A Reference Standard for Quaternary Solutions Used for Titrating Anionic Detergents

ACCURATELY STANDARIZED samples of linear alkylate sulfonates (LAS) are needed for standardization of quaternary titrants in diphasic titrations (1) and as standards in the ppm range for the APHA procedures (2). Commercial samples of LAS can be conveniently standardized against standard sodium hydroxide using a procedure similar to that described by House and Darragh (3) for estimating the mean mole weight of alkylaryl sulfonates. We have modified the procedure so that quaternary solutions are standardized directly against purified sulfonic acid, the molar concentration of which has been determined by titration with sodium hydroxide. The calculated molarity of a quarternary solution, such as Hyamine 1622 (Rohm & Haas), is thus not dependent on an accurate weight of hygroscopic sulfonic acids or their sodium salts. The original Epton procedure (1) required careful control of titrant volumes between 9.5 and 10.5 ml to obtain accurate results. By decreasing the molar concentration of the quaternary reagent and increasing the sample size it is possible to operate in the 20 to 25 ml titrant range with better precision.

For purification a 1.2 to 1.5 g sample of alkylarylsulfonic acids (90%), such as obtained by sulfonation of linear alkylates (chain length C_{11}–C_{14}), or their sodium salts is dissolved in water. Sulfonic acids are neutralized with sodium hydroxide using phenolphthalein, the solution transferred to a 250 ml separatory funnel, and about 2 g of sodium chloride added. The volume in the separatory funnel is adjusted to about 100 ml and the mixture is extracted with one 75 ml and two 50 ml portions of ethyl ether to remove any nondetergent oily matter. Vigorous shaking should be avoided to prevent emulsification. Concentrated hydrochloric acid (35 ml) is added to adjust the acidity to approximately 3 N, sulfonic acids are extracted with three 50 ml portions of ethyl ether, and the combined extracts are washed with three 15 ml portions of 3 N hydrochloric acid to remove sodium salts. Removal of the acidic washes must be complete even at the expense of small losses of the ethyl ether solution.

The washed ethyl ether extract is transferred to a 300 ml beaker and the ethyl ether evaporated on a steam bath. The beaker is placed over an open hole in the steam bath to remove all the residual hydrochloric acid. The absence of acid vapors can be checked with moist litmus paper. The sulfonic acids are then dissolved in 50 ml of neutralized 3A alcohol and titrated with standardized sodium hydroxide (0.1 N) using phenolphthalein indicator.

The titrated acids are quantitatively transferred to a 500 ml volumetric flask and diluted with water. A 100 ml aliquot is titrated for chloride following the Volhard procedure. If chloride is present, the milliequivalents of sodium hydroxide must be corrected by subtracting five times the millequivalents of chloride. If more than traces of chloride are found the extraction must be repeated as chloride affects the subsequent quaternary titration using methylene blue as indicator.

Standardization of the quaternary solution is accomplished as follows. An aliquot (10 ml) of the purified sodium sulfonate solution is transferred to a 100 ml glass-stoppered graduate. The following are added in sequence: 5 ml of 3A alcohol, 25 ml of methylene blue solution (0.03 g methylene blue chloride, 12 g concentrated sulfuric acid, and 50 g sodium sulfate per liter), and 15 ml of chloroform. Unnecessary premixing of the chloroform-water-alcohol system before the addition of the quaternary should be avoided. Add from a buret 18 ml of 0.0035 M quaternary solution (1.6 g Hyamine 1622 per liter), shake vigorously for 30 sec, and allow the phases to separate (the chloroform layer should be blue). Continue adding the quaternary solution in 1 ml increments until the endpoint is passed as evidenced by the transfer of the blue color from the chloroform layer to the aqueous phase. Repeat the titration using a second aliquot of the sulfonate standard adjusted to require between 20 to 25 ml of the quaternary solution. Add as large a volume as possible without overtitrating and shake for 1 min. Continue adding the quaternary in 0.1 ml increments (followed by shaking for 1 min) until the endpoint is reached. The point at which the intensity of color in the two phases is judged to be equal when viewed by transmitted light is taken as the endpoint. Using the milliequivalents of sodium hydroxide required to titrate the purified sulfonic acids and the proper dilution corrections the molarity of the quaternary solution can be calculated.

Any convenient commercial source of alkylarylsulfonic acids, e.g. branched (ABS) or linear (LAS) may be used for the standardization (Table I). There is no statistically significant difference between the molarities obtained using the two types of sulfonic acids as standards.

The mean molecular weight of the sulfonate can be estimated by transferring a 200 ml aliquot of the purified sodium sulfonate solution to a tared glass-stoppered Erlenmeyer flask. After evaporating the water, the salt is dried at 105C for 30 min and weighed. The weight of the salt is corrected for any residual water, determined by the Karl Fischer pro-

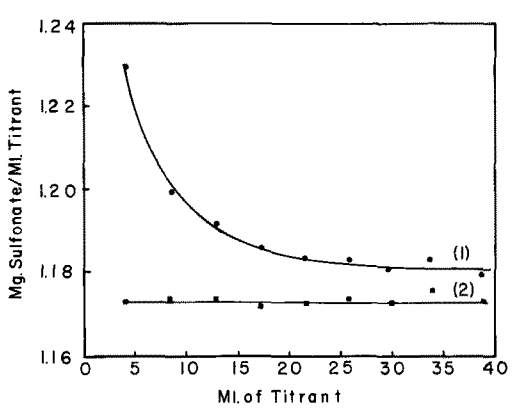

FIG. 1. Titrations of alkylarylsulfonate with Hyamine 1622. Curve 1, uncorrected; Curve 2, corrected.

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.

H. M. GARDNER
Lever Brothers Company
Research Center
Edgewater, New Jersey

REFERENCES

1. Epton, S. R., Trans. Faraday Soc. *44*, 226 (1948).
2. "Standard Methods for the Examination of Water and Wastewater," 12th Edition, Published by American Public Health Assoc. Inc., New York, N.Y. (1965).
3. House, R., and J. L. Darragh, Anal. Chem. *26*, 1492 (1954).
4. Weatherburn, A. S., JAOCS *28*, 233 (1957).

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

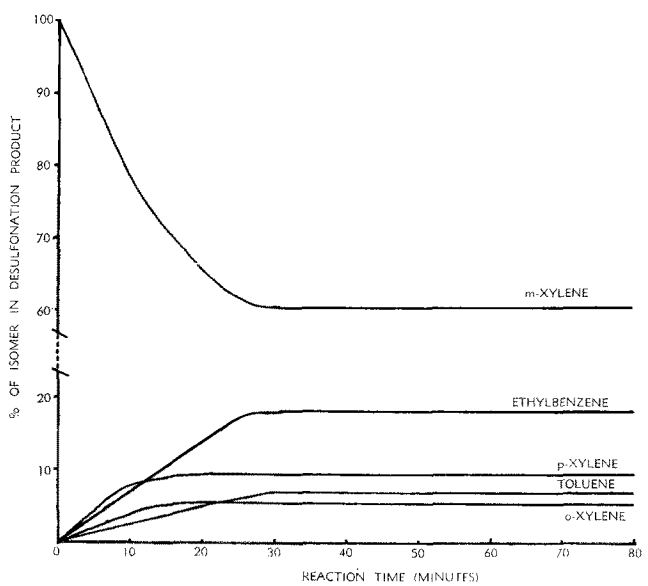

FIG. 1. Composition of desulfonation product obtained from a commercial sodium xylene sulfonate after various reaction times.