butterfat in 24 hr (e.g., $30 \times 454 \times .037 = 500$). It would appear from the above figures that serious consideration should be given to the possibility that rumen microbial lipids are significant contributors to the fatty acid composition of milk fat and other ruminant lipids.

Continuing the above line of thought for the case of the C_{15}-branched-chain acids, it is observed (Table II) that the milk fat contained 1.1% of these acids. This means that approximately 5.5 g of these acids were being secreted by the mammary gland in 24 hr. (e.g., $500 \times .011 = 5.5$). The rumen bacterial neutral lipid, free fatty acids, and polar lipid contained, respectively, 6.7, 1.9, and 20.3% of C_{15}-branched acids in their component fatty acids. Considering these values, together with the class composition in Table I, it is possible to make a rough calculation of the amount of C_{15}-branched acid of bacterial origin passing to the lower digestive tract in 24 hr. The assumptions in this calculation are that the neutral lipid is of the glyceride type and that the polar lipid is mainly phospholipid. A cephalin type phospholipid would contain approximately 65% fatty acid moieties of average C_{16} chain length. Calculations are:

$$29 \times .41 \times .067 = .80 \text{ g}$$
$$29 \times .13 \times .019 = .07 \text{ g}$$
$$29 \times .30 \times .203 \times .65 = 1.15 \text{ g}$$
$$\text{Total } C_{15} \text{ branched acid from bacterial lipid } \overline{2.02 \text{ g}}$$

This 2 g quantity of C_{15}-branched acid plus the 1 g of C_{15}-branched acid from the polar protozoal lipid (e.g., $113 \times .35 \times .65 \times .037 = .95$), passing to the lower digestive tract from the rumen during a 24 hr period, could easily account for more than half of the 5.5 g of C_{15}-branched acid in the butterfat.

It is now generally accepted that the major source of protein nitrogen for milk and meat production in ruminants is rumen microbial protein. Dietary protein and nonprotein nitrogen are largely converted to microbial protein in the rumen (23). The digestive mechanisms which make this microbial protein available to the animal would be expected to go hand in hand with mechanisms which would make the microbial lipid available. The presence of both proteolytic and lipolytic enzymes in the pancreatic and intestinal systems is well known.

This work is interpreted as providing support for the suggestion of Akachi and Saito (13) that the branched-chain acids of animal fats are derived from bacterial lipids in the gut. It also supports the suggestion of Reiser and Choudhury (11) regarding the possible rumen microbial origin of part of the stearic acid in ruminant body fats. Hydrogenation of dietary unsaturated fatty acids by rumen organisms has been recognized as being responsible for the characteristic *trans* fatty acid isomers in ruminant fats (26). It is suggested that attention should also be given to the probability of microbial synthesis of long chain fatty acids in the rumen from the volatile faty acids, which are always present in relatively high levels (e.g., 80–120 mmole VFA/l rumen fluid).

Current work in this laboratory involves a more detailed characterization study of rumen microbial lipids. It is anticipated that identification and quantitative determination of unique components of microbial lipids will provide natural markers which may be used for quantitative studies of the role of these lipids in animal nutrition. If it is found that the quantity of one or more of these compounds is proportional to the amount of bacterial protoplasm present, they might be used as markers to estimate the quantity of bacterial protoplasm in material leaving the rumen to the lower digestive tract, or in that intimately associated with plant fibers, or in material from various locations within the rumen, etc. For instance, if one assumes that protozoa do not synthesize C_{15}-branched-chain acids it can be estimated, based upon the quantities of these acids in the polar lipids, that 15–20% of the fatty acids in the polar protozoal lipid isolated in this study were of bacterial origin. This approach would be analogous to that of Weller *et al.* (23), who used diaminopimelic acid as a natural indicator of the quantity of bacterial nitrogen in the rumen.

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New Methods of Analyzing Industrial Aliphatic Lipids[1]

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Methods are described for the rapid fractionation of classes of lipids containing the hetero elements N, P, and S, such as primary amines, secondary amines, tertiary amines, and quaternary ammonium salts containing one, two, or three long-chain moieties; amides, nitriles, and other nitrogenous lipids; alkyl sulfates and sulfonates; alkyl phosphates and phosphonates.

