respect to the 4, 5 and 6 isomers as might be predicted (5). Also, from a consideration of the relative amounts of C_{12} and C_{14} chain lengths compared to C_{13}, as shown in Figure 1, an increasing rate of degradation with chain length should effect a decrease in the C_{14} to C_{13} ratio. The plotted data indicates that this is not occurring.

These divergences from results which would normally be anticipated from a knowledge of river water laboratory tests are not too surprising since the field conditions represent an open system and present a considerably different environment than a river water. Indeed, this possibility was pointed out by Swisher (10) and substantiated by the work of Sweeney (11) on a laboratory scale continuous sewage unit utilizing activated sludge. The work with activated sludge showed that the effects of molecular weight and phenyl position were smaller than in unacclimatized river water tests. It is important to emphasize that the mass spectral data and gas chromatographic data, particularly in respect to the effluents, are based on extremely small amounts of material. In the case of the latter two effluents this was less than one part per million of the total effluent.

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Dimensional Analysis Applied to Detergency

A. M. MANKOWICH, U. S. Army Coating and Chemical Laboratory, Aberdeen Proving Ground, Maryland

Abstract

Six fundamental soil and surfactant variables of the detergency process have been combined by dimensional analysis into a complete and valid set of three dimensionless products which represent the mechanism by a diagram comprising a family of curves of two of the products at fixed values of the third. Five soils and six surfactants have been combined into eighteen soil-surfactant systems to validate the dimensional analysis. The dependent parameter of soil removal, normally viewed as dimensionless, was assigned the dimensions of mass times length following more subtle considerations of the mechanism. This means of representing the detergency process is a considerable improvement over the previously established transcendental relationships of selected groups of soil-surfactant systems (2).

Introduction

DETERGENCY RESEARCH at this laboratory has been oriented towards the development of a detergency function that could be utilized for the scientific selection of surfactants for specific soil removal applications. From the beginning of the program (1), it has been felt that attainment of the objective involved the correlation of detergency with specific physiochemical factors of the detergency mechanism. Tending to confirm this premise have been our developments of linear detergency-micellar solubilization functions in the practical 90–100% soil removal range and relationships between the linearity constants of such functions and soil dipole moment, surfactant HLB, and soil-surfactant interfacial energy (2). While this was an advance in the field, reservations have been entertained concerning its pragmatic value because many of the functions were transcendental. It seemed logical at

TABLE I

Surfactant and Soil Data

Surfactants

Compound	Symbol	CMC–Molar		Surface tension at CMC	
		Commercial	Pure	Commercial	Pure
Polyoxyethylene–20–nonylphenol	NPEGE	0.000155 (9)	0.000140	32.6	39.0
Polyoxyethylene–30–nonylphenol	NPTGE	0.000275 (9)	0.000185	37.7	41.3
Polyoxyethylene–40–nonylphenol	NPTTGE	0.000450 (9)	0.000233	41.0	44.0
Polyoxyethylene–50–nonylphenol	NP50E	0.000788 (9)	0.000280	43.2	45.6
Sodium dodecyl benzene sulphonate	SDBS		0.00353		32.5
Sodium lauryl sulphate	SDS		0.0081		35.5 (14)

Notes: (a) Nomenclature of nonionics indicates average number of ethylene oxide units condensed with hydrophobe for commercial surfactants.
(b) SDBS is a branched chain ABS.
(c) CMC data at 25C.
Literature references for CMC given.

Soils

Name	Absolute viscosity, cp	Surface tension, dynes/cm	Dipole moment, debyes
Palmitic acid	5.517	—	0.79 (13)
Octadecylamine	2.868	21.7	1.3 (11)
Lauryl alcohol	2.758	28.3	1.7 (11)
Oleic acid	5.294	31.5	1.009 (12)
Linoleic acid	4.780	—	1.208 (20)

Notes: (a) Dipole moment literature references are given.
(b) Lauryl alcohol contains 58.7% 12–C plus varying amounts of 8–18C alcohols. 98% lauryl alcohol = 2.480 cp.
(c) Oleic acid is USP grade.
(d) Viscosity at 185F.

