Application of Silylation to Soaps, Alcohols and Amines in Aqueous Solutions

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Gas chromatographic analysis of many surfactants has been limited due to tailing and adsorption of the analyte on the stationary phase of the column by polar groups such as hydroxyl and amine functionalities. Silylation of these surfactants reduces these unfavorable interactions by replacement of the active hydrogen with a silyl group $Si\text{-}(CH_3)_3$. Although silylation generally is avoided in aqueous solutions, some surfactants have been silylated successfully in aqueous solutions. These include fatty acids and their hydroxamine soaps, fatty and other alcohols, fatty amines, and some inorganic acids. Quantitative results have been confirmed by stoichiometric, gas chromatographic and infrared data.

Surfactants commonly found in shampoos, detergents, metalworking fluids and paints, etc., contain numerous surface active agents which can be particularly difficult to analyze, especially when encountered at low concentrations as when working "oil in water" emulsions. This problem is due primarily to the nature of the surfactant molecule, which often contains hydroxyl, carboxylic or amine functionalities, and to the nature of the aqueous solution matrix. Analysis of these surfactants at low concentrations in aqueous solutions has been by numerable techniques, most importantly classical wet techniques, gas chromatography and liquid chromatography. Each methodology encompasses applicability to a vast array of surfactants, but each also is accompanied by its own particular set of advantages and disadvantages. For instance, gas chromatographic analysis has seen standard use in the analytical laboratory but necessitates that the analyte be sufficiently volatile that elution occurs within a reasonable time frame. This is dependent upon the molecular characteristics (molecular weight, hydrogen bonding, etc.) and the strength of the interactions between the stationary phase (or solid support) and the analyte. In particular strong polar groups such as hydroxyl and amine functionalities pose formidable problems due to tailing and adsorption of the analyte on the stationary phase of the gas chromatographic column.

For many of these compounds silylation has been a practical answer, although the approaches generally have involved silylation under anhydrous conditions (1, 2). This requires either extraction and/or dehydration steps which can be quite tedious. Silylation of compounds in aqueous solutions has been studied by numerable workers (3-5), with the article by Brittain, Sullivan and Schewe (6) being quite informative. These procedures generally consisted of silylation of the analyte (25-99% by weight in an aqueous solution), extraction of the silyl ether and injection into the gas chromatograph. In an alternative approach, Esposito (7) utilized on-column formation of trimethylsilyl ethers which accommodated aqueous and alcoholic solutions by injection of the aqueous solution followed by injection of the silylation reagent. The trimethylsilyl derivative is then formed on the column as the silylation reagent contacts the analyte. Most recently, Valdez (8) described a rapid silylation procedure useful for dilute hydroxy compounds in aqueous solutions using bis-trimethylsilyltrifluoroacetamide (BSTFA) and acetonitrile as a cosolvent. This work anticipated applicability of silylation only to simple hydroxy compounds such as the acetylenic alcohols, glycerol, etc., as reported. Excess amounts of silylation reagent were used to overcome problems associated with hydrolysis of the silylation reagent and the formed silyl ethers.

This paper describes the application of silylation to some common surfactants in aqueous solutions. Silylation appears to have a broader applicability in the study and analysis of surfactants in complex aqueous matrices than originally anticipated. Fatty acids and their hydroxamine soaps, fatty alcohols, glycolic alcohols, boric acid and its hydroxamine soap, and fatty amines are just a few of the compounds that can be analyzed by simple silylation techniques. The methodology described has the additional benefit that little sample preparation is needed, enabling rapid analyses for these types of components.

EXPERIMENTAL

Materials. Silylation reagents BSTFA and BSTFA + 10% TMCS (trimethylchlorosilane) were obtained from Regis Chemical Co. (Morton Grove, Illinois). Fatty alcohol and fatty acid standards were obtained from Supelco Inc. (Bellefonte, Pennsylvania), and the fatty amines from Chem Service Inc. (West Chester, Pennsylvania).