Thin-layer chromatography on silicic acid separates lipids according to classes of compounds. After isolation by thin-layer chromatography, each lipid class is amenable to further fractionation, according to chain length and de-

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gree of unsaturation, by complementary methods, such as paper chromatography and/or gas-liquid chromatography.

These procedures permit rapid analyses of complex mixtures of industrial lipids, such as surface-active agents, and identification of industrial compounds synthesized from fatty raw materials.

BECAUSE SYNTHETIC DERIVATIVES of natural lipids have become important industrial chemicals (1), methods for their fractionation and identification are urgently needed (2). The present communication describes the application of thin-layer chromatography (TLC) (4,38,39,40,45,46) to the analysis of technically important lipid derivatives, especially those containing nitrogen, phosphorus, and sulfur. It constitutes a continuation and expansion of work concerned with the analysis of complex mixtures of natural lipids (24, 27,28,29).

TLC on silicic acid fractionates all kinds of lipids by virtue of their differences in polarity according to classes of compounds; e.g., primary amines can be separated, as a class from secondary amines, which form another class, and from tertiary amines, which form still another class.

Subfractionations within one class of lipids, although perceptible, are pronounced only if extreme differences in chain length or degree of unsaturation exist within the group. Short-chain moieties or highly unsaturated compounds are more strongly adsorbed than are long-chain saturated constituents of a class of lipids. These subfractionations, however, do not usually interfere with class separations.

Several specific examples demonstrate the usefulness of combining TLC, which is usually an adsorption method, with complementary methods based on partition chromatography, such as reversed-phase paper chromatography (PC) and gas-liquid chromatography (GLC). Pure classes of lipids can be resolved by the latter two techniques into their individual components.

Methods and Materials

Apparatus. The apparatus[2] and procedures described by Stahl (38,39) for the preparation of thin layers (250 to 275 μ) of adsorbents—e.g., silicic acid ("Silica Gel G") diatomaceous earth, alumina, or cellulose on glass plates—were followed throughout this investigation. The fine grade adsorbents (60 μ or about 250 mesh), each containing plaster of Paris as a binder, were commercial products especially prepared for TLC.[2]

Reversed-phase PC was carried out as described elsewhere (25,26,27,35). The Whatman No. 1 paper[3] was cut across the fiber into strips (11.5 x 46 cm) which were dried for 2 hr at 120C. The dried strips then were drawn through a solution of 5% silicone in ether ("Dow Corning Fluid 200," viscosity 10 cs at 25C)[4] and air dried.

An "Electronic Densitometer Model 52-C[5]" was used for the quantitative evaluation of thin-layer chromatograms on glass strips (4 x 20 cm) (27,32, 33). The scanning stage of this instrument was easily adapted to permit use of standard square plates (20 x 20 cm) also. Paper chromatograms were evaluated in the same instrument.

[2] "Silica Gel G," "Kieselgur G" (i.e. diatomaceous earth), and "Aluminum oxide G," products of E. Merck A. G., Darmstadt, Germany, may be obtained from C. A. Brinkmann and Company, Inc., 115 Cutter Mill Road, Great Neck, Long Island, New York. This firm is also the U. S. representative of Excorna o. H. G., Mainz, Germany, the producer of cellulose powder for TLC, and of C. Desaga G.m.b.H., Heidelberg, Germany, the manufacturer of the equipment used for making the plates.

[3] H. Reeve Angel & Co., Inc., 9 Bridewell Place, Clifton, New Jersey.

[4] Dow Corning Corp., Midland, Michigan.

[5] Photovolt Corporation, 95 Madison Avenue, New York 16, New York.

All gas-chromatographic analyses were performed in a Beckman GC-2 Gas Chromatograph.[6] The various columns were prepared and operated under conditions stated in the literature (21,22).