TABLE II

Detergency, Physiochemical Data

Surfactant	Conc., molarity	% Soil removal	A Dynes/cm	S Mg Orange OT/100cc
Octadecylamine soil				
NPEGE	0.00636	92.6	14.1	14.1
	0.00740	96.2	14.1	17.0
	0.00954	99.0	14.1	22.0
	0.0110	99.2	14.1	23.0
	0.0127	99.3	14.1	27.3
NPTGE	0.000455	91.4	19.2	1.1
	0.000550	96.2	19.4	1.3
	0.000682	98.1	19.5	1.7
	0.000750	98.6	19.6	1.9
	0.000910	99.0	19.6	2.5
NPTTGE	0.000505	90.0	19.6	1.0
	0.000610	95.2	19.7	1.3
	0.000758	97.1	19.9	1.7
	0.000900	97.2	20.0	2.0
	0.00101	97.2	20.2	2.3
NP50E	0.000788	88.5	21.6	2.0
	0.000960	90.8	22.1	2.3
	0.00118	93.4	22.5	2.9
	0.00136	95.2	22.9	3.4
	0.00158	96.8	23.3	3.8
Oleic acid soil				
NPEGE	0.00124	86.6	4.4	3 5
	0.00152	90.0	4.3	4.2
	0.00249	96.5	4.7	6.9
	0.00291	96.5	4.8	8.0
NPTGE	0.000275	91.9	6.2	0.5
	0.000413	95.6	7.8	0.9
	0.000550	96.4	9.5	1.3
NPTTGE	0.000202	90.8	7.5	0.2
	0.000303	94.8	7.9	0.5
	0.000404	96.6	8.9	0.8
	0.000662	98.7	9.95	1.4
NP50E	0.000197	90.0	9.9	0.2
	0.000394	93.0	10.7	0.7
	0.000788	96.9	11.7	1.8
	0.00158	99.4	13.6	3.7
Lauryl alcohol soil (technical)				
NPEGE	0.000311	90.2	6.5	0.9
	0.000467	97.9	6.6	1.3
	0.000662	97.9	6.8	1.8
	0.000909	98.6	7.5	2.6
NPTGE	0.000069	89.6	7.6	0.1
	0.000138	91.8	8.4	0.2
	0.000207	94.7	9.0	0.3
	0.000275	97.6	9.4	0.5
	0.000550	97.6	12.4	1.3
NPTTGE	0.000113	91.9	10.3	0.1
	0.000225	93.3	10.6	0.2
	0.000450	95.7	12.7	0.9
	0.000900	98.8	13.4	2.0
NP50E	0.000099	80.3	12.85	0.1
	0.000149	90.6	12.7	0.1
	0.000223	94.7	13.4	0.2
	0.000298	95.8	14.0	0.4
PSML	0.000424	88.8	5.6	1.0
	0.000571	95.5	5.6	1.3
	0.000848	97.9	5.7	1.9
TDPGE	0.00132	93.6	3.1	2.9
	0.00192	97.0	3.7	3.9
	0.00264	97.4	3.6	5.2
SDBS	0.00900	89.7	4.1	2.3
	0.0120	95.5	3.7	3.5
	0.0180	95.5	3.3	5.9

this point to utilize the accumulated data in an attempt to derive a detergency function by dimensional analysis.

Dimensional analysis reduces a large number of variables of a process to a smaller number of dimensionless groups of the variables which often can be plotted on coordinate axes, thus giving a general correlation that is impossible with the original variables (3–5). The principal difficulty with the method is the selection of the independent parameters (6). With the exception of the dependent variable (detergency in this case), no other dependent parameter must be included in the analysis. Incorrect results are obtained when pertinent variables are overlooked, or when nonsignificant ones are present. Dimensional analysis consists of the calculation of the number (the "complete set") and the compositions of the dimensionless groups. The number of dimensionless groups in a complete set is usually determined by the Buckingham "pi" theorem which states that a complete set is equal to the total number of variables minus the number of fundamental dimensions involved. In this investigation, Langhaar's procedure using matrices is followed in calculating complete sets of dimensionless groups (5).

