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## Correlation of Hard Surface Detergency, Soil, and Surfactant

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### Abstract

In the practical detergency range between the 90% soil removal point (the CC-1 concentration) and the point at twice the CC-1 concentration (the CC-2 point), hard surface (steel) detergency (D) is a linear function of micellar solubilization (S) such that  $D = K_1 S + K_2$ , for glyceryl trioleate, oleic acid, and lauryl alcohol soils. Equations of this form were obtained for glyceryl trioleate systems using polyethenoxyethers of nonyl phenol and tridecyl alcohol, polyoxyethylene sorbitan monolaurate, sodium dodecyl benzene sulphonate, and sodium oleate.

It was shown that the constants  $K_1$  and  $K_2$  of the detergency equation possess more than mathematical significance. Analysis of the equations for the 15, 20, and 40 ethylene oxide mole ratio adducts of nonyl phenol with glyceryl trioleate soil revealed that  $K_1$  varied linearly with HLB of the adducts and that the  $K_2$ -log interfacial tension function (at the CC-1 point) was linear. Examination of the equations for the 20, 50, and 100 mole ratio adducts of nonyl phenol with oleic acid soil indicated also that  $K_1$  was a function of HLB and that  $K_2$  was a function of interfacial tension (at the CC-1 point). The detergency equations of a single surfactant (sodium dodecyl benzene sulphonate) and three soils (triolein, lauryl alcohol, and oleic acid) indicated  $K_1$  was a function of soil dipole moment, and  $K_2$  was a function of soil surface tension.

### Introduction

THIS REPORT presents the derivations of correlations between hard surface (low carbon steel) detergency, certain properties of soils, and certain physicochemical factors of surfactants.

Recent studies of hard surface detergency in this laboratory (1) showed that for glyceryl trioleate-carbon steel and oleic acid-carbon steel systems, soil removal at the CMC (critical micelle concentration)

was low, but increased sharply with increasing concentration to about 90% detergency (CC-1 point), at which point it leveled off and approached 100% at a considerably smaller rate. This pattern of detergency variation was exhibited by anionics of the alkyl aryl sulphonate and unsaturated fatty acid soap types and by nonionics such as polyethenoxyethers of an alkyl phenol, polyethenoxyethers of a higher alcohol, and a fatty acid ester of a polyethenoxyethylated anhydro-sorbitol.

One of the reasons for the importance of the CC-1 point is that it is a naturally-occurring cut-off concentration below which the surfactant is unable to produce soil removal of a practical level (90%). The detergency data of our first report (1) indicate the need for an upper cut-off concentration (CC-2 point), above which detergency need not be considered. The latter point, which in this laboratory has been set at twice the CC-1 concentration, is required because of the low rate of change of detergency with concentration above the CC-1 point (for those surfactant-soil systems in which detergency continues to approach 100%). Most of our previously reported detergency data (1) were carried only to the CC-2 points.

Hence, because of the practical considerations necessitating the establishment of the CC-1 and CC-2 points, the correlations derived in this investigation apply to the CC-1 to CC-2 concentration range only.

A conclusion of the original paper (1) was that no correlation existed between hard surface detergency and absolute micellar solubilization as determined by a dye solubilization technique; i.e., various surfactants having, e.g., 95% detergency at certain concentrations did not have the same dye solubilization value at these concentrations. Further analyses of the data in this investigation have revealed the existence of detergency-solubilization correlation for the individual surfactants.

### Experimental

The experimental techniques (micellar solubilization, detergency and interfacial tension) and most of

the soils (glyceryl trioleate, oleic acid, and octanoic acid) and surfactants have been described (1). It is to be noted that dynamic solubilization and detergency procedures were used. Lauryl alcohol was also used as a soil; it possessed the following properties: surface tension at 28C = 28.3 dynes/cm; density at 28C = 0.831; it contained 58.7% dodecanol and 10 to 18 carbon homologs. The following polyethenoxyethers of nonyl phenol were studied in addition to those previously mentioned (1):

nonyl phenyl pentacontaethylene glycol ether - NP50E - CMC = .000788 molar

nonyl phenyl decacontaethylene glycol ether - NP100E - CMC = .00100 molar

The CMC values were calculated from the formula of Hsiao, et al. (2).

