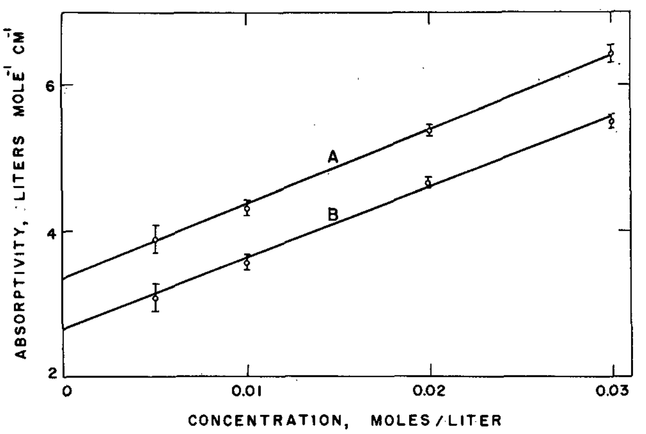

FIG. 5. Absorptivity at 3541 cm^{-1} versus concentration in CCl_4. (A) Methyl 12-hydroxystearate. (B) Methyl 10-hydroxystearate.

interactions similar to the medium-ring effect in cyclic compounds.

The IR-3 spectrophotometer is a single-beam instrument using a tape recorder to provide a reference spectrum. Since this permits the same light path and same absorption cell to be used for both blank and sample, the instrument, as modified in this laboratory, was capable of very sensitive differential spectrophotometry (22). Figure 4 shows a differential spectrum of methyl 12-hydroxystearate versus methyl 10-hydroxystearate, both at 0.01 molar in CCl_4. To check whether the 3541 cm^{-1} band could be due to intermolecular hydrogen bonding, measurements were made at several concentrations between 0.005 and 0.3 M. In interpreting spectra of substances capable of dimerization, it must be remembered that, in any mass-law equilibrium, there does not exist a concentration below which the proportion of dimer is exactly zero. The only reason that spectra can be observed that appear to be independent of concentration is that the concentration is taken sufficiently low that the effect of dimer is less than the experimental noise. It can be easily shown that the over-all absorptivity of an equilibrium mixture of monomer and dimer becomes a linear function of over-all concentration at low concentrations, with a slope that is not zero. Measurements which are made at concentrations where the slope is constant can then be extrapolated down through the experimental noise to obtain an intercept at zero concentration, as is common practice with electrochemistry, viscosity, light scattering, etc. Individual points were read from the curves of methyl 10- and 12-hydroxystearate in the range 3500–3600 cm^{-1} and were found to have absorptivities linear with concentration between 0.005 and 0.03 M. The absorptivities were therefore extrapolated by least squares to zero concentration at each wavenumber. Figure 5 illustrates the procedure for one wavenumber. The curve of absorptivity difference versus wavenumber at zero concentration shows a maximum at 3541 cm^{-1} similar to Figure 4, indicating that this peak must not be intermolecular.

Figure 4 could be interpreted to mean that a small fraction of the methyl 12-hydroxystearate is intramolecularly hydrogen bonded with an absorption band at 3541 cm^{-1}, at the expense of rotomers whose absorption bands would normally be at 3622 and 3594 cm^{-1}. However, the sensitivity of the differential method could also mean that we are merely seeing a trace of an impurity not detected by other methods. The most that can be done with the differential data is to place an upper limit of 1.5% on the fraction of the methyl 12-hydroxystearate molecules that could be in the intramolecularly hydrogen-bonded state in carbon tetrachloride. It does not appear that intramolecular factors could be responsible for the difference in chemical or physical properties of 10- and 12-hydroxyl derivatives of fats.

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Further Studies of Detergency Correlation

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Abstract

The significance of the relationships of the linearity constants of a previously reported detergency-micellar solubilization function (1) to surfactant HLB (hydrophile-lipophile balance), boundary tensions, and soil dipole moment was extended, first, by demonstrating their existence in systems of four homologous surfactants with one soil or four classes of soil with one surfactant, and second, by showing in every case that they are probably physical rather than random because they contain fewer constants than the number of points (four) used in their derivation.