Solvents. All separations were performed in a saturated atmosphere, i.e., in jars lined with filter paper. Solvents used for TLC and PC were purified and distilled (31). Five solvent mixtures were found useful for the fractionation, on thin layers of silicic acid, of lipid derivatives containing the hetero elements nitrogen, phosphorus, and sulfur (Tables I and II). These five solvent systems separate lipids on silicic acid into chemical classes.

TABLE I

Solvents for Thin-Layer Chromatography of Lipids Containing N, P, and S

I.	Petroleum hydrocarbon-benzene: 95 vol. of petroleum hydrocarbon (b.p. 60–70C) and 5 vol. of benzene.
II.	Benzene-aqueous ammonia: 100 vol. of benzene are equilibrated at 20C with 10 vol. of 1 *N* aqueous ammonia. The aqueous layer is discarded.
III.	Chloroform-methanol-aqueous ammonia: Chloroform is equilibrated at 20C with 1 *N* aqueous ammonia 10:1 v/v. 97 vol. of this ammoniacal chloroform and 3 vol. of methanol are used as the developing system.
IV.	Acetone-aqueous ammonia: 90 vol. of acetone and 10 vol. of conc. (14 *N*) aqueous ammonia.

TABLE II

Solvents for Thin-Layer Chromatography of Strongly Acidic Lipids on Modified Plates

V.	Chloroform-methanol-aqueous sulfuric acid: Methanol containing 5% of 0.1 *N* sulfuric acid is mixed with chloroform in various ratios, depending upon the polarity of lipids to be resolved. Typical solvent systems are:
	(A) 97 vol. of chloroform and 3 vol. of methanol-sulfuric acid.
	(B) 80 vol. of chloroform and 20 vol. of methanol-sulfuric acid.

Solvents I, II, III, and IV are arranged according to increasing polarity. They may be applied, consecutively, on one chromatoplate for stepwise fractionation of a complicated mixture of industrial lipids. Substances that do not migrate with the petroleum hydrocarbon-benzene system (I) may move with either solvent II, III, or IV. Substances that are resolved in the useful region of the chromatoplate (R_f 0.1–0.9) by one solvent system will be carried to the solvent front by any of the following ones. Lipids containing many polar functional groups such as polyethoxylated compounds or very acidic substituents (e.g., sulfates and sulfonates, phosphates and phosphonates) stay at the point of application with any of the four solvent systems listed above.

Strongly acidic lipids and also the amphoteric natural phospholipids are chromatographed on thin layers of silicic acid containing 10% by weight of ammonium sulfate. Such modified chromatoplates are prepared from a slurry of 25 g of Silica Gel G in a solution of 2.5 g ammonium sulfate in 60 ml of water. This slurry has to be applied to the glass plates quickly because it hardens even faster than do slurries of plain Silica Gel G.

[6] Beckman Scientific and Process Instruments Division, Fullerton, California.

On these modified plates, acidic lipids are separated with the solvent systems presented in Table II.

Free fatty acids, the starting material in the preparation of industrial aliphatic lipids, remain at the starting point with systems I, II, III, IV and are carried to the solvent front by system V. Solvent systems for the analysis of free fatty acids and other naturally occurring lipids were previously described (24,28).

The solvent systems used for the separation of homologous series by PC on siliconized Whatman No. 1 paper were aqueous acetic acid, aqueous acetonitrile, aqueous tetrahydrofuran, and a mixture of chloroform-methanol-water (25,27,35). Overlapping saturated and unsaturated lipids of one homologous series were resolved by PC in oxidizing solvents (26,27). Saturated lipids are well separated from each other and are stripped off overlapping unsaturated components by PC in solvents in which part of the water is substituted by perhydrol.