Methods. A Tracor 560 gas chromatograph was used with flame ionization detection. Analysis conditions were: injector and detector manifold 300 C; column oven, experiment dependent; nitrogen flow, 30 ml per min through a six-ft × 1/8" i.d. glass column packed with 3% OV-101 on 80-100 mesh chromosorb W-HP. Peak retentions and areas were recorded on an

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IBM-PC with Nelson Analytical software. A Nicolet MX-1 fourier transform infrared spectrometer was used for infrared analysis.

Single Step Silylation Method. Samples of 25 μl were placed into two ml vials followed by 175 μl of silylation grade acetonitrile. A butyl septum was secured on the vial followed by syring injection of 800 μl of BSTFA or BSTFA + 10% TMCS. The vial was agitated for 10-20 seconds during which a small amount of heat was generated. After one min of reaction time, a 2.5 μl injection was made into the gas chromatograph.

Two Step Silylation Method. Injection of 0.5 μl of the aqueous sample was followed by a 2.5 μl injection of BSTFA. Chromatographic analysis was then made.

Silylation for Stoichiometric Analysis. A 100 μl aliquot of a 1:1 (wt/wt) triethanolamine:water solution was added to a preweighed five ml micro reaction vessel containing a micro stir bar. After reweighing, 800 μl of acetonitrile was added to the sample. Then the reaction vessel was heated to 60 C in a water bath. While stirring, 3000 μl of BSTFA was added to the mixture. After three min the silylation reagent was evaporated slowly with a nitrogen purge. The reaction vessel was then dried off and placed in a dessicator to cool to ambient temperatures, whereupon the reaction vessel was reweighed and stoichiometric yields calculated. Spectra of the residue were taken for structural confirmation and completeness of the reaction. Small amounts of tetrahydrofuran were used in addition to the acetonitrile for the silylation of the fatty alcohols and the oleic acid due to their limited solubilities in water.

Reactions. Derivatization of aqueous solutions involves a competing reaction between water and the solute with the silylation reagent (3, 8).

$$CF_3C[OSi(CH_3)_3] = NSi(CH_3)_3 + H_2O \rightarrow (CH_3)_3SiOSi(CH_3)_3 + CF_3CONH_2 \qquad [1]$$

$$CF_3C[OSi(CH_3)_3] = NSi(CH_3)_3 + ROH \rightarrow (CH_3)_3SiOR + CF_3CONH_2 \qquad [2]$$

Because the reaction with water is rapid, the amount of derivatizing agent necessary for the silylation of the analyte should exceed the molar amount of water. The amount of BSTFA was in excess of the water by a 1 fold molar amount while also in excess of the analyte by a minimum 50 molar amount.

RESULTS AND DISCUSSION

Various methods have been used for the analysis of surfactants. Commonly found in surfactant solutions are fatty acids and their triethanolamine soaps (mono-, di-, tri-). The gas chromatographic analysis of fatty acids in aqueous solutions generally is made by extraction and methylation or by analysis of the free fatty acids. Methylation must be preceded by acidification and extraction of the fatty acids from the aqueous media, which can be a tedious procedure but often is the method of choice. The analysis of the free fatty acids can be made, but this is accompanied by relatively poor resolution due to peak tailing and band broadening. An additional problem is that direct injection of a fatty acid-triethanolamine soap often will result in a featureless chromatogram due to adsorption on the chromatographic column of both the fatty acid and the triethanolamine (Fig. 1). While the adsorption of the triethanolamine was expected, the adsorption of the fatty acid was not, because in the absence of triethanolamine the free fatty acids, even in aqueous solutions, will elute. Silylation overcomes this problem by simultaneous silylation of both the fatty acids and the triethanolamine. Figure 1 shows a typical chromatogram of the silylation adducts of aqueous fatty acid-triethanolamine soaps. Furthermore, a study of a 3:1 oleic acid:triethanolamine mixture in aqueous solution was shown to give linear results to levels well below 1% (Fig. 2).

