Dimensional Analysis of the Detergency Process for Systems Containing Multicomponent Soils

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Abstract

Dimensional analysis of the detergency process has been extended from soil-surfactant systems which contain a single polar soil to those with binary and ternary component soils which contain a nonpolar ingredient. This was made possible by replacement of the soil dipole moment variable by the proportional square root of orientation polarization (P_o) and by establishment of the validity of the empirical volume fraction additivity of the ingredient P_o values of binary polar—polar mixtures by using the classical dilute solution—solute (P_2) extrapolation procedure with a chemical oscillometer.

Introduction

EXTENSIVE DETERGENCY and physicochemical studies at this laboratory have led to the derivation by dimensional analysis of a valid set of three dimensionless products from six soil and surfactant variables of the detergency process (1–4). A log-log plot of two of the products at parameter values of the third form a detergency diagram for the 90–100% soil removal range which consists of a family of parallel lines with a 45° negative slope. The validations were obtained from data on soil-surfactant systems in which the surfactants were commercial, hard and soft ethoxylated alkylphenols, soft ethoxylated primary and secondary alcohols, hard and soft anionics. The soils, all single polar materials, included a fatty alcohol, an amine, an ester, and saturated and unsaturated fatty acids. Since a dimensional analysis cannot be performed with a dimensionless dependent variable, detergency or percentage of soil removal in this case, it is important to note that the analysis was made possible by accepting Schwartz's model of detergency (5) and postulating the dimensions of the latter as $M \times L$, where M = mass, L = length, and T = time. Percentage soil removal figures were used in the validation calculations because it was shown that they were proportional to $M \times L$.

This paper reports the results of work which was initiated to overcome the limitations of the previous studies. Since one of the variables in the valid dimensional analysis is soil dipole moment, nonpolar soils with zero dipole moment values could not be included among the systems previously represented in the detergency diagram. Furthermore, while the initial studies involved single polar soils, it is obvious that in actual practice soils may consist of mixtures of polar and nonpolar components. The elimination of these deficiencies was attempted by a series of dimensional analyses and corresponding validation checks involving a) the replacement of soil dipole moment by its proportional value, the square root of orientation polarization, b) validation of the assumption of volume fraction additivity of ingredient orientation polarizations of soil mixtures by using the conventional "dilute solution" method (11), and c) determination of the extent to which a) and b) permitted the use of polar-nonpolar and polar-polar soil mixtures with the dimensional analysis detergency correlation diagram.

Theory

The dimensionless products of the valid dimensional analysis (3) are

$$\pi_1 = \frac{D \times (\gamma CMC)^{0.8}}{(DM)^{1.6} \times C}$$

$$\pi_2 = \frac{C}{CMC}$$

$$\pi_3 = \frac{V}{(DM)^{0.2} \times (\gamma CMC)^{0.4} \times (CMC)^{0.5}}$$

The variables in these products and their dimensions are

Variable	Symbol	Dimensions
Detergency, % soil removal	D	ML
Concentration, molarity	C	M/L^3
Critical micelle concentration, molarity	CMC	M/L^3
Surface tension at CMC, dynes/cm	γCMC	M/T^2
Soil dipole moment, debyes	DM	$M^{0.5}L^{2.5}/T$
Soil viscosity, absolute, 185F, cp	V	M/LT

The relation of dipole moment to orientation polarization, P_o, follows from the Debye equation for the total polarization of a polar molecule:

$$P = P_E + P_A + P_o = P_E + P_A + \frac{4\pi N}{9kT}(DM)^2$$

where

P = total molar polarization
P_E = electronic polarization
P_A = atomic polarization
N = Avogadro's Number = 6.023×10^{23}
k = Boltzmann's constant = 1.38×10^{-16}
T = absolute temperature, °K

Thus at constant temperature (DM) is proportional to $(P_o)^{0.5}$, and at 25C, with (DM) expressed in debyes,

$$P_o = \frac{4\pi \times 6.023 \times 10^{23} \times 10^{-36} \times}{9 \times 1.38 \times 10^{-16} \times 298}(DM)^2 = 20.45\ (DM)^2$$

$(P_o^{0.5})$ may replace (DM) in products π_1 and π_3 to give the following:

$$\pi_1 = \frac{D \times (\gamma CMC)^{0.8}}{(P_o)^{0.8} \times C}$$

$$\pi_3 = \frac{V}{(P_o)^{0.1} \times (\gamma CMC)^{0.4} \times (CMC)^{0.5}}$$

Furthermore, in a dilute solution of a polar material in a nonpolar solvent, molar polarizations are additive,

$$P_{12} = x_1 P_1 + x_2 P_2$$

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TABLE I

Polar Soils

Material	Absolute viscosity, cp, at 185F	Dipole moment debyes	n_D at 25C	d_2 at 25C
Octadecylamine MP 47–51C	2.868	1.3 (6)		
Lauryl alcohol, 98%	2.480	1.6 (7)	1.4405	.831
Oleic acid, USP	5.294	1.009 (8)	1.4583	.888
Ethyl stearate MP 30–31C	2.200	1.7[a]		

[a] Calculated from group moments; dipole moment literature references given.