A study of a series of surfactant-soil systems consisting of a family of polyoxyethylated nonyl phenols and a family of saturated fatty acid soils (12–18 carbon) revealed linearity of the R-log (M/CMC) and surfactant HLB-log (M/CMC) functions for values of R (ethylene oxide mole ratio) between 15–50 and 20–100, respectively (M = surfactant concentration giving ca 100% removal of 16 and 18 carbon fatty acids, and CMC = critical micelle concentration). The validity of the semi-logarithmic functions was

confirmed by the fact that they indicated linearity between R and surfactant HLB as previously reported (2). Abnormally high nonyl phenol adduct concentrations (2.7–3.8%) were required to give good fatty acid removal. It was suggested that the initial decrease in detergency with increase of fatty acid soil HLB from 6.5–9.8, followed by increasing detergency as the soil HLB continued to increase to 11.25, was due to differences in the relative magnitudes of the soil-substrate adhesive forces and micellar solubilization existing in the soil HLB range.

Sodium dodecyl benzene sulphonate was a good detergent of the saturated fatty acids, soil removal being independent of soil HLB for the 12–18 carbon acids. The fatty acid soaps were poor detergents of these soils.

A "net ethylene oxide solubilizing power" method of computing HLB was proposed, based on known polar group hydrophobe-solubilizing values.

Introduction

AN EARLIER PAPER (1) from this laboratory reported a linear relationship between dynamic hard surface detergency and dynamic micellar solubilization of Orange OT dye, both determined at 180F, from a concentration at about 90% soil removal (CC-1 point) to one of twice that value (CC-2 point). This derivation was based on (a) the demonstrated linearity of the simple solubilization-concentration function in the relatively narrow CC-1 to CC-2 range, and (b) the approximately linear connection, within the precision of the gravimetric detergency method, between detergency and concentration in the same range. It followed mathematically, therefore, that if,

D = detergency, in % soil removal, between CC-1 and CC-2
S = micellar solubilization of Orange OT, in mg Orange OT per 100 ml, between CC-1 and CC-2
M = molar concentration
C_1 through C_{11}, and K_1 and K_2 = constants

Then,

$S = C_1 + C_2 M$ ....linear solubilization—concentration function

$$M = \frac{S}{C_2} - \frac{C_1}{C_2} = C_3 S - C_4$$

And,

$D = C_5 + C_6 M$ ....linear detergency—concentration function

$$M = \frac{D}{C_6} - \frac{C_5}{C_6} = C_7 D - C_8$$

Therefore,

$$C_7 D - C_8 = C_3 S - C_4$$
$$C_7 D = C_3 S - C_4 + C_8 = C_3 S + C_9$$
$$D = \frac{C_3}{C_7} S + \frac{C_9}{C_7} = C_{10} S + C_{11} = K_1 S + K_2$$

It was also shown previously (1) that the constants K_1 and K_2 were connected to surfactant HLB (hydrophile-lipophile balance) and soil dipole moment or boundary tension. The correlation of these constants with physicochemical factors was demonstrated for systems of three homologous surfactants with the same soil and for three classes of soil (fatty acid, alcohol, and ester) with the same surfactant.

This investigation extends the significance of these relationships in two ways: first, by demonstrating their existence in systems of four homologous surfactants with one soil or four classes of soil with one surfactant, and second, by showing that they are probably physical rather than fortuitous because in every case they contain fewer constants than the number of points (four) used in their derivation. In addition, systems of one surfactant with an homologous family of soils (the 12, 14, 16, and 18 carbon saturated fatty acids) are explored.