Indicators. As in TLC of natural lipid mixtures, iodine, 2′,7′-dichlorofluorescein, and oxidizing acids are used for detecting the spots of lipids on the chromatoplates (24,28). Iodine vapors indicate all unsaturated lipids as brown spots on a yellow background but saturated nitrogenous lipids with the exception of quaternary ammonium salts, are also deeply stained with this reagent. Most saturated and unsaturated lipids can be seen as yellow-green fluorescent spots under U. V. light,[7] after having been sprayed with a 0.2% alcoholic solution of 2′,7′-dichlorofluorescein.[8] This indicator is not very sensitive to phospholipids and fails completely with a few other lipid classes; e.g., long-chain ketones and sulfonated alkylphenols.

A saturated solution of potassium dichromate in concentrated sulfuric acid is superior to any other oxidizing acid solution for charring all nonvolatile organic compounds on the plates. With this solution, unsaturated lipids appear as light brown spots on a white background even before the chromatoplate is heated. Heating the plate yields further information on the chemical nature of the various compounds, as different colors appear at increasing temperatures.

These three indicators may be applied consecutively on one chromatoplate in the sequence iodine, dichlorofluorescein, chromic sulfur acid solution. The dichlorofluorescein on the plate does not show up during the subsequent charring process.

The indicators, iodine and α-cyclodextrin-iodine, used here in paper chromatography of industrial lipids have been described previously (25).

Lipid Material. Lipid samples were applied by means of 10–50 μl syringes,[9] as 1% solutions in ethyl acetate of less polar solvents in amounts of 0.001–1 mg per spot. The various classes of compounds investigated are represented in Figures 1 through 5. Several individual compounds of chain lengths C_{12}–C_{18} were tested in each class. Where feasible the corresponding unsaturated compounds at least of the oleic acid series were analyzed also. With compounds of chain lengths C_{12} and above and unsaturation up to 3 double bonds there was never subfractionation that could have interfered with the separation according to chemical class.

All lipid samples employed in this investigation were commercial preparations.

[7] "Mineralight," Ultra-Violet Products, Inc., San Gabriel, California.
[8] Eastman Kodak Company, Rochester 3, New York.
[9] Hamilton Company, Inc., Whittier, California.

Results

Thin-Layer Chromatography. Naturally occurring fats, oils, and waxes and their respective hydrolysis products such as fatty acids and alcohols, are well separated by TLC. These neutral or slightly acidic classes of lipids can be resolved on silicic acid with mixtures of petroleum hydrocarbon, diethylether, and glacial acetic acid in various proportions (20,24,28). Such developing systems, however, are not suitable for the fractionation of industrial fatty acid derivatives because the latter products usually contain free functional groups, either cationic or anionic, and thus they are more polar than are the biological lipids they have been derived from. Therefore, solvent systems had to be developed to permit the fractionation of polar lipids. The series of five solvent systems described above (I–V) allows the separation of complex mixtures of compounds ranging in polarity from the strongly basic quaternary ammonium bases to the highly acidic sulfonic acids.

Figure 1 illustrates the separation of a series of nonpolar lipid derivatives using solvent system I; i.e., petroleum hydrocarbon-benzene.

Fractionations of the prominent classes of nitrogenous lipids are shown in Figures 2 and 3. Solvent system II (Fig. 2) is particularly useful for the resolution of nitriles and tertiary amines, whereas solvent system III (Figure 3) yields efficient fractiontions of a wide range of nitrogenous lipids. Complete separation of primary, secondary, and tertiary amines, amides, and nitriles with solvent III is especially noteworthy. Nitriles migrate to the solvent front with this solvent. It is possible to follow the course of syntheses of these compounds and to check the purity of the final products. In the present investigation, secondary amines and unidentified impurities were found in several preparations of distilled primary amines. Primary and tertiary amines were found in secondary amines, and primary and secondary amines and several unidentified impurities were detected in tertiary amines. Amides were usually very pure. The sensitivity of TLC was checked with highly purified preparations of various amides, and 0.5% of contaminating nitrile could be detected when the plates were charred with chromic sulfuric acid solution. Only traces of unidentified contaminants were found in nitriles.

The resolution with solvent system IV of the cations of the quaternary ammonium salts containing one, two, or three long aliphatic chains and three, two, or one methyl groups, respectively, is illustrated in Figure 4. Alkylfurfuryl-dimethyl-quaternary ammonium ions migrate together with dialkyl-dimethyl-quaternary ammonium ions. The hydrohalides of amines migrate as amines and not in the ionogenic ammonium form as do the above types of quaternary ammonium salts.