TABLE II

Polar-Nonpolar Binary Soil Mixtures

Mixture	Mixture ratio, by weight	X_2 mole fraction solute
$\frac{\text{Lauryl alcohol}}{\text{TMPD}}$	1:19	.0704
	1:4	.2645
	1:1	.5899
	2:1	.7420
	3:1	.8119
	4:1	.8519
$\frac{\text{Oleic acid}}{\text{TMPD}}$	1:1	.4869
	2:1	.6549
	4:1	.7915

where

P_{12} = total polarization of the mixture, in ml
P_1 = molar polarization of the nonpolar component
x_1 = mole fraction of the nonpolar component
P_2 = molar polarization of the polar component
x_2 = mole fraction of the polar component

P_{12} is also given by the equation,

$$P_{12} = \frac{E_{12} - 1}{E_{12} + 2} \times \frac{x_1 M_1 + x_2 M_2}{d_{12}}$$

where

E_{12} = dielectric constant of the mixture
d_{12} = density of mixture
M_1 = molecular weight of nonpolar component
M_2 = molecular weight of polar component

Experimental Section

Materials

The polar soils were those previously used. Their constants are given in Table I. The liquid 2, 6, 10, 14-tetramethylpentadecane (TMPD), density = 0.780 and index of refraction (n_D) = 1.4369 at 25C, as determined in this laboratory, was the nonpolar ingredient in the binary polar-nonpolar soil mixtures. It provided as difficult a soil removal task as the polar soils, in contrast to other nonpolar substances examined. By using a two-minute screening test in hot water at 180F, detergencies of eicosane, paraffin oil of 135 SUS at 100F, and TMPD soils were 89%, 77%, and 41% respectively. Table II lists the polar-nonpolar mixtures prepared by weighing the components on an analytical balance, and their physical and chemical constants. Table III gives the polar-polar mixtures used, similarly prepared.

The following commercial, 100% active, ethoxylated nonionic surfactants were used in conjunction with the aforementioned soils and soil mixtures: a) 11 and 15 ethylene oxide (EO) mole ratio adducts of straight-chain nonylphenol; b) 12, 15, and 20 (EO) mole ratio adducts of a C_{13} average linear secondary alcohol; c) 20 (EO) mole ratio adduct of oleylalcohol; d) 9 (EO) mole ratio adduct of C_{12-15} ($C_{13.5}$ average) primary alcohol; and e) 7.4 (EO) mole ratio adduct of C_{12-18} (C_{14} average) primary alcohol.

Commercial grade sodium lauryl sulfate (SDS) and branched-chain sodium dodecyl benzene sulfonate (SDBS) were also used. Table IV gives the CMC and γCMC data for all surfactants studied; all data were obtained in this laboratory (9).

Methods

Detergency and surface tension were determined as outlined in previous papers (9). Index of refraction and density were obtained with an Abbe refractometer and a pycnometer equipped with a thermometer and a capped overflow tube respectively.

Dielectric constants were determined with a Sargent chemical oscillometer by using the small cell and holder with 10-ml samples. Cell constants were obtained at 24.8–25.2C by using USP chloroform and ACS benzene (.01% H_2O) as standards; dielectric constants were 4.800 and 2.274 respectively (10). The cell constants were checked by measuring the dielectric constants of ACS toluene (0.05% H_2O) and ACS CCl_4 (0.01% H_2O), obtaining values of 2.378 and 2.223 respectively, in comparison with the standard values of 2.379 and 2.228 respectively (10).

TABLE IV

Surfactant Surface Tension Data

Surfactant Hydrophobe	No. of EO[a]	CMC molarity	γCMC dynes/cm	Temp. °C
Straight-chain nonylphenol	11	.0000247	31.5	28
	15	.0000271	35.3	28
C_{13} average secondary alcohol	12	.0000867	31.4	28
	15	.000128	33.0	28
	20	.000226	33.9	28
Oleyl alcohol	20	.00000465	39.6	28
$C_{13.5}$ average primary alcohol	9	.0000149	30.2	28
C_{14} average primary alcohol	7.4	.0000173	28.0	28
Sodium lauryl sulphate		.00149	36.3	28
Sodium dodecyl benzene sulphonate (branched chain)		.00353	32.6	26

[a] Moles ethylene oxide.