Experimental

Materials—The surfactants, with the exception of the sodium oleate (a purified grade) and potassium laurate (prepared from a technical grade fatty acid), were commercial products, the same as those used in previous work (1,2); namely,

nonyl phenyl pentadecaethylene glycol ether	NPPGE
nonyl phenyl eicosaethylene glycol ether	NPEGE
nonyl phenyl triacontaethylene glycol ether	NPTGE
nonyl phenyl tetracontaethylene glycol ether	NPTTGE
nonyl phenyl pentacontaethylene glycol ether	NP50E
nonyl phenyl decacontaethylene glycol ether	NP100E
tridecyldodecaethylene glycol ether	TDDGE
tridecylpentadecaethylene glycol ether	TDPGE
polyoxyethylene (23) sorbitan monolaurate	PSML
sodium dodecyl benzene sulphonate	SDBS

Some of the soils have been described, lauryl alcohol (1) and triolein (3). USP grade oleic acid and octadecylamine MP 47–51C, were also used. The reagent grade fatty acids had melting points as follows:

lauric acid	42–43C
myristic acid	52–53C
palmitic acid	61–62C
stearic-acid	68–69.5C

Procedures—Most of the details of the dynamic methods employed in determining micellar solubilization and detergency, both at 180F, have been given in an earlier paper (2). Application of the fatty acids and the octadecylamine to the steel test panels was as follows: the molten material was brushed on one face of the weighed panel with a small camel's hair brush; the panel was then hung vertically in a 105C oven for a draining period depending on the material, as follows:

lauric acid	1½ min
myristic acid	2 min
palmitic acid	3 min
stearic acid	3 min
octadecylamine	2¼ min

the panel was next removed from the oven, cooled to room temperature, and reweighed (soil per panel was 53–60 mg).

Results and Discussion

1. *Oleic Acid Soil Removal by 20, 30, 50, and 100 Mole Ratio Ethylene Oxide Adducts of Nonyl Phenol*—A previous report (1) gives the micellar solubilization and oleic acid detergency data, together with the derived detergency (D)-solubilization (S) equations, for the 20, 50, and 100 mole ratio (R) adducts of nonyl phenol; viz.,

Adduct	R	Equation
NPEGE	20	$D = 1.31\ S + 85.75$
NP50E	50	$D = 1.66\ S + 82.62$
NP100E	100	$D = 0.60\ S + 89.06$

Table 1 lists similar data for the 30 R adduct, NPTGE, from which the following equation may be obtained as already described (1):

$$D = 3.52\ S + 91.52$$

Since the HLB values of the 20, 30, 50, and 100 R adducts are 16.00, 17.20, 18.18, and 19.05, respectively (⅕ of their oxyethylene weight percentages), and since $D = K_1 S + K_2$, it can be shown that K_1 is a trigonometric function of HLB, such that

$$K_1 = 0.80 - 2.1 \sin (\mathrm{HLB})$$

A relationship of the K_2 values of this system to the corresponding boundary tensions can be derived from the following pertinent information:

R	K_2	At adduct CC-1 concentration	
		Surface tension, $\frac{\text{dynes}}{\text{cm}}$	Antonow's "tension," A
20	85.75	35.8	4.3
30	91.52	37.7	6.2
50	82.62	44.6	13.1
100	89.06	46.3	14.8

The values given in the Antonow's "tension" column are differences between surfactant and soil (oleic acid, 31.5 dynes/cm) surface tensions, not mutually saturated. Therefore, strictly, they are not interfacial tensions as defined by Antonow's rule. It follows that K_2 is connected to A by the following function:

$$(K_2 - 87.0)^2 = 31.36 - (A - 9.7)^2$$

Agreement between calculated and actual values is fair for K_1 and excellent for K_2, as the following comparisons indicate (angular comparisons of K_1 are also given because it can be considered a slope mathematically):

R	Calculated			Actual		
	K_1	K_1 Slope	K_2	K_1	K_1 Slope	K_2
20	1.4	54° − 28′	85.58	1.31	52° − 38′	85.75
30	2.9	70° − 58′	91.37	3.52	74° − 8′	91.52
50	2.1	64° − 32′	82.55	1.66	58° − 56′	82.62
100	0.4	21° − 48′	89.31	0.60	30° − 57′	89.06

2. *Polyoxyethylene Sorbitan Monolaurate (PSML) Detergency of Four Types of Soil*—PSML micellar solubilization and triolein soil removal data have been reported previously (2), and the corresponding detergency function determined (1); viz., $D = 0.91 S + 86.44$.