Figure 5 shows separations of strongly acidic lipids on Silica Gel G containing 10% ammonium sulfate. The acidic solvent systems V (A) and V (B) effect complete resolution of mixtures of *N*-acylated sarcosine, oleic acid-ester of hydroxy sulfonic acid (i.e. of isethionic acid), and *N*-acylated short-chain amino acid (e.g. taurine), three widely used groups of detergents. Alkyl sulfates and sulfonates, also alkylphosphates and phosphonates, are separated with chloroform-methanol-aqueous sulfuric acid [V(A) and V(B)]. The acidic lipids investigated were particularly impure.

Turkey red oils (sulfated castor oils) and monopol oils (sulfated and sulfonated castor oils) can be an-

FRACTIONATION OF INDUSTRIAL ALIPHATIC LIPIDS

(Common legend to Figures 1–5)

The Figures 1, 2, 3, 4, 5(A), and 5(B) represent tracings of actual chromatograms obtained with solvent systems I, II, III, IV, V(A) and V(B).

The letters a, b, c, etc., relate to lipid classes.

Approximately 40 γ of each class was chromatographed. Major contaminating substances are indicated by dotted lines.

All chromatograms were run in saturated atmosphere for about 40 min to a height of 12 cm. 2',7'-Dichlorofluorescein was applied as the indicator in Figure 4, whereas chromic sulfuric acid solution was used in Figures 1, 2, 3, and 5.

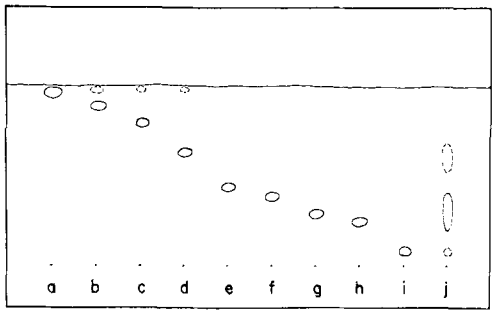

FIG. 1. (Solvent System I) a) alkylhalide; b) mercaptan; c) dialkylthioether; d) dialkylether; e) alkylthiocyanate; f) dialkylketone; g) alkylisocyanate; h) nitril; i) alkylphenol; j) dialkylphenol (crude).

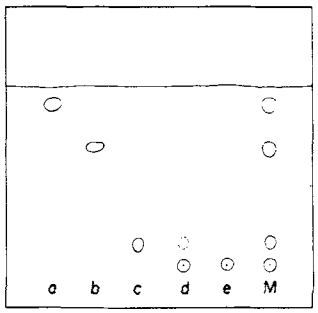

FIG. 2. (Solvent System II) a) alkylisocyanate; b) nitrile; c) trialkyl tertiary amine; d) dialkyl secondary amine; e) acetylated primary amine; M = mixture.

alyzed for their degree of sulfuration by TLC on modified chromatoplates with solvent system V (B).

Especially sharp separations of mixtures of natural phospholipids, such as lecithins, cephalins, and sphingomyelins, are also obtained on thin layers of Silica Gel G containing ammonium sulfate with the acidic solvent system V (B) or with any of the neutral or alkaline solvents described in the literature (5,11,15, 16,17,34,42,43,44). Phospholipids tend to streak when chromatographed on the more strongly adsorbing nonmodified Silica Gel G.

With all the compounds investigated Silica Gel G yielded better separations than did alumina or diatomaceous earth. Therefore, only Silica Gel G and modified Silica Gel G were applied for the separation of industrial lipids in the scheme described above.

Two techniques were applied for exploring the possibilities of quantitative analysis of mixtures of industrial lipids. With both methods, charring with chromic-sulfuric acid solution was used for visualizing the spots of lipids on the chromatoplates.