TABLE III

Polar-Polar Binary Soil Mixtures

Mixture	Mixture ratio by weight	Mole Fraction		Volume Fraction		E_{12}	Viscosity cp, 185F	d_{12} 25C	n_D 25C
		Oleic acid	Lauryl alc	Oleic acid	Lauryl alc				
$\frac{\text{Oleic acid}}{\text{Lauryl alcohol}}$	1:4	.14157	.85843	.18960	.81040	4.712	2.876	.841	1.4442
	1:3			.23777	.76223	4.436	3.003	.844	1.4450
	1:2			.31876	.68124	4.057	3.160	.849	1.4466
	1:1	.39746	.60254	.48342	.51658	3.427	3.559	.859	1.4496
	2:1			.65176	.34824	2.988	3.982	.868	1.4525
	4:1	.72517	.27483	.78917	.21083		4.396	.876	1.4549
$\frac{\text{Ethyl stearate}}{\text{Lauryl alcohol}}$	1:4			..........[a]	.83574		2.354		
	1:3			....	.79235		2.327		
	1:1			....	.55985		2.115		
$\frac{\text{Ethyl stearate}}{\text{Octadecylamine}}$	1:1	..........[c]					.....[b] 2.261		

[a] Volume fraction ethyl stearate = 1 − (volume fraction lauryl alcohol); density ethyl stearate = 1.057 at 20C.
[b] Viscosity at 185F of this system is meaningless due to interaction of ingredients with liberation of C_2H_5OH vapor. However, π_3 calculated from viscosity determined within 5 min of melting at 185F had a value of 72.8.
[c] Volume fraction octadecylamine = .56615; density octadecylamine = 0.81 at 20C.

In the first part of this investigation, in confirmation of the validity of substituting $(P_o)^{.5}$ for (DM) in dimensionless products π_1 and π_3, P_o was obtained from the equation given in the previous section, $P_o = 20.45\ (DM)^2$, by using the (DM) values of Table I. The calculated polarizations in ml were 59.10, 52.35, 34.56, and 20.82 for ethyl stearate, lauryl alcohol, octadecylamine, and oleic acid, respectively.

The next phase of this report covered the study of lauryl alcohol-TMPD and oleic acid-TMPD, polar-nonpolar soil mixtures, all of which were solutions at ambient room temperatures in the ratios listed in Table II. It was found that a simple treatment of the data of these mixtures gave surprisingly consistent, usable, and valid detergency diagram plots. The value of P_o of the polar ingredient was used in calculating dimensionless product π_1 of the mixtures. The log-log detergency diagram plots of the π_1–π_2 points for all ratios of lauryl alcohol-TMPD mixtures fell on the π_3 parameter of lauryl alcohol alone, using the same surfactant. Similarly π_1–π_2 plots of all ratios of oleic acid-TMPD mixtures fell on the π_3 parameter of the oleic acid alone; the same surfactant was used in all cases.

In order to treat polar-polar binary soil detergency data by dimensional analysis, it was necessary to adopt a working hypothesis, which assumed first that such a mixture possessed an effective or resultant orientation polarization and, second, that the latter could be determined experimentally with the "dilute solution" extrapolation method (11) by considering it to be an individual entity. By using C_6H_6 as the nonpolar solvent, six to seven mixture polarizations, P_{12} (for example, of C_6H_6 solutions of a definite weight ratio of oleic acid and lauryl alcohol), were obtained in the 0.006–0.02 x_2 (total polar solute mole fraction) concentration range from corresponding measurements of dielectric constant (E_{12}) and density (d_{12}), as follows:

$$P_{12} = \frac{E_{12} - 1}{E_{12} + 2} \times \frac{x_1M_1 + x_2M_2}{d_{12}}$$

M_2 was the average molecular weight of the oleic acid-lauryl alcohol mixture and was calculated in the usual manner. The constant P_1 of C_6H_6 was calculated by the Mosotti-Clausius equation from measurements of its dielectric constant and density:

$$P_1 = \frac{E_1 - 1}{E_1 + 2} \times \frac{M_1}{d_1}$$

The P_2 values in the C_6H_6 solutions followed from the equation:

$$P_2 = \frac{P_{12} - P_1}{x_2} + P_1$$

Extrapolation of the P_2 values to $x_2 = 0$, using least squares, gave $P_{2\infty}$, the effective or resultant molar polarization of the oleic acid-lauryl alcohol mixture at infinite dilution. P_{2E} was then calculated by the Lorentz-Lorenz equation:

$$P_{2E} = \frac{M_2}{d_2}\ \frac{n_2^2 - 1}{n_2^2 + 2}$$

where M_2 was the average molecular weight of the oleic acid-lauryl alcohol mixture and n_2 was its refractive index. Finally, by taking P_{2A} as 5% of P_{2E}, the effective orientation polarization of the mixture was obtained:

$$P_o \text{ mixture} = P_{2\infty} - P_{2E} - P_{2A}$$

In this study the effective orientation polarization values of 1:4, 1:1, and 4:1 ratios by weight of oleic acid and lauryl alcohol were determined as just outlined. The second part of the working hypothesis, adopted for use with polar-polar binary soils and incorporated to keep the dimensional-analysis, detergency-correlation method as free as possible from time-consuming experimental work, was the assumption that the effective orientation polarization of such mixtures could be estimated by the volume fraction additivity of the orientation polarization values of the two ingredients. The latter values, of course, are calculated from literature dipole moments.

