TABLE I

Comparison of the Molarity of a Hyamine Solution Standardized Against Branched and Linear Sulfonic Acids

Sulfonic acids	Molarity $\times 10^{-4}$	Standard deviation $\times 10^{-4}$
Branched (ABS)	33.67	±0.057 (N=4)
Linear (LAS)	33.58	±0.057 (N=4)

cedure, and any chloride as previously determined by the Volhard procedure. The mean molecular weight is then calculated from this corrected weight and the normality of the LAS standard.

An apparent nonlinear relationship has been demonstrated for the reaction of anionic detergents with cationic titrants such as Hyamine 1622 (1,3,4). This is illustrated in Fig. 1. The cause of the apparent nonlinearity is the arbitrary selection of the endpoint (4). Initially all the methylene blue (MB) is in the chloroform layer. Addition of excess cationic displaces the MB to the aqueous layer. The generally chosen endpoint is the indication of equal intensities of the blue color in the two phases. Since only the MB-anionic complex imparts color to the chloroform layer, the presence of color in this phase at the selected endpoint indicates that the equivalence point has not been reached. It is this small consistent amount of untitrated anionic that is responsible for the apparent nonlinearity. With Weatherburn corrections (4), linearity was obtained over the entire titration range (Curve 2 of Fig. 1). Thus by applying a small constant correction to all titrant volumes it is not necessary to restrict the titrant range.

For routine analyses it is more convenient to ignore the Weatherburn correction and restrict the titrant volume in both standardization and analysis to the 20–25 ml range. The levels of anionic active, calculated using either the Weatherburn method or the uncorrected restricted volume method agree within ± 0.05% absolute.

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Rapid Desulfonation of Alkylbenzene Sulfonates

VARIOUS INSTRUMENTAL techniques, e.g. gas chromatography, infrared and mass spectrometry, have been used to identify the hydrophobic base of alkylbenzene sulfonates employed in detergent systems. In order to carry out such investigations the hydrocarbon fraction must first be obtained by desulfonation of the sulfonate. The original procedure (1) for such desulfonations involved refluxing with 85% phosphoric acid at 215C for 90 min. Later, Setzkorn and Carel (2) reported a microdesulfonation technique. This involved refluxing the sulfonate, in a microdesulfonation apparatus, with phosphoric acid for 60 to 90 min. Recently, Wright and Glass (3) have described a desulfonation procedure based on heating the sulfonate with concentrated hydrochloric acid in a sealed tube at 200C for 3 hr. It has been found that, using phosphoric acid and elevated pressure, such desulfonations can be carried out in 15 min.

Sufficient sample to contain 50 to 100 mg of sulfonate was placed in a 4 in. × 7/16 in. O.D. glass stoppered test tube and 2 ml of 85% phosphoric acid added. The test tube was inserted in a pressure tube, which has been described earlier (4), and sealed. The pressure tube was then placed in a heating block, maintained at 250C, for 15 min. The pressure tube was cooled under running water and the test tube removed.

Petroleum ether (1 ml, 40–60C boiling range, aromatics free) was added to the tube, the contents of the tube shaken and the ethereal layer transferred, with the aid of a dropper, to a second test tube. The acidic residue was reextracted with a further 1 ml portion of petroleum ether and the ethereal extracts combined. Sodium hydroxide (1 ml, 15% solution) was added to the tube containing the ethereal extract and the contents agitated by inversion. The ethereal layer was transferred to another tube and again washed with 1 ml of 15% sodium hydroxide. The ethereal layer was then transferred to a tapered micro test tube and the hydrocarbon obtained by evaporation of the solvent. This latter step was not carried out when low molecular weight alkyl benzene sulfonates, e.g. that of xylene, were desulfonated. In this case the petroleum ether solution of the hydrocarbon was chromatographed directly.

The gas chromatographic separations were carried out on a "Pye" 104 (Model 4) chromatograph. Low molecular weight alkyl benzenes were analyzed at 100C on an 18 ft 80/100 mesh Chromosorb W column containing 11.5% silicone oil and 11.5% Bentone 34. Higher molecular weight alkyl benzenes, e.g. detergent alkylates, were analyzed at 190C on a 9 ft 60/80