Details and Preliminary Work

Previous detergency correlation studies at this laboratory were based on experimental data obtained at 180F and primarily in the 90–100% soil removal range. These data were used in dimensional analysis. CMC and soil dipole moment (25C) were obtained from the literature and are referenced in Table I. Surface tensions of liquid soils were determined at ambient room temperature (ca. 25C); solid tensions were calculated by Zisman's method (7). HLB (hydrophile-lipophile balance), one of the variables in our original detergency functions (2), is a dimensionless quantity representing the difference between hydrophilic and hydrophobic tendencies of a surfactant. As such, it was omitted from the actual computation in our dimensional analyses, but may be included with the calculated dimensionless groups as an additional parameter. Noninclusion of suspending power as a significant variable was due to prior selection of soil dipole moment. Earlier experiments at our laboratory (8) emphasized the importance of specific soil-surfactant adsorbability as one of the factors of the suspendibility action (peptization and induced zeta potential were others). Anionic surfactants were greatly superior to nonionics in suspending polar powders, while nonionics were better suspending agents for nonpolar particles. The dipole moment parameter, a polarization index, included the influence of suspending power.

The parameters selected for the first dimensional analysis were those that had been included in the detergency functions previously derived at this laboratory (2); namely, detergency—D, micellar solubilization—S, soil dipole moment—DM, Antonow's tension—A, critical micelle concentration—CMC, and HLB (which was omitted from the actual analysis, as explained above). It is to be noted that "A" reflects both wetting power and emulsification characteristics, the former because of its surface tension component and the latter due to its boundary surface nature. The advisability of separating "A" into its components, soil and surfactant surface tensions, was considered subsequently. Variables such as contact angle, spreading coefficient, adhesion tension and work of adhesion, are related to the components of "A"; and hence are not independent parameters. Similarly the surfactant concentration variable influences both detergency and micellar solubilization, and was considered redundant in the first analyses. Temperature was not a variable because the process took place at 180F. Time was also standardized. It is important to indicate the considerations leading to the assignment of dimensions to the detergency variable. Detergency is normally expressed as percent soil removal, and as such is dimensionless. A dimensionless dependent variable makes the analysis impossible. Detergency, however, may be regarded simply as a mass of soil removed from a certain location to another. Abitrarily representing by 100 mass units (e.g., milligrams) the original amount of soil in any application, detergency may be considered as the milligrams of soil transferred a unit distance away from the surface being cleaned. This is numerically equal or proportional to percent by weight soil removal. The dimensions of detergency may then be considered to be mass times length.

Utilizing the fundamental dimensions of mass (M), length (L), and time (T), the selected detergency parameters and dimensions of the first dimensional analysis were:

Parameters	Units	Dimensions
D	"% Removal" (see above)	ML
S	Mg per 100 cc	M/L^3
A	Dynes per cm	M/T^2
CMC	Gram moles per 1	M/L^3
DM *	Debye	$M^{1/2}L^{5/2}/T$

* Dipole moment equals the product of one of the electrical charges of a dipole unit by the distance between the two charges; that is,

$$\frac{M^{1/2}L^{3/2}}{T} \times L = M^{1/2}\,L^{5/2}/T$$

Several analyses were then made, some including soil density (at 185F) and soil melting point as additional parameters. Melting point temperature (absolute) was considered both as a fourth fundamental dimension and as proportional to kinetic energy with dimensions of the latter, ML^2/T^2. An analysis was also made with the Antonow tension parameter replaced by its components, detergent surface tension (γd) and soil tension (γs). In the latter analysis γ_{CMC} (surface tension at the CMC) was used for γd since these values are approximately equal above the CMC. No set of dimensionless products from these analyses could be validated by the data of the surfactant-soil systems listed in Tables I and II.

It seemed at this point that the nonvalidity of these preliminary analyses might be due to the following factors:

1. Omission of a significant soil variable, that of molten soil viscosity (at 185F). The increasing difficulty in deterging mineral oil of increasing viscosity is well known. Table I gives absolute soil viscosity (V) data for subsequent use.