The photodensitometric method recently described for the evaluation of thin-layer chromatograms of mono-, di-, and triglycerides (33) and of "aldehydic cores" derived from unsaturated glycerides by reductive ozonolysis (32) has been found useful for the quantitative analysis of model mixtures of saturated primary amines, amides, and nitriles in the range of

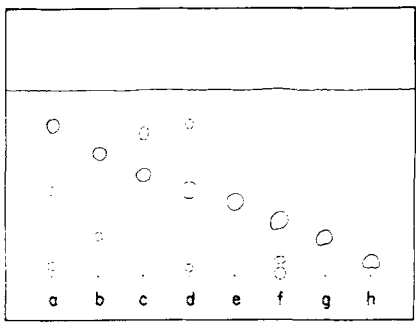

FIG. 3. (Solvent System III) a) trialkyl tertiary amine; b) acetylated *N*-2-ethoxy amide; c) acetylated primary amine; d) dialkyl secondary amine; e) amide; f) alkyldimethyl tertiary amine; g) *N*-2-ethoxy amide; h) primary amine.

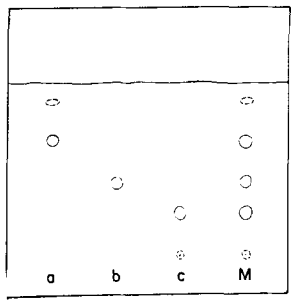

FIG. 4. (Solvent System IV) a) trialkyl methyl ammonium chloride; b) dialkyl dimethyl ammonium chloride; c) alkyl trimethyl ammonium chloride; M = mixture.

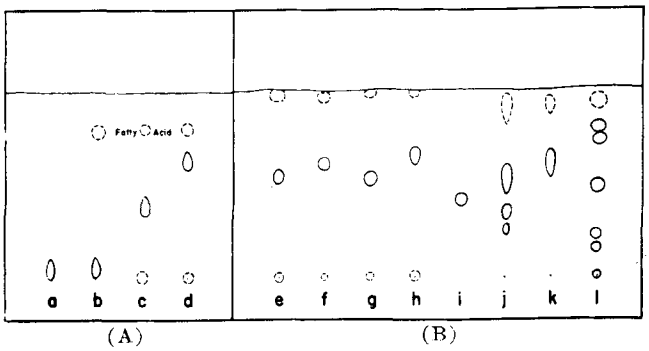

FIG. 5(A). [Solvent System V(A)] a) triethanolamine; b) triethanolamine oleate; c) diethanolamine-stearic acid condensate; d) lauryl sarcosine.

FIG. 5(B). [Solvent System V(B)] e) sodium salt of N-acylated short-chain amino sulfonic acid (Igepon T-type); f) sodium salt of oleic acid-ester of hydroxy sulfonic acid (Igepon A); g) sodium lauryl sulfate; h) sodium dodecyl benzene sulfonate; i) sodium salt of α-sulfo-lauric acid; j) alkyl ammonium salt of alkylphosphonamides; k) sodium capryl polyphosphate; l) soybean phosphatides.

5–35 γ per class of compound, with an error of ± 8%. It is mandatory to chromatograph and scan "unknown" mixtures alongside model mixtures on the same plate.

Measurement of spot areas (36,37) on photostats obtained from thin-layer chromatograms was found to permit quantitative analyses of industrial lipids in a range of 30–130 γ per class of compound with an error of ± 5% (18).

Combined Methods (TLC—PC, GLC)

Classes of lipids, after having been separated by TLC, can be scratched off the chromatoplate and eluted from the adsorbent by repeated slurrying with a suitable solvent (24) in a test tube and decanting. The eluate is filtered through a sintered glass funnel and concentrated by evaporating most of the solvent in a stream of nitrogen. The various classes of lipids

isolated by thin-layer adsorption chromatography are then amenable to further fractionation by complementary chromatographic methods based on partition, such as PC and GLC, or by other techniques (8).

Most industrial lipids have high boiling points because of their polarity and/or their high molecular weight. Therefore, PC is most suitable for resolving any class of lipids according to chain length and degree of unsaturation.

