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[Received February 26, 1964—Accepted May 7, 1964]

Identification of Surface Active Agents in Admixture by Thin Layer Chromatography[1]

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Abstract

The qualitative identification of the surface active agents commonly used in household detergent formulations is possible using thin layer chromatography (TLC). Successful separations have been made when the samples are spotted on Aluminum Oxide G and developed with isopropanol. A variety of specific reagents may be used to color the spots and thereby supplement the Rf values as a means to identify the surfactants. The analysis can be made semi-quantitative if the separations are made using an aluminum oxide column and collecting the fractions eluted with isopropanol and methanol.

Introduction

THE SEARCH for a quicker method of identification for the surfactants present in detergent formulations is a continuing project. Currently the analysis of a detergent is centered around the alcohol soluble portion of the formulation. This portion is subjected to instrumental and chemical testing and further separated by ion exchange chromatography to isolate the nonionic surface active agents. IR analysis of the nonionic portion will indicate the presence or absence of fatty amides by an absorption band near 6 μ which is characteristic of the amide carbonyl vibration and the presence of alkylphenol ethoxylates with be indicated by a series of bands which includes the strong C—O—C band near 9 μ. It may be possible to determine the relative concn of an alkylphenol ethoxylate by UV spectroscopy if the assumption is made that the surfactant is a particular adduct of *n* moles of ethylene oxide to a particular alkylphenol. The IR spectrum of the alcohol soluble portion is sometimes useful, but at other times limited in value because of the overlap of absorption bands of the multicomponent system. The more components present, the less positive any identification can be. Therefore, a definite need exists for a procedure which will separate completely, and give identity to, the components in a detergent mixture.

Gas chromatography, which has become a very useful analytical tool, does not lend itself to the complete separation of surface active species. However, paper chromatography has been used by Drewry (1) in England for the qualitative identification of detergents. The anionic, cationic and nonionic agents, soaps and hydrotropes have been identified on a single chromatogram by a method of consecutive spraying. The sprays, when applied in a definite sequence, develop specific colors with the particular surfactants and thereby make their identity known. This work of Drewry's looked very promising but it required 16–18 hr for the solvent front to rise the necessary 20 cm to develop the chromatogram (solvent system of *t*-butanol-ammonium hydroxide-water).

Separations of a variety of mixtures had been reported in 30 min time when TLC (2–7) was used. In addition to speed, an additional advantage of this technique is that a TLC chromatoplate could be sprayed with sulphuric acid and heated to char any organic material on the plate. This would give a rapid indication of the success of the separation and give an idea as to the number of components in a mixture.

Since TLC, where applicable, gives a rapid separation of multicomponent systems and, since techniques used with paper chromatograms to develop colors with various components of detergent formulations were known, we decided to attempt the separation and identification of detergent formulations by thin layer chromatography.

Qualitative Identification

Reagents

Aluminum Oxide G (according to Stahl)
Isopropanol
Pinacryptol Yellow (K & K Laboratories, Inc., 177-10 93rd Avenue, Jamaica, N.Y.)
Iodine
Surface Active Agents (commercial samples)

Apparatus

Comprehensive TLC Apparatus (Brinkman Instruments, Inc., 115 Cutter Mill Road, Great Neck, Long Island, N.Y.)
UV Light

Preparation of Plates. Both 5 x 20 cm and 20 x 20 cm glass plates were cleaned with concd chromic acid, rinsed with water and then wiped dry. A 1:2 slurry of Aluminum Oxide G and water was prepared and stirred until it was uniform and free of entrapped air. A Desaga applicator was used to draw down a 0.25-mm layer of the aluminum oxide on the plates. The

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plates were left undisturbed for ten min and then placed in racks in an oven to dry at 75C for four hr. The dried plates were stored in a desiccator until used.

Preparation of Samples. One g of the alcohol soluble portion of the sample was dissolved in the min amt of methanol in a 100-ml volumetric flask and the sample further diluted to the mark with acetone. Later, we found that 3 g of a liquid formulation could be diluted to 100 ml with acetone.

Spotting and Development. A 10-μ syringe was used to spot the plates. The syringe was clamped above a plate and the tip of the needle pressed firmly into the aluminum oxide coating. To ensure a smooth flow from the syringe, the plunger was slowly depressed so that the spots were no more than 15 sq mm in area. The spots were positioned 1.5 cm from the lower edge of the plate so that they would not be covered by the developing solvent. The plate was allowed to dry for two min to remove the spotting solvent and then the plate was lowered into a battery jar containing isopropanol to a depth of 0.5 cm. The jar was lined with a piece of filter paper on one side to provide a solvent saturated atmosphere for faster equilibration. The solvent front was allowed to rise to a line, previously marked on the plate, ten cm above the center of the spots.