Oleic acid detergency by PSML is given in Table I and pertinent solubilization data has been reported (2). The following detergency function may then be calculated as previously described: $D = 1.33 S + 89.01$.

TABLE I

Detergency—Micellar Solubilization Data

soil	surfactant	molarity × 10^4	% soil removal	micellar solubilization, mg Orange OT/100 ml
oleic acid	NPTGE	2.75	91.9	0.395
		4.13	95.6	......
		5.50	96.4	1.39
oleic acid	PSML	13.1	91.5	......
		17.0	96.8	......
		26.1	98.3	......
lauryl alcohol	PSML	4.24	88.8	1.0 at .000425 M
		5.71	95.5	......
		8.48	97.9	1.9 at .000850 M
octadecylamine	PSML	106	92.9	22.5
		159	99.5	......
		212	99.6	56.3
lauryl alcohol	NPEGE	3.11	90.2	0.8 at .000310 M
		5.45	97.9	......
		6.22	97.8	1.9 at .000620 M
octadecylamine	NPEGE	63.6	92.6	14.1
		95.4	99.0	......
		127	99.3	27.3

Table I contains detergency and solubilization data for PSML-lauryl alcohol and PSML-octadecylamine systems. The data yields the following detergency functions:

lauryl alcohol soil, $D = 8.14 S + 82.60$
octadecylamine soil, $D = 0.13 S + 92.10$

Taking the previously referenced (1) dipole moments of triolein, oleic acid, and lauryl alcohol as 3.08, 1.009, and 1.7 debyes, respectively, together with the value of 1.3 debyes for octadecylamine (4), it can be shown that K_1 conforms approximately to the trigonometric relationship,

$$K_1 = 2.8 - 3.0 \sin (6.283\ \mathrm{DM})$$

where, DM = dipole moment, in debyes

The connection of K_2 to boundary tensions may be determined from the following applicable information:

Soil	Soil surface tension dynes/cm	K_2	At CC-1 concentration (PSML)	
			surface tension	Antonow's "tension," A
Triolein..................	31.6	86.44	34.1	2.5
Oleic acid................	31.5	89.01	34.1	2.6
Lauryl alcohol........	28.3	82.60	33.9	5.6
Octadecylamine......	21.7	92.10	33.8	12.1

The surface tension of octadecylamine, a low surface energy solid, has been estimated from its critical tension of wetting, 22 dynes/cm (5), and the observation (6) that critical surface tensions of such solids differ little (ca 0.3 dynes/cm) from the surface tensions of liquids of similar molecular structure. It is found that the following parabolic equation holds:

$$K_2 = 98.73 - 5.24\,A + 0.379A^2$$

The agreement between actual and calculated values of K_2 is good; viz.,

A	K_2	
	calculated	actual
2.5	88.00	86.44
2.6	87.67	89.01
5.6	81.28	82.60
12.1	90.82	92.10

3. *NPEGE Detergency of Four Types of Soil*—NPEGE solubilization and triolein detergency data have been reported previously (2) and the corresponding detergency function calculated (1); viz., $D = 2.55 S + 80.09$.

The NPEGE-oleic acid detergency function has been determined (1): $D = 1.31 S + 85.75$.

Table I shows the detergency and solubilization data for NPEGE-lauryl alcohol and NPEGE-octadecylamine systems. The following detergency functions may be calculated as previously described (1):

lauryl alcohol soil, $D = 5.20 S + 87.83$
octadecylamine soil, $D = 0.36 S + 89.58$

Analysis of the K_1 values and the corresponding soil dipole moments (given in preceding section) indicates approximate conformance to the following trigonometric equation:

$$K_1 = 3.0 - 3.05 \sin (6.283\ \mathrm{DM})$$

The correlation between K_2 for the NPEGE-soils system and boundary tensions may be derived from the following pertinent information:

K_2	Soil	soil surface tension	At CC-1 concentration (NPEGE)	
			surface tension	Antonow's "tension," A
80.09	triolein	31.6	35.9	4.3
85.75	oleic acid	31.5	35.8	4.3
87.83	lauryl alcohol	28.3	34.8	6.5
89.58	octadecylamine	21.7	35.8	14.1

Again the values given in the Antonow's "tension" column are differences between surfactant and soil surface tensions, not mutually saturated; and are not interfacial tensions as defined by Antonow's rule. Mathematical analysis of the K_2 data reveals the existence of the following relationship between K_2 and A:

$$(K_2 - 82.13)^2 = 60.53 - (A - 11.8)^2$$

There is extremely good agreement between calculated and actual values of K_2; viz.,

A	Calculated K_2	Actual K_2
4.3	80.06	80.09
6.5	87.83	87.83
14.1	89.56	89.58

4. *Saturated Fatty Acid Detergency by Anionic Surfactants*—Table II shows that fatty acid soaps are poor detergents of the solid saturated fatty acids.

TABLE II

Detergency of Saturated Fatty Acids by Anionic Surfactants

surfactant	molarity × 10^4	% fatty acid-soil removal			
		12C	14C	16C	18C
sodium oleate	11. – CMC	......	10.4	16.9	10.4
	132.	15.4	22.2	......	......
	264.	55.0	58.4	48.5	zero
	792.	78.0	49.5	*	*
	1056.	42.0	3.7	......	*
potassium laurate	140.	37.8	56.1	......	*
	233. – CMC	98.1	77.5	41.9	*
	466.	98.3	58.6	*	*
	932.	......	*	......	......
SDBS	15. – CMC	......	13.4	......	18.2
	30.	23.3	20.4	......	22.4
	60.	93.0	84.3	81.5	71.2
	75.	......	96.8	95.3	99.0
	90.	......	99.7	......	98.7
	120.	99.3	......	......	......

* Residual soil greater than original soil.

The detergency isotherms of the 12, 14, 16, and 18 carbon acid soils with both soaps (with the exception of the potassium laurate-lauric acid system) attain a low maximum and then fall to "negative" detergency (residual soil > original soil). At the same soap concentration, detergency decreases with increasing number of carbons in the soil (that is, with decreasing soil HLB). A partial explanation of these results has been advanced in connection with a study (7) of the adsorption of long chain polar compounds on metal surfaces from non-polar solutions; viz., the binding energy of the fatty acid molecules to the steel substrate consists of the adsorptive energy of their polar carboxyl groups to the metal plus the van der Waals cohesive forces between their hydrocarbon chains; hence the greater the chain length, the more strongly the fatty acid is adsorbed. It is now suggested, therefore, that the greater the chain length, the more difficult the fatty acid is to deterge. Since the polar groups of the soap detergents are also carboxyl, preferential adsorption of detergent ions on the substrate is minimized. The chief action is adsorption between the hydrocarbon chains of the acid soil and the fatty acid soap, and this increases (with consequent decrease in detergency) with increasing chain length of the former and concentration of the latter.

The alkyl aryl sulphonate data of Table II indicates that SDBS is a good detergent of solid fatty acids, the detergency isotherms of all four soils approaching 100% removal. Detergency is substantially independent of the chain length of the acids. It is reasonable to suppose that the principal detergent action in the SDBS-fatty acid soil system is preferential wetting of the substrate by the polar sulphonate group. The low binding energy of the latter in wetting agents and hydrotropes would seem to indicate that surfactant HLB is a more pertinent factor in the preferential adsorption mechanism than the surfactant polar group. Such a conclusion is not substantiated by the data in Tables II and III, which reveal good fatty acid soil removal by both SDBS and NP100E, with HLB values of 11.70 and 19.05, respectively. It is evident that HLB, although a measure of the hydrophilic and hydrophobic characteristics of an amphipathic molecule, is not an index of its binding energy (adsorptive energy of its polar group plus van der Waals cohesive forces between its hydrophobic groups).