Suitable solvents for paper-partition chromatography of a given class of lipids can be chosen after studying the behavior of this lipid in adsorption chromatography. Lipid classes that are chromatographed on Silica Gel G with solvent systems I or II can be further resolved by reversed-phase chromatography on siliconized paper with a solvent system consisting of 25 vol. of chloroform, 75 vol. of methanol, and 5 vol. of water, or with 75–95 vol. of acetic acid or acetonitrile and 25–5 vol. of water. Compounds differing by two methylene groups and one double bond, such as palmitonitrile and oleonitrile, overlap. Such "critical pairs" are resolved by chromatographing in oxidizing solvents by which the saturated lipids are well separated, whereas all superimposing unsaturated compounds are quantitatively oxidized and carried to the solvent front (26,27). As an example, nitriles can be resolved on siliconized paper with solvent systems consisting of 75 vol. of acetic acid and 25 vol. of water, or 70 vol. of acetonitrile and 30 vol. of water. A mixture of 65 vol. of acetic acid, 10 vol. of peracetic acid,[10] and 25 vol. of water, or a mixture of 70 vol. acetonitrile, 10 vol. of perhydrol and 20 vol. of water was used for separating overlapping saturated and unsaturated nitriles.

The more polar classes resolved by TLC with solvent system III can be further fractionated by reversed-phase PC with about equal portions of water with acetic acid, or acetonitrile, or tetrahydrofuran. Acetylated primary amines as an example can be separated on siliconized paper with either 60 vol. of acetonitrile or tetrahydrofuran and 40 vol. of water (27).

Procedures for the chromatographic separations on impregnated or unimpregnated paper of quaternary ammonium salts isolated with solvent IV have been described (6,9,13,14,30).

The acidic lipids that are fractionated into classes by thin-layer chromatography on Silica Gel G containing ammonium sulfate may also be further resolved by chromatography on impregnated or plain paper according to procedures reported in the literature (7,13).

Gas-chromatographic methods for the analysis of the most prominent classes of nitrogenous lipids, primary amines, amides, and nitriles have been described. Primary amines and nitriles analyzed directly (21,22,41), whereas amides are reduced with lithium aluminum hydride and are then resolved by GLC as amines (23).

Discussion

Procedures for the fractionation of complex mixtures of naturally occurring lipids are well worked out. Adsorption chromatography on columns, on chromatoplates, or on impregnated paper is commonly used for the isolation of lipid classes, while methods of partition chromatography are subsequently applied for their further resolution.

In contrast, no scheme has yet been developed for the fractionation of synthetic lipid derivatives. A first attempt towards a systematic analysis of such lipids was made a decade ago by Holman (12) who separated alkyl halogenides, mercaptans, hydrocarbons, nitriles, amides, alcohols, and esters as classes by displacement chromatography on charcoal columns. Other workers have described procedures for separating members of a homologous series by paper partition chromatography (6,7,9,13,14,19,27) by gas-liquid chromatography (21,22,41), or by paper electrophoresis (8,). The methods of partition chromatography are applicable only to pure lipid classes; mixtures of different homologous series cannot be efficiently resolved (3).

Thin-layer chromatography on silicic acid permits rapid fractionation of industrial lipids according to classes. This technique may be used in combination with existing methods of partition chromatography to the complete analysis of complex mixtures of industrial lipids.

The course of synthesizing procedures, the yields of intermediates, and the purities of the final products can be evaluated by thin-layer adsorption chromatography, paper partition chromatography, and gas-liquid chromatography.

The lipid moieties of polyethoxylated cationic and nonionic surface active agents can only be analyzed after cleavage from the polyoxyethylene chains (10).

As an extension of this paper, refined methods for the analysis of very hydrophilic lipid derivatives by chromatography on thin layers of ion exchangers will be reported in a forthcoming publication.

[10] Becco Chemical Division, Food, Machinery and Chemical Corp., Buffalo 7, New York.

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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 linearily 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 polyethenoxylated anhydrosorbitol.

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