Silylation of the triethanolamine and the fatty acid by the two-step method of Esposito was not successful in eluting either the fatty acid or the triethanolamine, indicating that not only adsorption, but also a possible condensation reaction between the two on the column surfaces was occurring. Therefore, in the single injection method silylation must be occurring in the reaction vessel. This was implied earlier (8) but not confirmed by experimental evidence. As further proof the silylation procedure was performed on a larger scale for triethanolamine, oleic acid and octadecanol. After reaction the solvent was stripped off under a nitrogen blanket and infrared spectra were taken of the residue (Figs. 3-5). In the case of the silylation of the oleic acid, the carbonyl frequency of 1720 cm^{-1} agreed well with literature values (9). Although this value is lower than normally encountered in ordinary esters, it has been suggested this is due to either a bulk substituent effect or to electron release from silicon to oxygen (10). Other typical frequencies due to silylation

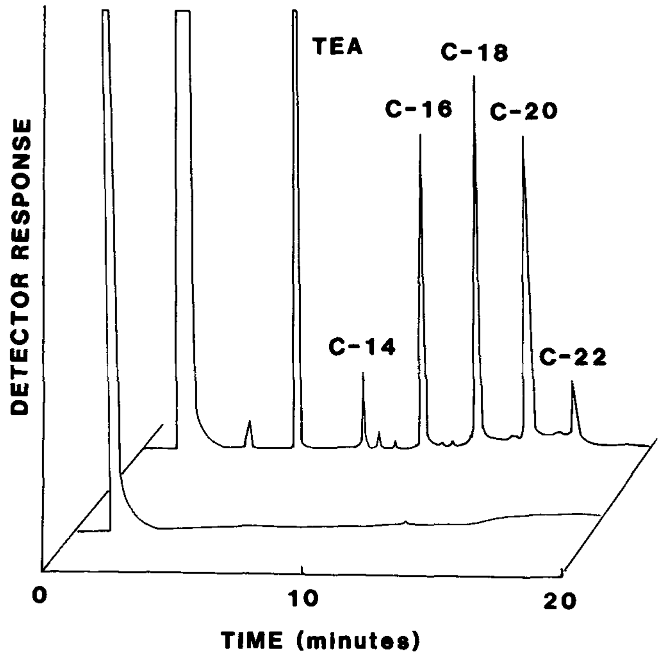

FIG. 1. Gas chromatographic analysis of an aqueous fatty acid-triethanolamine mixture with (upper) and without (lower) silylation. The fatty acids are labelled C-14 – C-22, and the triethanolamine is designated as TEA.

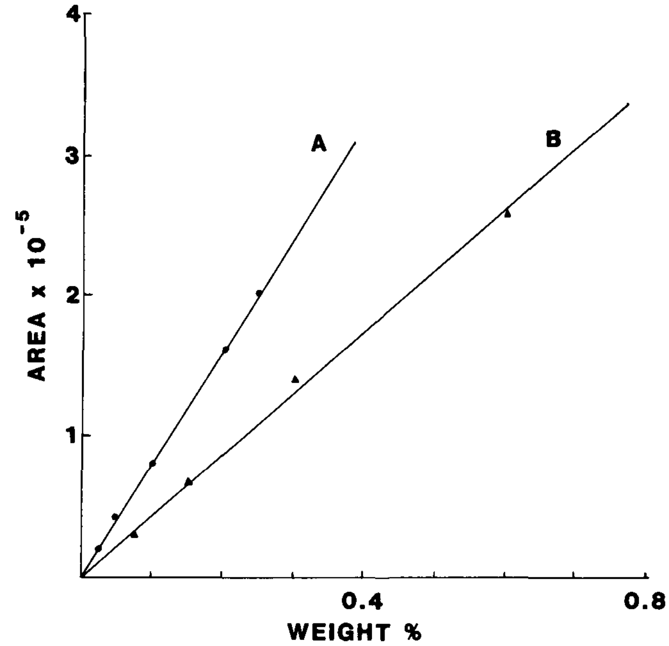

FIG. 2. Calibration curve for a silylated 3:1 oleic acid:triethanolamine soap in aqueous solution. The weight % indicates the concentrations of the individual components in water where A and B designate triethanolamine and oleic acid, respectively.