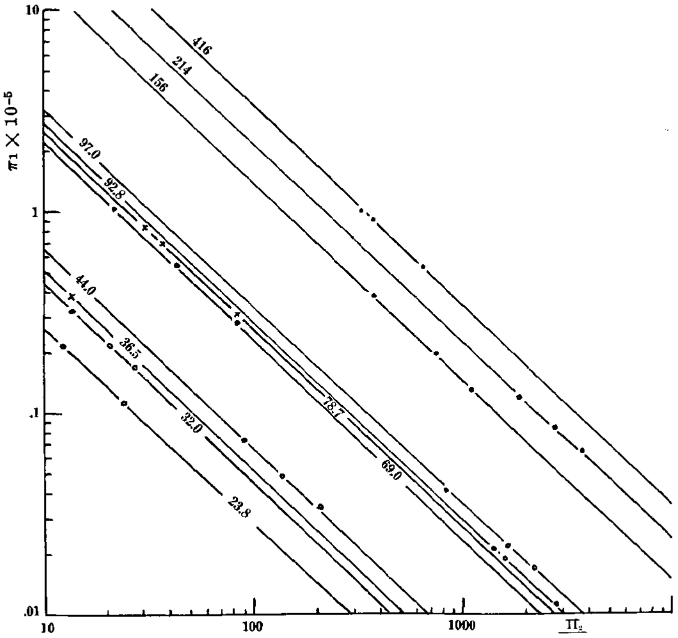

FIG. 1. Dimensional analysis No. 9-C with (DM) = K $(P_o)^{.5}$—validating systems at π_3 95, 74, 39.6, 24.1, and 10.3 not shown.

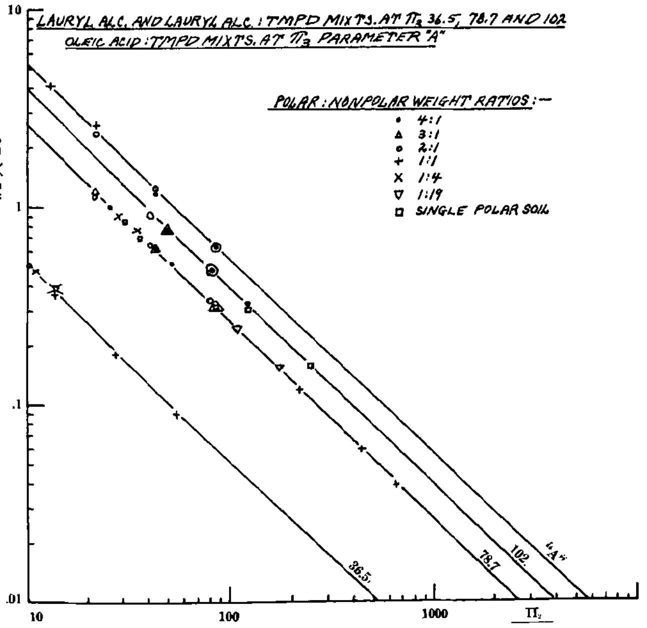

FIG. 2. D.A. No. 9-C with polar-nonpolar soil mixtures; π_3 78.7 and "A"—15 (EO) adduct of straight-chain nonylphenol; π_3 102—12 (EO) adduct of 13.5C average primary alcohol; π_3 36.5—15 (EO) adduct of 13C average secondary alcohol.

Comparisons of the experimentally determined "effective" or "resultant" orientation polarizations of the 1:4, 1:1, and 4:1 weight ratio mixtures of oleic acid and lauryl alcohol with calculated values, which were based on volume fraction additivity of the ingredient orientation polarizations, showed good agreement. The deviations averaged −6.7% and were smaller for the mixtures that contained a larger proportion of the more polar ingredient (it was speculated that the agreement would be even better when ingredient polarities were nearly the same). Based on the preceding tests, detergency diagram π_1 and π_3 values for soil-surfactant systems containing binary polar-polar soil mixtures were obtained by using calculated "effective" mixture orientation polarizations.

TABLE VI

Experimental and Calculated Orientation Polarization Data

Material	Experimental P_o ml	Calculated P_o[a] ml	Percentage of deviation
Oleic acid	17.23		
Lauryl alcohol	60.59		
Ethyl stearate[b]	58.19		
1 oleic acid:4 lauryl alcohol by wt	55.86	52.37	− 6.2
1 oleic acid:1 lauryl alcohol by wt	40.86	39.63	− 3.0
4 oleic acid:1 lauryl alcohol by wt	29.61	26.37	−10.9

[a] On basis of volume fraction additivity of ingredient experimental P_o values given in column 2.