Octanoic acid soil removal by the 15, 20, 30, and 40 mole ratio ethylene oxide adducts of nonyl phenol, the 12 and 15 mole ratio adducts of tridecyl alcohol, and the nonionic PSML could be represented graphically by approximately linear detergency-concentration functions with zero slope and detergencies of about 63 to 70%. The 50 and 100 mole ratio adducts of nonyl phenol and the two soaps, sodium oleate and potassium laurate, gave octanoic acid detergency-concentration functions that were approximately linear with small positive slopes, detergency increasing from about 70% at the CMC to 90% at 6 (CMC) to 12 (CMC), Lauryl alcohol-carbon steel systems were characterized by CC-1 and CC-2 points.

The equations derived herein are based on the results of the original investigation (1), as well as on additional data on the previously reported soil-surfactant systems and new data on lauryl alcohol-surfactant systems.

Development of Detergency Functions

Although it has been shown (2) that over long concentration ranges (3 to 4 multiple spreads) at 100F the log solubilization-log concentration function is linear, examination of similar data at 180F (1) revealed the linearity of the simple solubilization-concentration function in the shorter CC-1 to CC-2 range (Fig. 1). In the latter range, plots of typical detergency-concentration data at 180F (Fig. 2) gave approximately linear relationships within the precision of the gravimetric detergency method. Since both detergency and solubilization were linear with respect to concentration in the CC-1 to CC-2 range, each with a positive slope, it followed mathematically that in this range the detergency-solubilization function was linear, as follows:

if,

- D = detergency, in % soil removal at 180F
- S = micellar solubilization, in mg Orange OT per 100 ml at 180F
- M = molar concentration
- C<sub>1</sub>, C<sub>2</sub>, C<sub>3</sub>, C<sub>4</sub>, C<sub>5</sub>, C<sub>6</sub>, C<sub>7</sub>, C<sub>8</sub>, C<sub>9</sub>, C<sub>10</sub>, C<sub>11</sub>, K<sub>1</sub>, K<sub>2</sub> = constants

then,

$$S = C_1 + C_2 M \text{---Figure 1}$$

$$C_2 M = S - C_1$$

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

and

$$D = C_5 + C_6 M \text{---Figure 2}$$

$$C_6 M = D - C_5$$

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

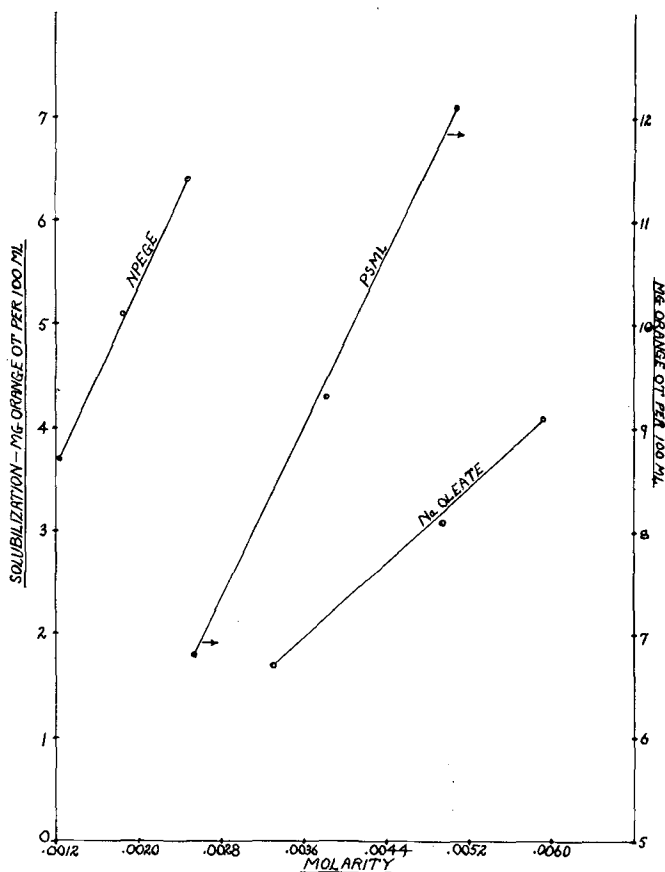


Fig. 1. Solubilization isotherms at 180F.

