21.7 dynes/cm from its critical surface tension of wetting according to the Zisman procedure (27). Now mathematical analysis of these data reveals parabolic relationships between K_1 and HLB, and between K_2 and A, as given in Table VI; viz:

$$K_1 = -402.76 + 45.93 \, (HLB) - 1.296 \, (HLB)^2$$
and, $$K_2 = 25.74 + 8.25 \, A - 0.264 \, (A)^2$$

The second part of Table VI shows that agreement between the calculated and experimental values of K_1 and K_2 is good to excellent. If calculated values of K_1 are used in the corresponding detergency functions, the maximum deviation of a calculated detergency at the CC-1 point from the experimental is only 2.7%.

Further correlation of physicochemical factors with detergency exists in this series of surfactant-soil systems. Figure 3 shows a linear connection between HLB and the reciprocal of the ethylene oxide mole ratio, R, for the polyoxyethylene nonyl phenols (5). The equation for this relationship is:

$$HLB = 19.45 - \frac{66.8}{R}$$

Workers at the Bureau of Mines (21) have found that CMC and R of these adducts are connected logarithmically by the equation given in the figure:

$$ln \, (CMC) = 0.056 \, R + 3.87$$

Where, CMC is in micromolar units. It then follows, Figure 3, that CMC and HLB are connected by the equation:

$$\log \, (CMC) = \frac{1.68 \, (20.42 - HLB)}{19.45 - HLB}$$

K_1 values, and therefore detergencies, in this series of surfactant-soil systems are thus related to CMC.

Detergency Correlation in a Multi-Soil, Common Surfactant, Series of Systems

We will now show the derivation of the detergency correlation existing in a multi-soil, common surfactant, series of systems. The surfactant in this study will be PSML, the 23-mole ratio ethylene oxide adduct of sorbitan monolaurate, and the soils are triolein, oleic acid, lauryl alcohol, and octadecylamine (28). Table VII has the detergency and solubilization data and calculated detergency functions for each of these four systems in the CC-1 to CC-2 range. Table VIII lists the K_1 and K_2 constants for this series of systems

TABLE IX
Detergency Correlation of Linearity Constants of Selected Soil-Surfactant Systems

1. 20,30,40 and 50 R adducts of nonyl phenol with octadecylamine soil:
$K_1 = -402.76 + 45.93 \, (HLB) - 1.296 \, (HLB)^2$
$K_2 = 25.74 + 8.25 \, A - 0.264A^2$
Notes: R = ethylene oxide mole ratio
100 R adduct has no CC-1 point
2. 20,30,40,50 and 100 R adducts of nonyl phenol with lauryl alcohol soil:
$K_1 = 67 + 62 \sin (10.485 \, HLB)$
$K_2 = 88.65 + 3.65 \sin (4.40A)$
3. 20,30,40,50 and 100 R adducts of nonyl phenol with stearic acid soil:
$K_1 = 80.47 - 9.775 \, (HLB) + 0.297 \, (HLB)^2$
$K_2 = 238.5 - 10.8A + 0.183A^2$
4. 20,30,50 and 100 R adducts of nonyl phenol with oleic acid soil:
$K_1 = 0.80 - 2.1 \sin (HLB)$
$(K_2 - 87.0)^2 = 31.36 - (A - 9.7)^2$, or $K_2 = 88.1 + 5.5 \sin (1.28A)$
5. 30,40,50 and 100 R adducts of nonyl phenol with linoleic acid soil:
$\log K_1 = 5.2755 - 0.2625 \, (HLB)$
$K_2 = 118.11 - 5.733A + 0.268A^2$
6. PSML with triolein, oleic acid, lauryl alcohol, and octadecylamine soils:
$K_1 = 2.90 - 3.00 \sin (6.283 \, DM)$
$K_2 = 98.73 - 5.24 \, A - 0.379A^2$
7. 20 R adduct of nonyl phenol with triolein, oleic acid, lauryl alcohol and octadecylamine soils:
$K_1 = 3.00 - 3.05 \sin (6.283 \, DM)$
$(K_2 - 82.13)^2 = 60.53 - (A - 11.8)^2$,
or $K_2 = 87.30 + 7.20 \sin (2.43A)$

together with the soil dipole moments and surface tensions, the former values being taken from the literature. This section also gives surfactant and Antonow's tensions at the CC-1 concentrations. Mathematical analysis of these data indicates a trigonometric K_1-dipole moment relationship and a parabolic K_2-Antonow's tension connection, as shown in the table. The bottom part of Table VIII shows fair agreement between calculated and experimental values of K_1, and good agreement between calculated and experimental values of K_2.

Summary

It is felt that it would be of interest to conclude this paper by showing some of the correlations already established for selected soil-surfactant series of systems, with particular reference to the variation of the linearity constants K_1 and K_2 of these systems with corresponding soil or surfactant physicochemical factors. Table IX gives the detergency functions for these multi-soil, common surfactant, and multi-surfactant, common soil, series of systems.

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