[b] Calculated P_o of ethyl stearate (based on dipole moment of 1.7 debyes determined from group moments) = 59.10 ml.

Results

Orientation Polarization in Dimensionless Products π_1 and π_3. Fig. 1, a graphical representation of detergency and dimensionless product data of 16 soil-surfactant systems, for which π_1 and π_3 were calculated with $(P_o)^{.8}$ and $(P_o)^{.1}$, substituted for the $(DM)^{1.6}$ and $(DM)^{.2}$ terms respectively, indicates the validity of the substitutions, as was expected theoretically. Since $(P_o)^{.5}$ is proportional to (DM), it may replace the latter in the dimensionless products (14).

Dimensional Analyses of Systems with Binary Polar-Nonpolar Soil Mixtures. Fig. 2 is a plot of the detergency and dimensionless product data; the latter were obtained with the P_o variable, instead of dipole moment, for 13 systems consisting of three surfactants and lauryl alcohol:TMPD soil mixtures with weight ratios ranging from 4:1 to 1:19, also for three systems containing oleic acid:TMPD soil mixtures with weight ratios of 4:1, 2:1, and 1:1. Similar plots for systems of lauryl alcohol soil and each of the three surfactants that were used with the binary mixtures are also given. It will be noted that Fig. 2 consists of a family of four parallel π_3 parameters labelled 36.5, 78.7, 102, and "A," also that π_3 78.7 is the regular π_1–π_2 plot of the system containing the single soil, lauryl alcohol, and the nonionic 15 ethylene oxide (EO) mole ratio adduct of straight-chain nonylphenol, NP-15(EO). It is also seen that the π_1–π_2 plots of the six polar-nonpolar lauryl alcohol-TMPD soil mixture systems with NP-15(EO) fall on the π_3 78.7 parameter. It will be remembered from the Methods section that plots of systems containing a binary polar-nonpolar soil on the dimensional analysis detergency diagram are made possible by using the P_o value of the polar component of the mixture in calculating π_1 and disregarding the normally-calculated π_3 value. This purely empirical but practical and usable procedure is confirmed by analogous results obtained with the π_3 parameters 36.5 and 102. Parameter "A," the plot of the π_1–π_2 dimensional analysis data for all three oleic acid-TMPD soil mixture (4:1, 2:1, and 1:1, by weight) systems with NP-15(EO), provides a further validation of the procedure. Since NP-15(EO) cannot give 90–100% detergency of oleic acid soil alone under the standard soil removal conditions (9), no π_1–π_2–π_3 data are available for this system (0.60% NP-15[EO] solution gives 88.3% soil removal; but in 1.2% NP-15[EO] solution, detergency falls off to 82%). The numerical value of parameter "A" may be estimated from its proximity to known parameters.

Dilute Solution-Extrapolation Determination of Orientation Polarization. As stated previously, it was thought that, in order to be a practical tool in detergency correlation, the dimensional analysis procedure must not be involved in experimental determinations of soil mixture P_o data. The latter test methods were used, however, to establish the validity of an empirical volume fraction additivity of the ingredient P_o values of a binary polar-polar soil mixture to obtain an "effective" mixture, P_o, for subsequent use in computing π_1 and π_3. Tables V and VI contain some of the data accumulated in a series of tests which indicate good agreement between such calculated "effective" orientation polarizations and experimental values determined by the conventional dilute solution-extrapolation method outlined in the Methods section (11). In Table V dielectric constant (E) and density (d) measurements of the single polar materials, ethyl stearate, lauryl alcohol, and oleic acid, each in benzene solution at a number of low concentrations, are reduced in each case to a series of molar solute polarizations, P_2 (Methods section). The latter were plotted against the solute mole fraction, x_2, and extrapolated to $x_2 = 0$; $P_{2\infty}$ of ethyl stearate was obtained by a

TABLE V

Dilute Solution-Extrapolation Data for Determining P_o of Single Polar Materials, 25 ± 0.2C[a]

Mixture	Approx. Mixt. Ratio, by weight	x_2	E_{12}	P_{12}	x_1P_1	x_2P_2	P_2	d_{12} at 25C
Ethyl stearate Benzene	1:30	.00830	2.301	27.77	26.47	1.30	156.63	0.872
	1:25	.00996	2.308	28.01	26.42	1.59	159.64	0.872
	1:17	.01470	2.323	28.66	26.30	2.36	160.54	0.871
	1:10	.02503	2.357	30.10	26.02	4.08	163.00	0.869
	1:8	.02918	2.370	30.65	25.91	4.74	162.44	0.869
Lauryl alcohol Benzene	1:52	.00820	2.305	27.48	26.47	1.01	123.17	0.870
	1:28	.01504	2.331	28.15	26.29	1.86	123.67	0.870
	1:19	.02241	2.358	28.87	26.09	2.78	124.05	0.869
	1:14	.02927	2.379	29.47	25.91	3.56	121.63	0.869
Oleic acid Benzene	1:33	.00841	2.280	27.36	26.47	0.89	105.83	0.873
	1:19	.01468	2.282	27.82	26.30	1.52	103.54	0.873
	[illegible]	.02222	2.283	28.36	26.10	2.26	101.71	0.873
	1:9	.02932	2.286	28.90	25.91	2.99	101.98	0.873

[a] For benzene: $E_1 = 2.273$; $d_1 = 0.872$ at 25C; $P_1 = 26.69$ by Mosotti-Clausius equation; and $x_1 = 1 - x_2$.