2. Use of CMC data of commercial surfactants. It was felt that the use of CMC data of the homogeneous surfactant in each case would tend to give more valid products. Such a procedure, the use of more significant but yet closely related data, is not without precedent in detergency studies. Sawyer and Fowkes related susceptibility to foam stabilization of detergent solutions to increasing surface tension of the pure surfactants, not to that of the built solutions (14). In this laboratory, it was found that in P-C-436b alkaline cleaners (15) increasing detergency was directly connected to increasing surface tension and CMC of the unbuilt anionic surfactant and to increasing surface tension of the pure nonionic additive (2). CMC data on pure polyoxyethylated nonylphenols (branched chain) were available in the literature (16), and are shown in Table I which includes an interpolated value for the 40 ethylene oxide mole ratio adduct, NPTTGE. The table also gives surface tension at the CMC values, as estimated from surface tension-log concentration curves (16). The surface tension-log concentration curve of the SDBS used in this study showed a sharp break and practically zero slope at the apparent CMC (2). Hence the SDBS was considered homogeneous. Its CMC data and that of pure sodium lauryl sulfate (SDS) were given in Table I.

3. Use of too high a value for the dipole moment of lauryl alcohol. A further literature search revealed that 1.6 debyes might be a more suitable value (17,18).

4. Use of a technical grade of lauryl alcohol. A 98% grade material was obtained; and its detergent data, Table III, was used.

TABLE III

Data, Dimensional Analysis No. 9

Soil	Surfactant	π_3	% Soil removal	Solubilization $\text{mg}\ \frac{\text{Orange OT}}{100\ \text{cc}}$	$\pi_1 \times 10^{-6}$	$\pi_2 \times 10^{-3}$
98% Lauryl alcohol	NPEGE	44	90.3	0.8	5.700	5.36
			98.8	1.1	6.236	7.86
			98.8	1.4	6.236	10.0
	NPTGE	37.5	93.5	.07	4.675	0.350
			93.5	.08	4.675	0.410
			98.5	.09	4.925	0.490
	NPTTGE	32.6	91.4	.08	3.817	0.340
			93.0	.09	3.884	0.400
			94.8	.1	3.959	0.470
			97.5	.2	4.072	0.690
	NP50E	29.3	90.6	.04	3.240	0.140
			98.2	.05	3.512	0.180
			98.2	.06	3.512	0.210
	SDS	6	97.7	1.0	0.099	0.130
			98.2	2.2	0.099	0.270
Octadecylamine	NPTGE	45	91.4	1.1	6.371	5.95
			96.2	1.3	6.705	7.03
			98.1	1.7	6.838	9.24
			99.0	2.5	6.900	13.2
	NPTTGE	39.3	90.0	1.0	5.240	4.46
			95.2	1.3	5.542	5.49
			97.1	1.7	5.653	7.08
			97.2	2.0	5.656	8.54
			97.2	2.3	5.656	9.79
	NP50E	35.3	88.5	2.0	4.412	7.00
			90.8	2.3	4.527	8.10
			93.4	2.9	4.656	10.3
			95.2	3.4	4.746	12.0
			96.8	3.8	4.826	13.5
Oleic acid	NPEGE	103	86.6	3.5	11.429	24.6
			90.0	4.2	11.878	30.0
			96.5	6.9	12.736	49.0
			96.5	8.0	12.736	57.1
	NPTGE	87.7	91.9	0.5	9.608	2.43
			95.6	0.9	9.995	4.86
			96.4	1.3	10.079	7.03
			97.4	1.6	10.183	8.65
	NPTTGE	76	90.8	0.2	7.929	0.815
			94.8	0.5	8.279	2.15
			96.6	0.8	8.436	3.35
			97.1	0.9	8.479	3.86
			98.7	1.4	8.619	6.01
	NP50E	69	90.0	0.2	6.730	0.540
			93.0	0.7	6.955	2.43
			96.9	1.8	7.246	6.36
			99.4	3.7	7.433	13.3
	SDBS	22	92.0	1.1	0.416	0.310
			98.3	1.7	0.445	0.480
			98.3	3.5	0.445	0.990
	SDS	14	98.7	0.6	0.209	0.072
			99.2	1.0	0.210	0.130
Linoleic acid	SDS	12.3	99.2		0.146	
			96.0		0.152	
			99.7		0.158	
	SDBS	19.2	93.9		0.319	
			98.7		0.335	
			99.7		0.338	
Palmitic acid	SDS	15.4	91.6		0.287	
			98.9		0.310	
			99.4		0.311	
	SDBS	24.2	88.6		0.593	
			97.9		0.655	
			98.9		0.662	