TABLE III

Fatty Acid Detergency by Nonionic Surfactants

surfactant	molarity × 10^4	% fatty acid soil removal			
		12C	14C	16C	18C
NPPGE	1.1 – CMC	3.0	4.2	......	1.8
	11.0	......	6.5	......	9.2
	33.0	......	......	......	......
	132.	......	11.2	......	22.7
	264.	47.7	19.2	29.2	35.6
	396.	78.1	73.4	77.0	81.1
	528.	91.0	......	......	......
NPEGE	1.6 – CMC	5.0	3.7	......	1.8
	58.2	......	7.6	......	......
	116.	......	13.5	......	......
	232.	......	20.9	......	73.5
	261.	66.9	27.1	92.2	94.9
	290.	......	......	......	98.7
	349.	80.6	80.6	ca 100	98.9
NPTGE	2.8 – CMC	10.5	6.5	......	18.9
	44.	......	16.6	......	......
	66.	64.1	20.8	......	48.9
	132.	89.7	29.5	81.8	98.4
	176.	69.3	68.2	99.7	ca 100
	220.	......	98.2	......	......
NPTTGE	4.5 – CMC	......	10.6	......	17.4
	26.4	......	17.4	......	......
	52.8	62.4	33.3	27.2	43.3
	79.2	90.9	......	43.4	65.4
	106.	95.7	......	57.5	94.9
	158	93.2	49.2	99.4	ca 100
NP50E	7.88 – CMC	45.0	14.2	25.5	44.6
	15.8	94.0	......	......	......
	21.7	99.3	......	......	......
	23.6	......	......	......	63.5
	31.5	......	42.2	......	......
	43.3	98.3	......	28.9	89.5
	63.0	......	......	53.0	ca 100
	126.	......	72.6	99.5	ca 100
	189.	......	99.8	......	......
NP100E	10. – CMC	98.8	40.0	24.1	62.8
	20.	98.5	......	31.3	89.3
	30.	......	37.1	49.2	96.4
	60.	......	80.8	99.3	99.6
	80.	......	99.4	......	......
TDDGE	1.48 – CMC	......	4.1	17.3	zero
	213.	3.8	*	8.3	12.4
	426	13.7	8.2	......	9.4
TDPGE	1.65 – CMC	......	5.1	16.0	zero
	211.	14.9	8.5	16.7	21.6
	422.	40.8	56.6	66.6	72.1
PSML	1.1 – CMC	......	5.2	......	zero
	10.6	......	11.2	......	......
	106.	37.9	22.7	34.4	42.4
	212	76.7	32.0	45.3	58.8
	318	......	45.1	......	......

* Residual soil greater than original soil.

5. *Fatty Acid Soil Removal by Nonionic Surfactants*

—Table III shows that the 15, 20, and 30 ethylene oxide mole ratio (R) adducts of nonyl phenol are poor detergents of the 12–18 carbon saturated fatty acids at normal concentrations (to 1%). Detergency increases with increasing chain length of the 14, 16, and 18 carbon acid soils at the same concentration of the 30, 40, 50, and 100 R adducts. Removal of 12 carbon acid by the latter three adducts is considerably better than 14 carbon soil removal, and is substantially equivalent to the good detergency of the 18 carbon soil by these surfactants. Table IV emphasizes the abnormally high nonyl phenol adduct concentrations required to give good fatty acid detergency (2.7–3.8%). The results indicate that at the same concentration of 30, 40, 50, or 100 R adduct, detergency decreases as fatty acid soil HLB is decreased from 11.25–9.8, but then increases as soil HLB continues to decrease to 6.5. It is suggested that this is due to differences in the soil-substrate adhesive forces and in the extent of micellar solubilization existing in the soil HLB range. As soil HLB is decreased from 11.25–9.8 (going from a 12–14 carbon fatty acid), detergency is decreased because of the increase in the binding energy of the myristic acid to the substrate brought about by the increased van der Waals forces between the longer hydrocarbon chains. Further decrease of soil HLB from 9.8–6.5 (from a 14–18 carbon acid) results in increased micellar solubilization which more than counteracts the increased binding energy of the longer chain soil molecules, thus causing increased soil removal.