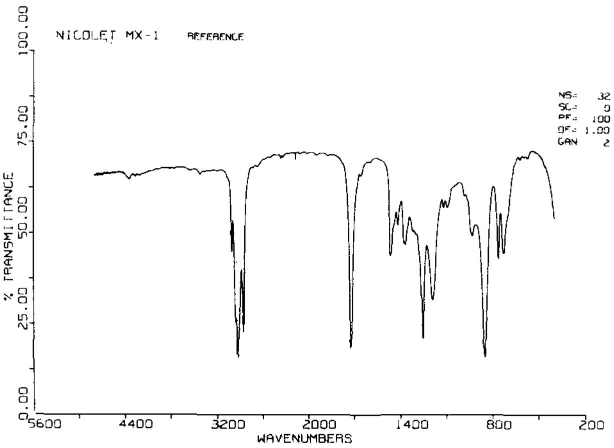

FIG. 3. Infrared spectra of the silylation adduct of oleic acid.

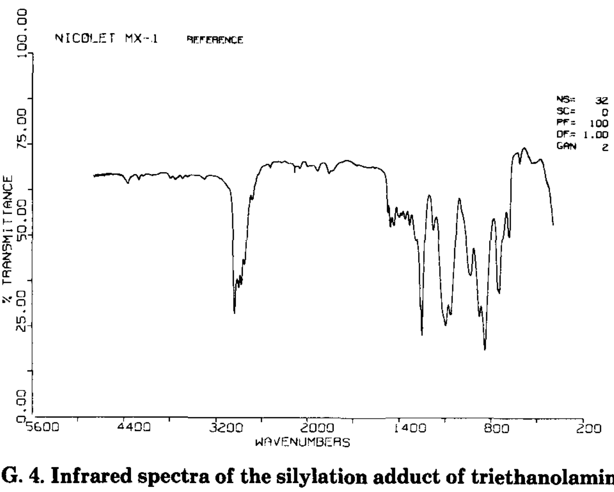

FIG. 4. Infrared spectra of the silylation adduct of triethanolamine.

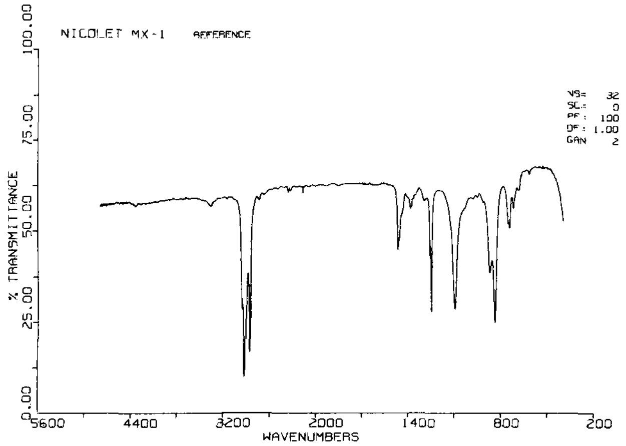

FIG. 5. Infrared spectra of the silylation adduct of octadecanol.

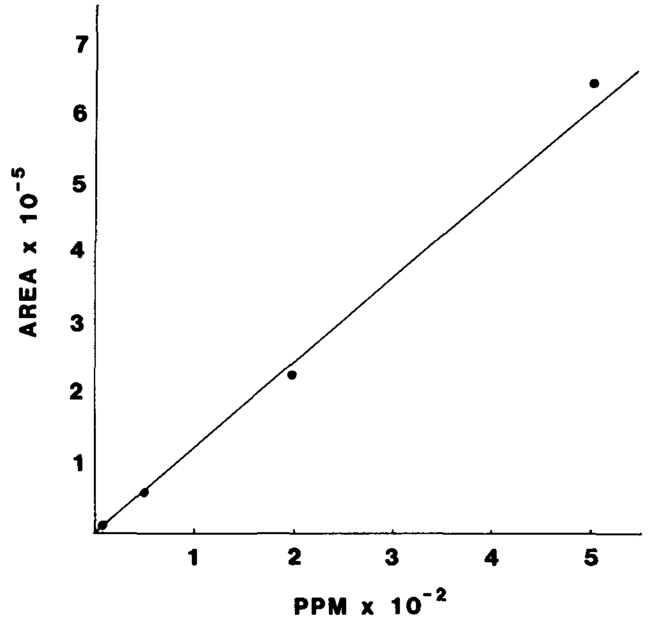

FIG. 6. Calibration curve for the silylation of boric acid in aqueous solutions ranging in concentration from 5 to 500 ppm.