Dimensional Analysis No. 9

A dimensional analysis (No. 9) was now made incorporating the preceding changes (1,2,3 and 4). The parameters and their dimensions were:

D..........ML

S..........M/L^3

γ_{CMC}..........M/T^2

CMC..........M/L^3

DM..........$M^{1/2}L^{5/2}/T$

V..........M/LT

A dimensional matrix of the above was prepared as follows:

$$\begin{array}{c|cccccc|}
 & D & V & S & DM & \gamma_{CMC} & CMC \\
\hline
M & 1 & 1 & 1 & \frac{1}{2} & 1 & 1 \\
L & 1 & -1 & -3 & 5/2 & 0 & -3 \\
T & 0 & -1 & 0 & -1 & -2 & 0 \\
\hline
 & a & b & c & d & e & f
\end{array}$$

Note that the matrix consists of three rows, one for

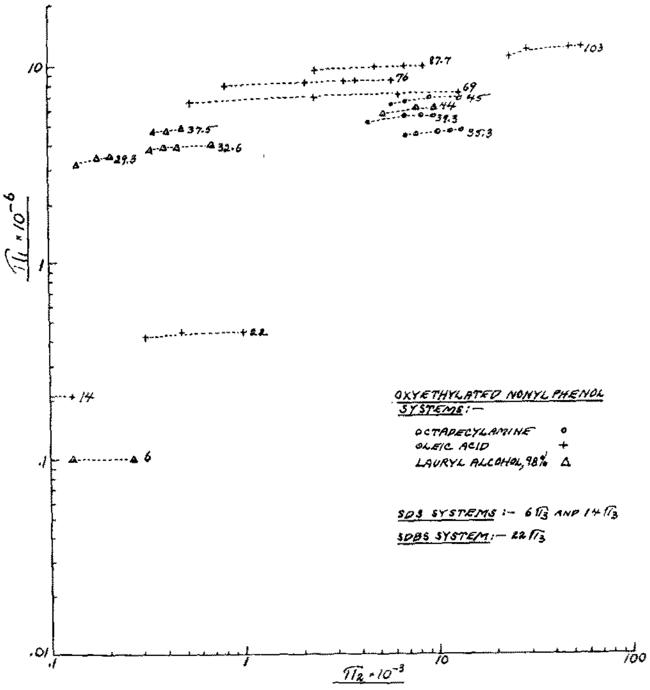

FIG. 1. Dimensional analysis No. 9

$$\pi_1 = \frac{D \cdot (\gamma_{CMC})^{4/5}}{DM^{8/5} \cdot CMC} \qquad \pi_2 = \frac{S}{CMC}$$

$$\pi_3 = \frac{V}{DM^{1/5} \cdot (\gamma_{CMC})^{2/5} \cdot CMC^{1/2}}$$

each of the fundamental dimensions, and six columns, each column representing one of the parameters and containing the appropriate exponents of its dimensional expression. The dependent variable, D, was placed in the first column; and a, b, c, d, e and f are the exponents of the parameters in the dimensionless products to be calculated. A determinant of the third order was formed from the last three columns at the right side of the dimensional matrix, giving the following:

$$\begin{vmatrix} \frac{1}{2} & 1 & 1 \\ 5/2 & 0 & -3 \\ -1 & -2 & 0 \end{vmatrix} = \Delta$$

Expansion of this determinant yielded a value, Δ, of −5. Now, since the dimensional matrix contained a third order, nonzero determinant, its rank was equal to that of the determinant; namely, 3. According to theory, the number of dimensionless products in a complete set is equal to the difference between the number of variables and the rank of their dimensional matrix. In this analysis, the number was 6 − 3 = 3. The next step was to set up homogeneous linear equations for each row of the dimensional matrix, as follows:

$$a + b + c + \tfrac{1}{2}d + e + f = 0$$

$$a - b - 3c + 5/2d - 3f = 0$$

$$-b - d - 2e = 0$$

Since there are 6 unknowns and 3 equations, it was convenient to determine d, e and f in terms of a, b and c. Arranging the solutions in matrix form gave:

$$\begin{array}{c|cccccc|}
 & D & V & S & DM & \gamma_{CMC} & CMC \\
\hline
\pi_1 & 1 & 0 & 0 & -8/5 & 4/5 & -1 \\
\pi_2 & 0 & 1 & 0 & -1/5 & -2/5 & -\frac{1}{2} \\
\pi_3 & 0 & 0 & 1 & 0 & 0 & -1 \\
\hline
 & a & b & c & d & e & f
\end{array}$$