Least Squares treatment. It is to be noted that the P_2 values of lauryl alcohol and ethyl stearate decrease with decreasing x_2 (ethyl alcohol exhibits the same characteristics in C_6H_6 solution, according to Reference 11) whereas the P_2 values of oleic acid increase with decreasing x_2 (the more usual phenomenon). Table VI has the P_o values of these polar materials, resulting from the extrapolations and further treatments with the Debye equation. These experimental values are used in the subsequent volume fraction additivity checks. Similar data to those in Table V, for benzene solutions of varying low concentrations of 1:4, 1:1, and 4:1, by weight, mixtures of oleic acid and lauryl alcohol lead to the "effective" mixture P_o values listed in Table VI. The total solute molar polarization in each case increased with the decreasing total solute mole fraction; and the value at infinite dilution for each mixture was determined by Least Squares. The agreement between calculated and experimental P_o values of the polar-polar mixtures in Table VI is considered good; the average deviation is −6.7%. On this basis it was decided to use volume fraction additivity of ingredient P_o values for determining the "effective" P_o of binary polar-polar soil mixtures in subsequent dimensional analysis correlation studies.

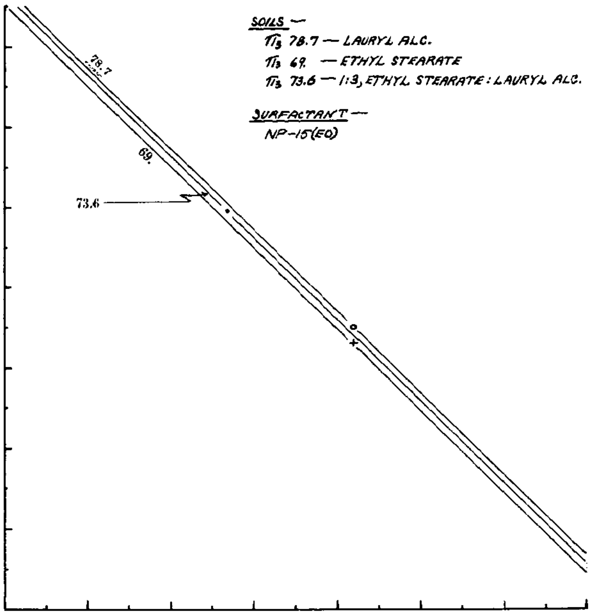

FIG. 4. D.A. No. 9-C with polar-polar, ethyl stearate:lauryl alcohol soils and NP-15 (EO).

Dimensional Analyses of Systems with Binary Polar-Polar Soil Mixtures. Fig. 3 is a plot of detergency and dimensional analysis data of soil-surfactant systems containing binary polar-polar soils; the dimensionless products were obtained by using "effective" P_o values calculated with the volume fraction additivity hypothesis and relating to oleic acid:lauryl alcohol soil mixtures (80:20 to 20:80% by weight oleic acid to lauryl alcohol) and the anionic surfactant, sodium lauryl sulfate (SDS). It is to be noted that these systems correlate perfectly (in π_3 value and position) between themselves and with the two systems representing the individual soils, oleic acid and lauryl alcohol; the same surfactant was used. Fig. 4 represents detergency and dimensional analysis data for a series of soil-surfactant systems comprising polar:polar, ethyl stearate:lauryl alcohol soil mixtures in various ratios by weight with the nonionic surfactant NP-15(EO) together with the two systems consisting of the ingredients alone with NP-15(EO).