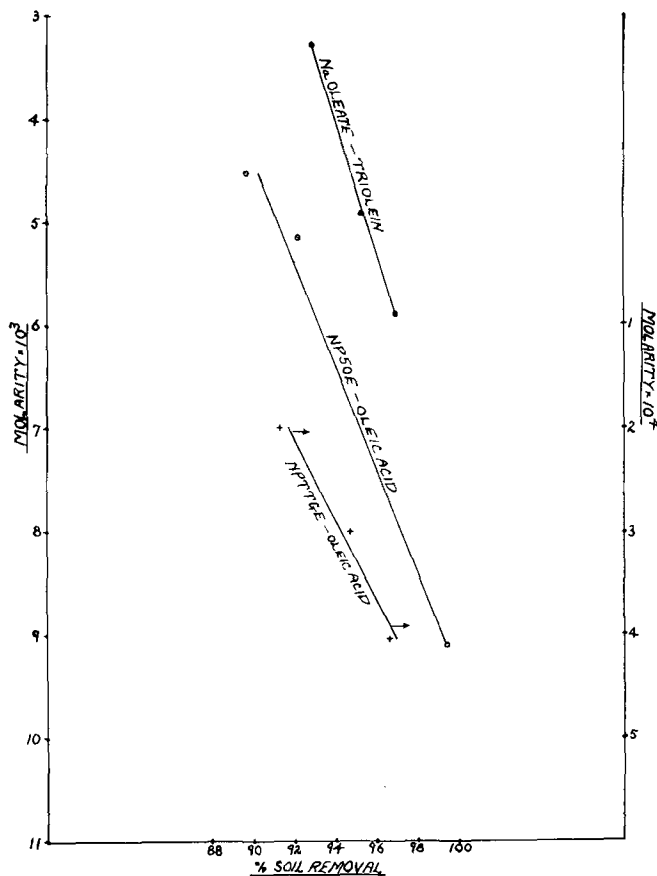


Fig. 2. Detergency isotherms at 180F.

therefore,

$$\begin{aligned} C_3 S - C_4 &= C_7 D - C_8 \\ C_7 D &= C_3 S - C_4 + C_8 = C_3 S + C_9 \\ D &= \frac{C_3}{C_7} S + \frac{C_9}{C_7} = C_{10} S + C_{11} \end{aligned}$$

or,

$$D = K_1 S + K_2$$

The linear plots of Figure 3 are considered to represent approximately the detergency-solubilization relationships in the relatively small but practical detergency range between the CC-1 and CC-2 points, for steel surfaces and glyceryl trioleate, oleic acid, and lauryl alcohol soils.

#### A. Detergency-Solubilization Equations for Glyceryl Trioleate Systems

Using the CC-1 to CC-2 data previously reported for glyceryl trioleate systems (1), the following equations can be obtained for the linear detergency-solubilization functions of the various surfactants studied:

##### Polyethenoxyethers of nonyl phenol

nonyl phenyl pentadecaethylene glycol ether -  
NPPGE -  $D = 3.20 S + 84.46$

nonyl phenyl eicosaethylene glycol ether -  
NPEGE -  $D = 2.55 S + 80.09$

nonyl phenyl tetraconta ethylene glycol ether -  
NPTTGE -  $D = 1.60 S + 89.22$

##### Polyethenoxyethers of tridecylalcohol

tridecyl dodecaethylene glycol ether -  
TDDGE -  $D = 1.59 S + 82.53$

tridecyl pentadecaethylene glycol ether -  
TDPGE -  $D = 1.15 S + 85.33$

polyoxyethylene sorbitan monolaurate -  
PSML -  $D = 0.91 S + 86.44$

sodium dodecyl benzene sulphonate -  
SDBS -  $D = 0.40 S + 88.13$

sodium oleate -  $D = 1.63 S + 90.20$

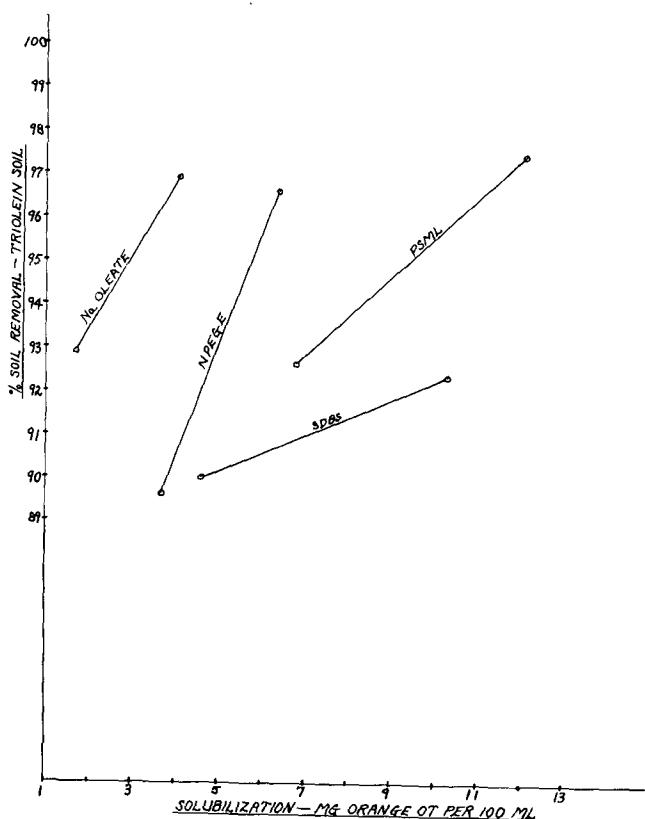


Fig. 3. Detergency-solubilization functions CC-1 to CC-2 range.

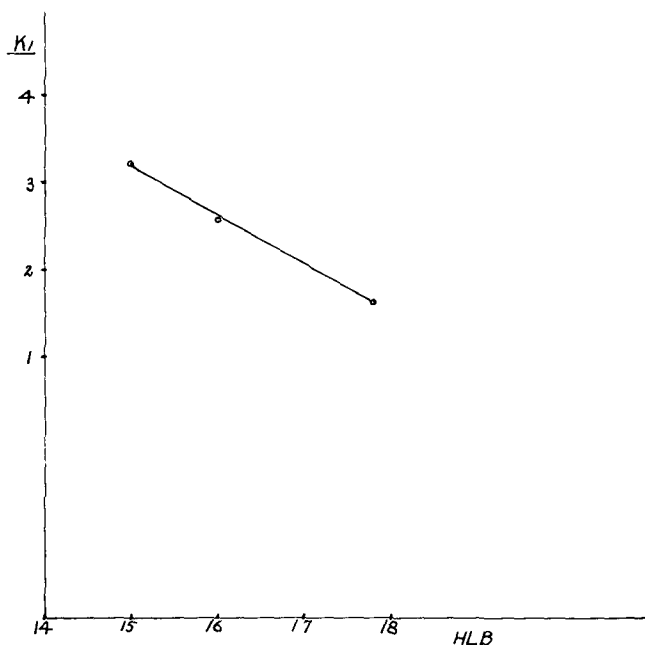


Fig. 4.  $K_1$ -HLB function for ethylene oxide adducts of nonyl phenol and triolein soil.

It is interesting to note that further analysis of the equations for the three analogs of nonyl phenol polyethenoxyethers led to more significant relationships. Since the equations are in the form of  $D = K_1 S + K_2$ , it can be shown that  $K_1$  varies linearly with the HLB values of the corresponding analogs (Fig. 4) and that the  $K_2$ -log interfacial tension (at the CC-1 point) function is also linear (Fig. 5). The data are as follows:

Analog	Mole ratio	$K_1$	$K_2$	HLB	Interfacial tension, ergs/cm <sup>2</sup> (at CC-1)
NPPGE	15	3.20	84.46	15.00	0.6
NPEGE	20	2.55	80.09	16.00	0.3
NPTTGE	40	1.60	89.22	17.78	1.3

The  $K_1$ -HLB function of Figure 4 may be expressed as:

$$K_1 = 11.95 - 0.58 (\text{HLB})$$

The equation for the  $K_2$ -interfacial tension relationship is:

$$K_2 = 87.59 + 14.34 \log (\text{IT})$$

where IT = interfacial tension at the CC-1 point, glyceryl trioleate soil, in ergs per cm<sup>2</sup>.