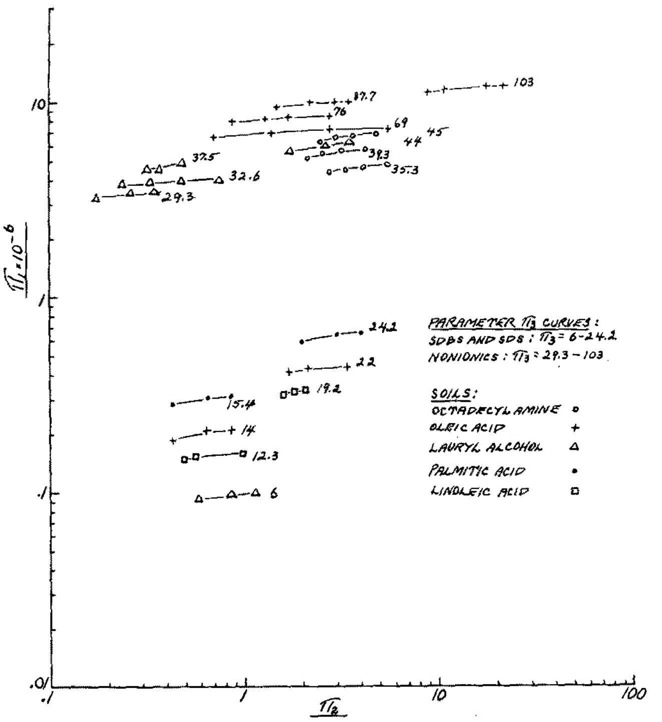

FIG. 1″. Dimensional analysis No. 9-B

$$\pi_1 = \frac{D \cdot (\gamma_{CMC})^{4/5}}{DM^{8/5} \cdot CMC} \qquad \pi_2 = \frac{C}{CMC}$$

$$\pi_3 = \frac{V}{DM^{1/5} \cdot (\gamma_{CMC})^{2/5} \cdot CMC^{1/2}}$$

And the dimensionless products were (renumbering the πs for convenience):

$$\pi_1 = \frac{D \cdot (\gamma_{CMC})^{4/5}}{DM^{8/5} \cdot CMC}$$

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

$$\pi_3 = \frac{V}{DM^{1/5} \cdot (\gamma_{CMC})^{2/5} \cdot CMC^{1/2}}$$

These products were checked with the data of the soil-surfactant systems for oleic acid, octadecylamine and 98% lauryl alcohol soils given in the tables. The calculated results were listed in Table III; and plotted as a family of curves in Figure 1, with π_3 as the parameter. According to the diagram, these dimensionless products gave a valid representation of the detergency processes of 14 soil-surfactant systems including three soils and six surfactants. It is to be noted that because of the complexity of the problem the analysis is considered valid if π_1–π_2 curves with the same π_3 parameter cover the same π_1 range, although not coinciding. Such curves are of almost zero slope at the 90–100% soil removal level studied.

From a practical standpoint it would be preferable that, instead of the variable "S" (micellar solubilization), the variable "C" (surfactant concentration) be used in dimensionless product π_2. This is permissible because both variables have the same dimensions, those of M/L^3. Making the change, product π_2 becomes C/CMC. The advantage of the change is the replacement of the experimental parameter "S" by a nonexperimental one, "C". Figure 1″ shows the detergency diagram constructed with $\pi_2 = C/CMC$, and π_1 and π_3 remaining the same. The diagram and products are valid and meaningful. Note the addi-