The value and position of the π_3 parameter of the soil mixture system correlate with the values and positions of the π_3 parameters of the ingredients and the same surfactant. In this region of the dimensional analysis diagram the experimental accuracy, although adequate for estimating the detergency of a soil (or soil mixture)-surfactant system, is not sufficient to differentiate between π_3 parameters varying 1–2 units in value. Thus parameter π_3 73.6 of Fig. 4 is not significantly different from parameter π_3 74.5, a system which is not plotted. Fig. 5 represents a system comprising a polar:polar, ethyl stearate:octadecylamine soil mixture with the nonionic NP-15(EO), also systems of the ingredients with the same surfactant;

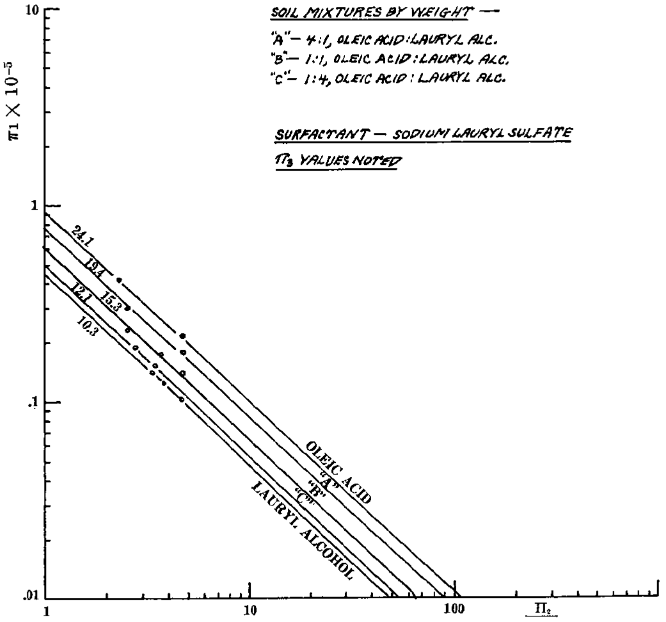

FIG. 3. Dimensional analysis No. 9-C with polar-polar soil mixtures. Soil mixtures by weight.

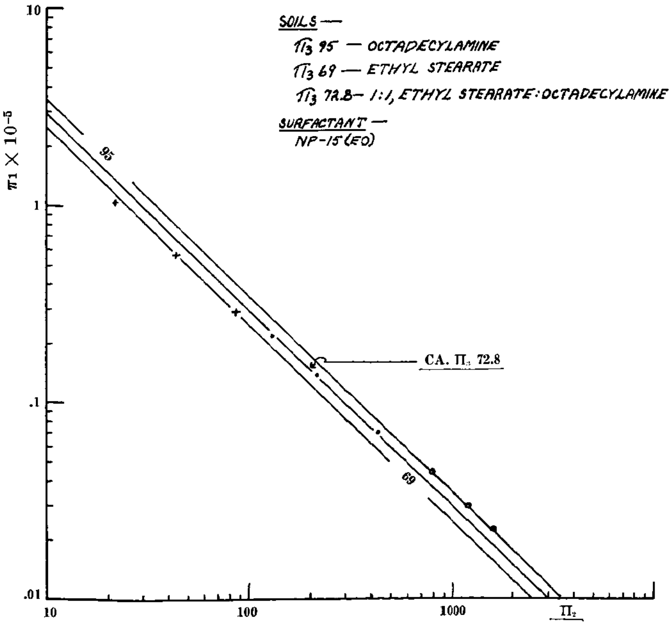

FIG. 5. D.A. No. 9-C with polar-polar, ethyl stearate-octadecylamine soils and NP-15 (EO).

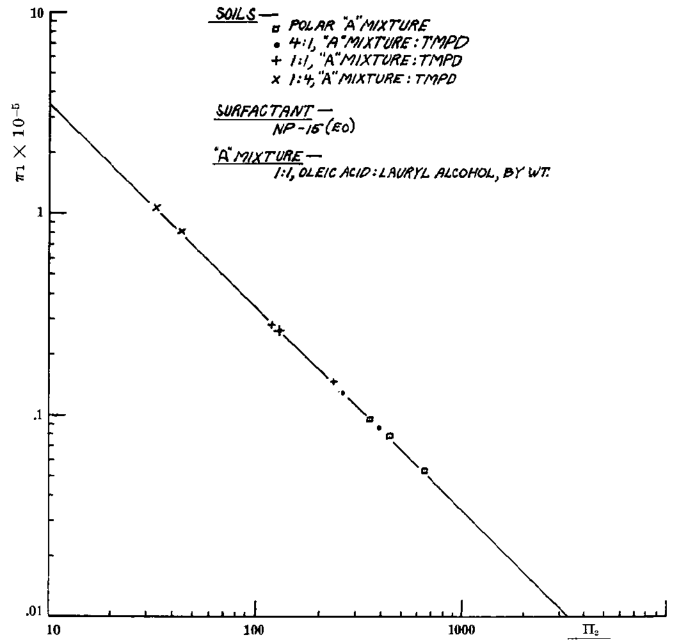

FIG. 6. D.A. No. 9-C with ternary soil mixtures, one nonpolar ingredient.