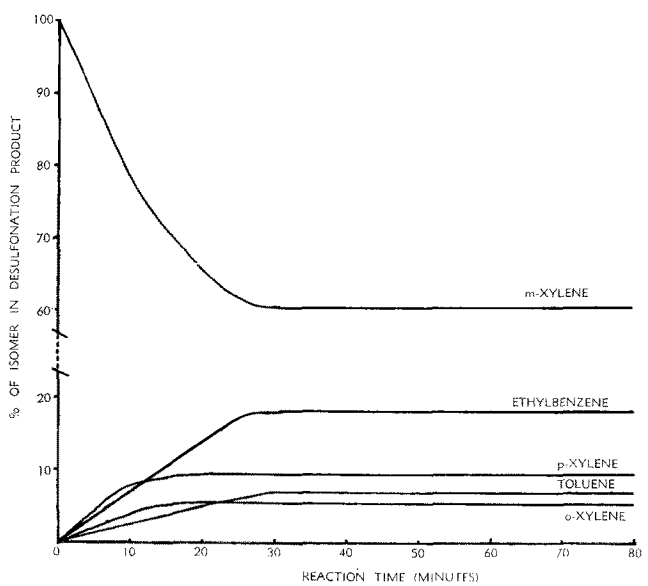

FIG. 1. Composition of desulfonation product obtained from a commercial sodium xylene sulfonate after various reaction times.

mesh Chromosorb P column containing 20% silicone grease.

The chromatogram of the material obtained by desulfonation of a detergent sulfonate was quantitatively identical to that of the parent alkylate. When the procedure was applied to a formulated detergent product containing at least 5% of the sulfonate the chromatogram of the desulfonation product was again quantitatively identical to that of the original alkylate. In addition, the chromatogram contained one or two extra peaks, of low retention times, which did not interfere with the peaks due to the alkylate. These extra peaks were due to decomposition of other components in the formulated product. These results showed that the desulfonation process linearly converted detergent sulfonates to the parent alkylate.

It can be seen (Fig. 1) that in order to obtain a constant composition in the case of a commercial sodium xylene sulfonate solution, the reaction time for hydrotrope samples must be increased to 30 min, a reflection of the greater difficulty encountered in desulfonation of toluene and ethyl benzene isomers. Using the normal reflux procedure (1) for such samples, at least six hours' heating was required to obtain constant composition.

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The Relationship Between Alkyl Furans and the Reversion Flavor of Soybean Oil

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FLAVOR REVERSION in soybean oil is the development of a characteristic beany and grassy flavor prior to the inception of rancidity. This off flavor may develop in soybean oil when its peroxide number is still less than one meq/kg. In a recent communication (1) we have reported the identification of 2-pentyl furan in the volatile flavor compounds isolated from a reverted-but-not-rancid soybean oil and that this compound at concentrations of 1–10 ppm imparts to an oil a characteristic beany and grassy odor and flavor reminiscent of those of a reverted soybean oil. Expert organoleptic panels at four different laboratories consistently identified a bland freshly deodorized cottonseed oil containing 5 ppm of 2-pentyl furan as a reverted soybean oil.

We have postulated that the compound, 2-pentyl furan is produced through the autoxidation of linoleic acid (1). Since soybean oil contains approximately 7% of linolenic acid, it was considered possible that 2-ethyl furan produced from linolenic acid might also contribute to the reversion flavor of soybean oil, and perhaps have an even stronger odor and flavor potential than 2-pentyl furan. The compound, 2-ethyl furan, was therefore synthesized (by K & K Laboratories, Inc., Plainview, N. Y.). Its infrared spectrum is shown in Fig. 1. The flavor characteristic of this compound was evaluated in a bland freshly deodorized cottonseed oil.

It was found that 2-ethyl furan had a higher flavor threshold than 2-pentyl furan and that it did not contribute any beany and grassy type of reversion odor and flavor to an oil. Careful examination of the gas chromatograms of the volatile flavor compounds isolated from a reverted-but-not-rancid soybean oil also did not yield any peak which had a retention time corresponding to that of 2-ethyl furan. It was therefore concluded that 2-ethyl furan does not contribute to the reversion flavor of soybean oil although 2-pentyl furan does. Why 2-pentyl furan is formed in soybean oil in quantities sufficient to cause beany and grassy flavor, but not so in cottonseed oil, is now being investigated.

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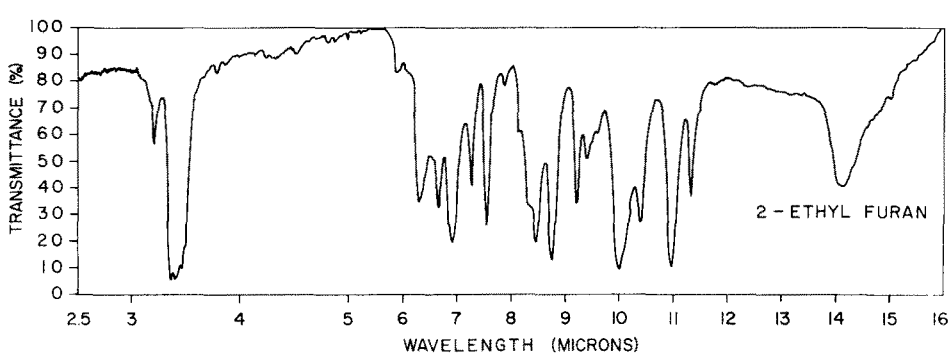

FIG. 1. Infrared spectrum of 2-ethyl furan.