Hence the detergency-micellar solubilization correlation for polyethenoxyethers of nonyl phenol and glyceryl trioleate soil is:

$$D = [11.95 - 0.58(\text{HLB})] S + 14.34 \log (\text{IT}) + 87.59$$

It is of added interest that, for the aforementioned analogs, HLB is related to CMC (1) as follows:

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

Hence, the constants in the detergency equation,  $D = K_1 S + K_2$ , may possess more than mathematical significance.  $K_1$  seems to be a function of CMC and HLB. The latter is an important factor of the cryoscopic theory of detergency (3), which maintains that detergency results from the production of lamellar micelles in anisotropic solutions and that such formation is favored by low HLB nonionic agents.  $K_2$  of

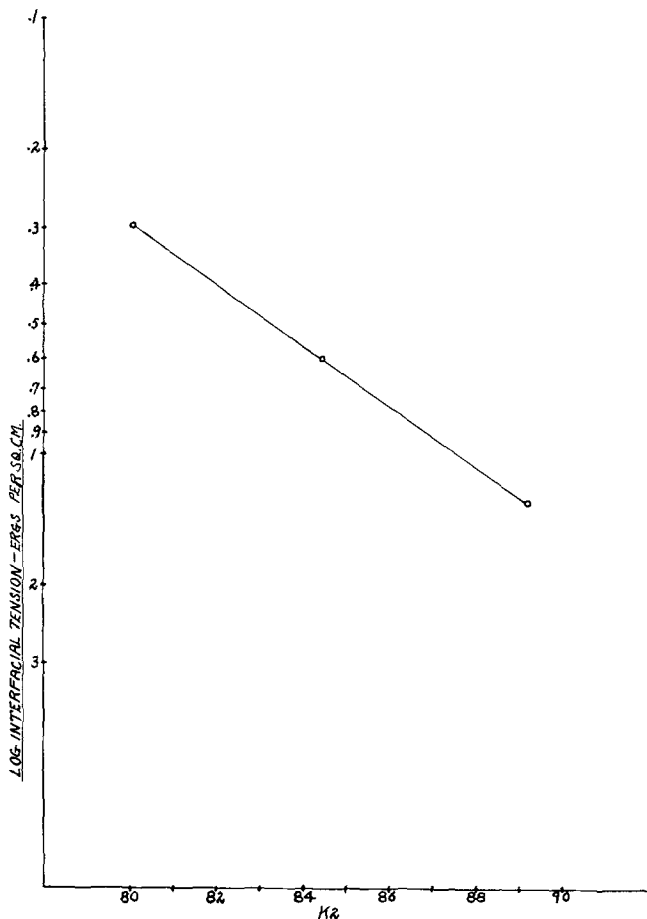


Fig. 5. Log interfacial tension function for ethylene oxide adducts of nonyl phenol and triolein soil.

the detergency equation could be considered a soil factor since it is a function of interfacial tension.

**B. Effect of Soil on Detergency-Solubilization Correlations of SDBS**

In preceding section A, interesting detergency relationships were developed for a series of analogs of nonyl phenol for a glyceryl trioleate soil. This section will consider the variation in the developed detergency-solubilization function ( $D = K_1 S + K_2$ ) of a single surfactant caused by variation of the soil. It should be remembered that the derivations are based on the unsophisticated relationship that the increase in detergency in the CC-1 to CC-2 range is linear. This relationship is reasonably reliable because differences between experimental soil removals and values calculated from linear detergency-concentration functions are of the order of the experimental error (2%).