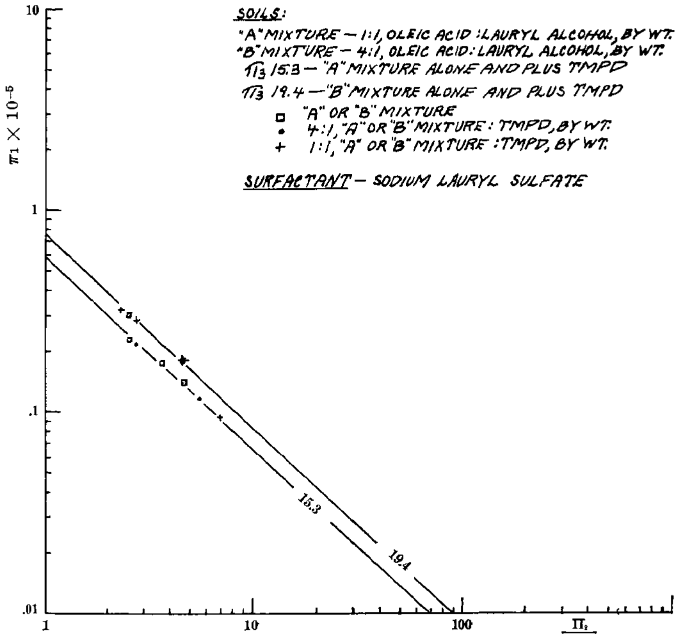

FIG. 7. Dimensional analysis No. 9-C with additional ternary soils.

it is another confirmation of the applicability of the dimensional analysis to systems containing a binary polar:polar soil mixture. The π_1–π_2 plot of the soil mixture system correlates with plots of the systems which contain the individual soils and the same surfactant. It is to be noted that, although these ingredients (ethyl stearate and octadecylamine) interact at the temperature of the viscosity determination (185F), an estimate of the latter, based on measurements made immediately after melting at 185F, permits the calculation of a parameter π_3 value which correlates with those of the systems of the component soils.

Dimensional Analyses of Soil-Surfactant Systems with Ternary Soil Mixtures. Fig. 6 is a plot of detergency and dimensional analysis data for soil-surfactant systems containing ternary soil mixtures which consist of various ratios by weight of polar oleic acid and lauryl alcohol dissolved in various amounts of nonpolar tetramethylpentadecane, TMPD. It provides an important confirmation of the results obtained with dimensional analyses of systems of binary polar-nonpolar soil mixtures. Reference to Fig. 2 shows that, for the latter, the π_3 parameter of the single polar soil system is identical with that of the binary polar-nonpolar soil mixture system. Similarly Fig. 6 indicates that the π_3 parameter of a system which contains a polar-polar soil mixture is identical with the π_3 of the system of a ternary soil mixture which consists of the same polar-polar soil mixture dissolved in a nonpolar material. Fig. 7 gives additional validation for soil-surfactant systems with ternary soil mixtures.

Discussion

Numerous physicochemical and detergency tests of soil-surfactant systems have established the validity of a modified dimensional analysis of the detergency process in which the soil dipole moment variable is replaced by the proportional property of the square root of orientation polarization, P_o. The resulting dimensionless products are

$$\pi_1 = \frac{D \times (\gamma\text{CMC})^{.8}}{(P_o)^{.8} \times C}$$

$$\pi_2 = \frac{C}{\text{CMC}}$$

$$\pi_3 = \frac{V}{(P_o)^{.1} \times (\gamma\text{CMC})^{.4} \times (\text{CMC})^{.5}}$$

where P_o is expressed in milliliters, and other symbols are as given in the Theory section.

An empirical volume fraction additivity of the ingredient P_o values of a binary polar-polar mixture was established by using the classical dilute solution-solute (P_2) extrapolation procedure with a chemical oscillometer. The agreement between calculated and experimental "resultant" P_o values of the polar-polar mixtures which were studied was considered good. Confirmation of the relationship extended the application of the dimensional analysis from soil-surfactant systems which contained a single polar soil to those with multicomponent soils met in practice.

The dimensionless-product, $\log \pi_1$–$\log \pi_2$ plots and parameter π_3 values of soil-surfactant systems the soils of which are binary polar-nonpolar or ternary polar-polar-nonpolar mixtures, are identical with the corresponding plots (extended, if necessary) and π_3 values of systems the soils of which are the corresponding single polar ingredient or binary polar-polar mixture respectively using the same surfactant, of course. The π_1 value for a system with a multicomponent soil containing a nonpolar ingredient is computed by using the "resultant" P_o value of the polar ingredients, or P_o or the single polar ingredient in the case of a binary polar-nonpolar soil. The π_3 value is not calculated for such a system; instead it has the π_3 value of the system with which its $\log \pi_1$–$\log \pi_2$ plot coincides.

$\text{Log}\, \pi_1$–$\log \pi_2$ plots of soil-surfactant systems the soils of which are binary polar-polar mixtures, with π_1 and π_3 values obtained by using "resultant" or effective P_o values based on volume fraction additivity of the ingredient polarizations, correlate perfectly in position and π_3 value with the plots of systems of the ingredient soils.

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