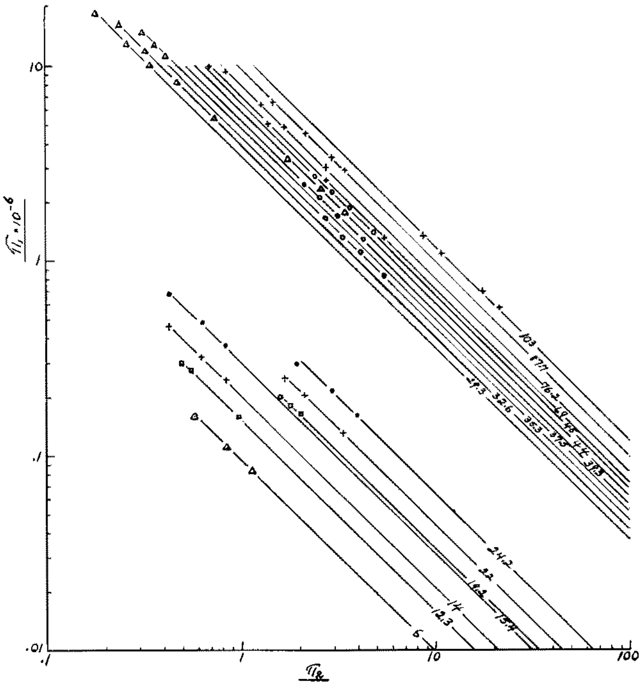

FIG. 2. Dimensional analysis No. 9-C

$$\pi_1 = \frac{D \cdot (\gamma_{CMC})^{4/5}}{DM^{8/5} \cdot C} \qquad \pi_2 = \frac{C}{CMC}$$

$$\pi_3 = \frac{V}{DM^{1/5} \cdot (\gamma_{CMC})^{2/5} \cdot CMC^{1/2}}$$

tional soil-surfactant systems using palmitic and linoleic acid soils.

It is now possible to form a still more useful set of dimensionless products from the set plotted in Figure 1″. A new π_1 can be obtained by dividing π_1 by π_2 of Dimensional Analysis 9–B of Figure 1″. When this is done the variable "C" replaces "CMC" in the denominator of π_1. Products π_2 and π_3 remain the same. Figure 2, a plot of these products, which we term the results of Dimensional Analysis 9–C, gives a much more convenient detergency diagram. The π_1–π_2 function on a log–log scale is a series of parallel lines with a negative slope of approximately 45°.

Further study will probably yield more suitable sets of dimensionless products of the detergency process. Improvement will result also from the use of more accurate constants (i.e., soil dipole moment and CMC). However, Figure 2 (Dimensional Analysis 9–C) now provides a valid, simple and practical detergency diagram that represents the mechanism by log–log curves of dimensionless products π_1 vs π_2 for fixed values of the parameter π_3. These products and the diagram are a vast improvement over the transcendental relationships established previously for selected groups of soil-surfactant systems (2). In fact it would seem that the eventual extension of the diagram's utility to prediction of detergency in various soil-surfactant applications is within reach.

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Studies on the Fatty Acid Composition of Crayfish Lipids[1]

D. A. WOLFE,[2] P. VENKATA RAO, and D. G. CORNWELL, Department of Physiological Chemistry, Ohio State University, Columbus

Abstract

The fatty acid composition of carcass and exoskeleton lipids was determined for the freshwater crayfish *Orconectes rusticus.* Lipid fractions were isolated by column and thin-layer chromatography. Fatty acid methyl esters and alcohol acetates were then prepared and analyzed by gas-liquid chromatography. Peak identities were established from retention time data for methyl esters, hydrogenated methyl esters, and saturated, monoene, diene, and polyene methyl esters separated as acetoxy-mercuri-methoxy derivatives. Minor component acids were estimated from their relative compositions in these fractions.

The triglyceride, cholesteryl ester, and astaxanthin ester fractions exhibited a typical freshwater fatty acid composition. Carcass free fatty acids, present in unusually high amts, contained less 16:0 and 16:1, and more 10:0, 20:4, and 20:5 acids than the neutral lipids. The crayfish phospholipid fraction contained elevated amts of 20:4, 20:5, and 22:6 acids. A selective mobilization of triglyceride at lower temps may therefore contribute to the seasonal variation in relative C_{20} polyunsaturated fatty acid content reported for crustacea. Relative retention time data suggest that crayfish fatty acids belong to the 9,12-octadecadienoic acid and 9,12,15-octadecatrienoic acid structural types.

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[2] Present address: U. S. Bureau of Commercial Fisheries, Radiobiological Laboratory, Beaufort, N.C.