TABLE I

Additional SDBS Detergency and Solubilization Data at 180F

Molarity	Soil	Detergency, % soil removal	Micellar solubilization, mg orange OT per 100 ml
.00900, CC-1	Lauryl alcohol	89.7	2.1
.0120		95.5	3.5
.0180		95.5	6.0
.00600, CC-1	Oleic acid	92.0	1.1
.00760		98.1	....
.0120		98.3	3.5

Table I lists detergency-solubilization data at 180F for SDBS-oleic acid and SDBS-lauryl alcohol systems (SDBS = anionic sodium dodecyl benzene sulphate). Figure 6 is a graphical representation of

this data showing the linear solubilization isotherm and averaged linear detergency isotherms, from which the detergency-solubilization functions may be derived as previously described herein. The results of such calculations give the following:

$$\begin{aligned} \text{lauryl alcohol soil} - D &= 0.95 S + 89.85 \\ \text{oleic acid soil} - D &= 1.55 S + 92.87 \end{aligned}$$

For glyceryl trioleate soil, the function (derived previously herein) is:

$$D = 0.40 S + 88.13$$

Again remembering that these functions are in the form of  $D = K_1 S + K_2$ , it can be shown that  $K_1$  is a simple function of soil polarity expressed in terms of dipole moment. The data are:

Soil	$K_1$	Dipole moment-Debyes	Dipole moment reference
Glyceryl trioleate.....	0.40	3.08	4
Lauryl alcohol.....	0.95	1.7	5
Oleic acid.....	1.55	1.009	6

The figures indicate linearity between  $K_1$  and log of dipole moment, as follows:

$$K_1 = 1.53 - 2.34 \log (\text{dipole moment})$$

It seems significant and more than fortuitous that the effect of soil variation on the detergency-solubilization function of a surfactant is related, in part at least, to polarity of the soil. A correlation exists between the constant  $K_2$  and soil surface tension. Taking the surface tensions of glyceryl trioleate, lauryl

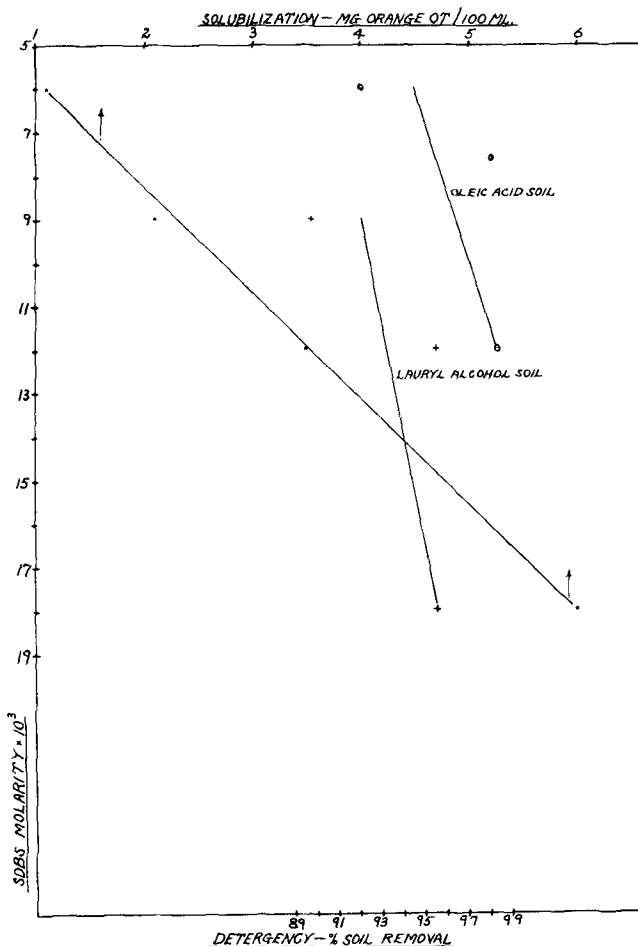


Fig. 6. Detergency and micellar solubilization isotherms for SDBS at 180F.

alcohol, and oleic acid as 31.6, 28.3, and 31.5 dynes per cm, respectively, it can be shown that:

$$(K_2 - 90.5)^2 = 6.45 - (\gamma - 30.8)^2$$

where,  $\gamma$  = soil surface tension in dynes per cm.

### C. Correlation of Detergency of Nonyl Phenol Polyethenoxyethers Using Oleic Acid Soil

In section A of this report, analyses of the detergent-solubilization equations for the three analogs of the nonyl phenol polyethenoxyethers using triolein soil indicated that the  $K_1$  of the equations varied linearly with the HLB values of the analogs and that the  $K_2$ -log interfacial tension function (at the CC-1 point) was linear.