Detection and Characterization. When dry, the plate was sprayed with a pinacryptol yellow solution made by dissolving 0.05 g of the reagent in 100 ml ethanol and filtered to remove any undissolved material. The plate was then examined under UV light and the color of the spots recorded along with their Rf value. The Rf value is the distance traveled by the spot divided by that traveled by the solvent front. The Rf values may vary with the mol wt of the compounds (5) and, therefore, must be used in conjunction with the color of the spots for identification. The plates were then placed in a jar containing iodine crystals until yellow spots were visible. This treatment confirms the position of any spots which do not fluoresce brightly under UV light and in particular helps to identify alkanolamides which do not exhibit UV fluorescence. After standing for several min the iodine spot from a dialkanolamide will fade, while that from a monoalkanolamide will not fade as much. The plate may now also be sprayed with a cobalt-thiocyanate solution which will give a blue color to ethoxylates and amine-oxides. Table I summarizes the characteristic color with pinacryptol yellow and the approximate Rf value of the surfactant.

Semi-quantitative Analysis

The large difference in distance of travel on the plates between the ionic and nonionic components indicated that they might be separated quantitatively, in amounts large enough to permit IR identification, by using the same solvent-adsorbent system in a column. To accomplish this the following procedure was developed.

A small plug of cotton dipped in isopropanol was inserted in a chromatography column 1.5 cm in diam and 15 cm in length. One-half cm of clean sand was sprinkled on the cotton and any sand sticking to the sides of the column was washed off with a little isopropanol. Reagent grade aluminum oxide was stirred in a beaker with sufficient isopropanol to keep it mobile until all the trapped air was removed. Enough aluminum oxide was poured into the column so that there was a 10-cm layer on top of the sand. The sides of the column were washed again and the column tapped to ensure that the adsorbent was well packed and level at the top. Another 0.5-cm layer of sand was added and the column filled with 10 ml isopropanol, which was allowed to drain no further than the top of the sand.

TABLE I

Identification of Components
Pinacryptol Yellow Reagent-Ultraviolet Light

Surfactant type	Color developed	Rf value[a]
Alkylarylsulphonates	Yellow	0.0–0.1
Soaps	Blue	0.0
Xylene sulphonates	Orange-Yellow	0.0
Toluene sulphonates	Orange-Red	0.0
Sulphated alcohol ethoxylates	Pale Blue	0.0–0.2
Sulphated alkylphenol ethoxylates	Pale Blue	0.0
Amine oxides	White	0.3–0.5
Alkanolamides	....	0.5–0.7
Ethoxylates	Pale Blue	0.7–0.9

[a] These values are valid for chromatoplates having a 0.25-mm layer of aluminum oxide G developed with isopropanol. The Rf values vary with the mol wt of the compound and, therefore, must be used in conjunction with the color of the spots for identification.

If the sample was the alcohol soluble portion of a detergent, 0.5 g was dissolved in 5 ml methanol, placed on the column and moved on the adsorbent by allowing the column to drain to the top of the sand. If the sample was a liquid detergent, 2 ml (which in a 25% active detergent will give 0.5 g surfactant) were allowed to drain on to the column followed by 5 ml methanol to move the sample further into the column.

Elution with isopropanol was now begun. To hasten the process a pressure head was kept on the column by inserting a glass tube through a cork in the top of the column and attaching it with a piece of plastic tubing to a large dropping funnel filled with isopropanol. The stopcocks on the dropping funnel and column were open and the eluant collected in 25-ml fractions. Most of the nonionic appeared in the first 25 ml; so if two nonionics were present (detected previously by TLC) samples were taken every 5 ml. Samples may be evaporated to dryness, weighed and examined by IR spectroscopy for identification. After 100–150 ml isopropanol have been used, most of the nonionic will have washed off the column. Many nonionics contain alkyl-benzene derivatives as the hydrophobic portion so that the degree to which the eluant is free of nonionic may be easily checked by examining a portion of the eluant in the UV region at 275 mμ.

If it appeared that little nonionic was being eluted by the isopropanol, a dropping funnel containing methanol was substituted for the isopropanol. The first 15–25 ml eluant collected after the introduction of the methanol in the column contained the remainder of the nonionic not eluted by the isopropanol. The rest of the methanol eluted contained the ionic components. Ca. 100 ml methanol was usually sufficient to scrub the column clean. The eluant again may be checked for surfactant by examining a portion in the ultraviolet region; an alkyl benzene sulphonate absorbs at 265 mμ. The complete removal of the ionic surfactants from the column was a definite advantage over the use of ion exchange resin for these separations. Finally, the column may be eluted with water to remove materials like builders or inorganic salts that may remain adsorbed on the aluminum oxide.

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[Received December 9, 1963—Accepted May 5, 1964]