(11) can be seen in all three spectra, such as Si-CH_3 deformation at 1255 cm^{-1}, Si-$(CH_3)_3$ stretch at 840 cm^{-1}, and C-O-Si absorption at 1100 cm^{-1}, while the features due to OH groups are now absent.

Stoichiometric analysis of the residue gave conversion efficiency values for the triethanolamine, oleic acid and the octadecanol. The expectations were a single silylation site for the fatty acid and fatty alcohol while the triethanolamine would be silylated at all three hydroxyl sites. Based on this, the conversion efficiencies were found to be 94, 96 and 92% for the triethanolamine, oleic acid and octadecanol, respectively.

Analyses of boric acid (H_3BO_3), and boric acid-ethanolamine soaps were again easily made by the single step silylation technique. A linearity study is shown in Figure 6 for concentrations of boric acid at 5 to 500 ppm in aqueous solutions. Of particular interest to us was the form of the boric acid-triethanolamine adduct as to whether it existed in solution as a soap or a true condensation product. Silylation of these materials in an aqueous matrix indicated that a true condensation product had not formed because the levels of both the boric acid and the triethanolamine were quantified at their dissociated levels. This suggested only ionic interactions between them. Analysis of other inorganic acids, such as phosphoric, sulfuric and their organic analogs appears to be practical using this method, although we had difficulty in getting reproducible results. This may have been the result of inadequate reaction times, lack of solvent optimization or the necessity of using an acid washed column. The recent work of Bauer and Vogt (12) is most helpful in this area.

Silylation of the fatty amines in aqueous solutions proved to be more difficult than the silylation of the other functionalities (hydroxyl and carboxyl). Silylation by BSTFA alone was found to be inadequate, while BSTFA + 10% TMCS allowing 3-5 min of reaction time at 60 C achieved reproducible results. Silylation of both amine protons is suggested based on the fact that silylation of anhydrous amines using similar silylation reagents produced disubstituted TMS derivatives (13). Also, polar solvents such as acetonitrile are reported to favor disubstitution of the amine functionality. Chromatographic plots of C-12, C-14, C-16 and C-18 fatty amines are shown in Figure 7. Reinjection of the silylation mixture after several hours yielded equivalent peak heights, indicating that the silyl adducts were resistant to hydrolization.

Several hydroxy compounds such as butoxytriglycol, fatty alcohols, and the acetylenic alcohols have been successfully silylated by the single-step method. Silylation of this category of compounds has been covered in an earlier paper (8). In the absence of amines most hydroxy compounds will readily be silylated by the two-step method employing on-column formation of the silyl ethers. In fact this may be the method of choice in these cases, because the ratio of silylation reagent to analyte is smaller making lower detection limits possible. In any case, many types of surfactants found at low concentrations in aqueous solutions can be readily silylated by one or both methods, producing quantitative as well as qualitative results.

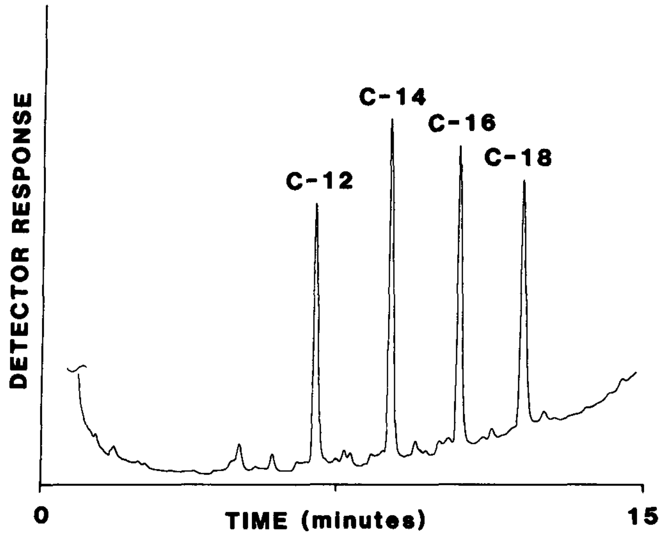

FIG. 7. Chromatographic plot of silylated C-12 to C-18 fatty amines at 0.1% levels in an aqueous glycol emulsion.

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