It was now considered essential to determine the correlation, if any, existing for analogs of the same surfactant when using oleic acid as the soil. Table II contains the detergency-solubilization data at 180F, using oleic acid soil, for the 20, 50, and 100 ethylene oxide mole ratio adducts of nonyl phenol. The 30 and 40 mole ratio analogs were not included in this analysis because their detergency isotherms deviated in part from the normal characteristics of our CC-1 system. While both possessed CC-1 and CC-2 points,

TABLE II  
Nonyl Phenol Polyethenoxyether Detergency-Solubilization Data at 180F—Oleic Acid Soil

Adduct	Ethylene oxide mole ratio	Molarity	Detergency, % soil removal	Micellar solubilization, mg orange OT per 100 ml
NPEGE	20	.00152, CC-1	90.0	4.2 at .00145M
		.00291, CC-2	96.5	8.18
		.00249	96.5	7.0
NP50E	50	.00455, CC-1	89.7	5.07
		.00910, CC-2	99.4	10.08
		.00517	93.5	.....
NP100E	100	.00351, CC-1	90.1	7.4
		.00702, CC-2	97.7	14.5
		.00400	97.7	.....

the CMC of the former coincided with its CC-1, and the CMC of the latter was larger than its CC-2 concentration. From the data of Table II, the following equations were computed, the terms having the same significance as heretofore:

Adduct	Ethylene oxide ratio	Equation
NPEGE.....	20	$D = 1.31 S + 85.75$
NP50E.....	50	$D = 1.66 S + 82.62$
NP100E.....	100	$D = 0.60 S + 89.06$

Remembering that the equations are in the form of  $D = K_1 S + K_2$ , and utilizing the following additional information:

Adduct	$K_1$	$K_2$	HLB	Interfacial tension at CC-1, ergs per cm <sup>2</sup>
NPEGE.....	1.31	85.75	16.00	3.0
NP50E.....	1.66	82.62	18.18	3.4
NP100E.....	0.60	89.06	19.05	3.2

It can be shown that  $K_1$  varies parabolically with HLB; viz.,

$$K_1 = 2.24 - \frac{(\text{HLB} - 17.3)^2}{1.85}$$

A relationship also exists between  $K_2$  and the interfacial tension, as follows:

$$(K_2 - 86.25)^2 = 264.06 - (\text{IT} - 19.25)^2$$

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## Graphic Aid for Interpreting Gas Chromatograms<sup>1</sup>

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### Abstract

A simple semilogarithm plot of elution volumes can be constructed as an aid to identify components that are members of the same homologous series. This technique is especially useful in organoleptic and flavor studies for identifying small peaks in any gas chromatogram. The method is applicable to chromatograms containing 20 or more peaks, which do not have to be completely resolved. Any member of the homologous series within 4 or 5 carbons of the unknown can be used as a standard for identification. The tentative plots also help in examining chromatograms obtained with hydrogen flame or with  $\beta$  ray-type detector equipment where samples are too small for collection and identification by chemical and physical tests.

THE LINEAR RELATIONSHIP of the carbon number to the logarithm of the retention volume has been widely used for identification and expression of results in the terms of one component (2,5,6).

<sup>1</sup> Presented at fall meeting, American Oil Chemists' Society, 1961.

<sup>2</sup> This is a laboratory of the Northern Utilization Research and Development Division, Agricultural Research Service, U.S.D.A.

The log-log plot (2-4) allows a fairly accurate identification of unknown constituents when more than one suitable standard is available. Many extracts of natural products present a whole series of unknowns in a single sample, such as the volatiles from autoxidation of fats and the flavor essence of natural fruits. In many cases standards for the identification of these materials are not available. Because many of these substances are homologs, they follow the linear plot of carbon number vs. the logarithm of the retention volume. The problem of identifying the unknowns is helped tremendously if they can be grouped together as a homologous series. The usual preliminary separations involving alkali washing, preferential solubility, or removal of insoluble derivatives all tend to concentrate certain of the homologs. The graphic technique aids in the identification of a large number of unknown components where many of them belong to one or more homologous series.

Retention volumes or retention times are plotted in the usual fashion on a semilogarithm paper. At each retention time lines are drawn across the full width of the paper, i.e., parallel to the carbon number base. If colored lines are drawn to contrast with the lines