TABLE IV

Practical Level Detergency by Polyoxyethylated Nonyl Phenols

surfactant	R	molarity × 10^4			% fatty acid soil removal			
		HLB	M*	M/CMC	12C	14C	16C	18C
NPPGE	15	15.00	396.	360	78.1	73.4	77.0	81.1
NPEGE	20	16.00	349.	225	80.6	80.6	ca 100	98.9
NPTGE	30	17.20	176.	64	69.3	68.2	99.7	ca 100
NPTTGE	40	17.78	158	35	93.2	49.2	99.4	ca 100
NP50E	50	18.18	126.	16	......	72.6	99.5	ca 100
NP100E	100	19.05	60.	6	......	80.8	99.3	99.6

*—concentration giving ca 100% removal of 16 and 18 carbon soils.
CMC—critical micelle concentration.

Table IV also shows a sharp decrease in the M/CMC ratio with increasing ethylene oxide mole ratio, R, of nonyl phenol (where M = surfactant concentration giving ca 100% removal of 16 and 18 carbon fatty acid soil, and CMC = critical micelle concentration). Mathematical analysis reveals linearity of the R-log (M/CMC) and surfactant HLB-log (M/CMC) functions for values of R between 15–50 and 20–100, respectively. The validity of these semi-logarithmic functions is confirmed by the fact that they indicate linearity between R and surfactant HLB, a relationship previously reported (2). All adducts, with the exception of the 15 mole ratio one, give ca 100% removal of the 16 and 18 carbon acids.

6. *Fatty Acid HLB Values*—Because of the time required in determining either HLB (8) or hydrophile-lipophile characteristics by water titration (9) and cloud point (10), fatty acid HLB values were calculated from polar group hydrophobe-solubilizing powers. Since a carboxyl or hydroxyl group is equivalent to three methylene or methyl groups (11), and one ethylene oxide group is equivalent to one methylene group (11), while a carboxyl or hydroxyl group equals three ethylene oxide groups (10), hydrophile-lipophile characteristics of surfactants of known HLB can be calculated in terms of "net ethylene oxide solubilizing power" (NSP). First the value of the phenyl group which appears in many of the surfactants used to correlate HLB and NSP must be obtained. A comparison is made of the "NSP" values of two surfactants of the same HLB, one of which has a phenyl group. Negative values of the equivalent ethylene solubilizing powers are assigned the hydrophobic groups, and since the "NSP" values of the two surfactants are equal, the value of the phenyl group may be obtained as follows for two agents of 16.00 HLB:

NPEGE: $C_9H_{19}\cdot C_6H_4\cdot (OC_2H_4)_{20}\cdot OH$
$NSP = +20 + 30 - 9 - (C_6H_4) = 14 - (C_6H_4)$
TDPGE: $C_{13}H_{27}\cdot (OC_2H_4)_{15}\cdot OH$
$NSP = +15 + 3 - 13 = 5$
hence, $14 - (C_6H_4) = 5$
and, $(C_6H_4) = 9$

that is, nine ethylene oxide groups solubilize one phenyl group. Table V lists nonionic surfactants of known HLB whose "NSP" values have been computed as above. Fatty acid "NSP" values are now calculated (example following for palmitic acid) giving −8, −10, −12, and −14 for the 12, 14, 16, and 18 carbon members, respectively.

TABLE V

New Ethylene Oxide Solubilizing Powers (NSP)

surfactant	HLB	NSP
NP100E	19.05	85
NP50E	18.18	35
NPTTGE	17.78	25
NPTGE	17.20	15
NPEGE	16.00	5
NPPGE	15.00	0
NP9E *	12.20	− 6
NP6E *	10.80	− 9
NP4E *	8.80	−11
tetraethylene glycol monostearate	7.65	−13
diethylene glycol monostearate	4.73	−15

* ethylene oxide adduct of nonyl phenol with the number indicating ethylene oxide mole ratio.

palmitic acid: $C_{15}H_{31}\cdot COO\cdot H$
$NSP = 3 - 15 = -12$

Fatty acid HLB values may now be obtained by interpolation in Table V.

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