• *Short Communication*

Determination of Cationic Surfactant in the Presence of Alcohol Sulfate Surfactant Using Orange II Dye

During washing and conditioning treatments, both anionic and cationic surfactants may come in contact with human hair or textile fibers and attach to their surfaces. To study these interactions, an analytical procedure was required for the determination of cationic surfactant in the presence of fatty alcohol sulfate. A colorimetric method, described by Few and Ottewill (1) and recently modified by Scott (2), for the determination of cationic surfactants was selected for a study of the conditions which would make the method applicable to this problem of mixed surfactant analysis.

The apparatus and reagents used in this study have been described previously (2). The recommended procedure is as follows: Weighed aliquots (0.1–0.6 g) of quaternary solution (approximately 2.4 mg quaternary/g) with an equivalent or less of sodium lauryl sulfate (SLS), are refluxed with 10 ml 4N HCl for 1½ hr. After the reaction mixture cools to room temperature, the pH is adjusted to 8.0 with 0.8N sodium hydroxide. The mixture is transferred to a 125 ml extraction cylinder, diluted to 100 ml volume with deionized water and the remainder of the analysis performed as described by Scott (2).

Tables I through IV summarize the results of the Orange II analysis of the two quaternaries dodecyltrimethylammonium bromide (DTAB) and hexadecyltrimethylammonium bromide (CTAB). Analyses were performed in the absence and in the presence of SLS at different ratios of sulfate to quaternary. Analysis for quaternary in the presence of SLS is accomplished by acid hydrolysis of the alcohol sulfate, a technique which has been described previously to prevent fatty alcohol sulfate interference in mixed surfactant determinations (3). The data show no significant differences between the ratios of quaternary-absorbance in the absence of SLS and in the presence of SLS when hydrolysis is employed. From these data, assuming a 1:1 stoichiometry between alcohol sulfate and cationic, one may calculate the amount of alcohol sulfate. In sample 1, Table I, the amount of SLS is 0.59 μmoles by calculation and 0.71 μmoles by measurement. Thus, the agreement between calculated and measured values for cationic determination in the presence of SLS by this scheme is good; however, the method provides only for a rough estimation of fatty alcohol sulfate surfactant.

In addition to hydrolysis, manipulations which are required to prevent SLS interference in this determination include pH adjustment to neutralize excess acid, and dilution to a salt (sodium chloride) concentration of less than 0.5 M to avoid salting out of uncombined Orange II to the chloroform phase. Presumably, fatty amines or amine oxides which are stable to acid hydrolysis, and capable of forming water-insoluble chloroform-soluble adducts with Orange II can be analyzed in the presence of alcohol sulfate surfactant by controlling the extraction pH (2) in this procedure.

The technique as described should make the Orange II method a useful tool for studying the interactions of anionic and cationic surfactants in solution. One instance of usefulness is demonstrated in a study of the interaction of these two surfactant types in the presence of keratin fibers (4).

TABLE I

Analysis of DTAB in the Presence of SLS

Sample No.	Absorbance	Mg (DTAB)	Mg DTAB / Absorbance units	Molar $\frac{\text{SLS}}{\text{DTAB}}$ Ratio
1	0.429	0.502	1.17[a]	0.44
2	0.356	0.265	0.744[b]	0.80
3	1.25	0.935	0.746[b]	0.23
4	0.675	0.503	0.745[b]	0.42
5	0.706	0.526	0.745[b]	0.40

[a] No hydrolysis was employed.

[b] Hydrolysis was employed. The mean ratio of mg quaternary/A = $\bar{x}$ for samples 2–5 is 0.745.

TABLE II

Analysis of DTAB in the Absence of SLS

Sample No.	Absorbance	Mg (DTAB)	Mg DTAB / Absorbance units[a]
1	0.323	0.242	0.749
2	0.650	0.485	0.746
3	0.971	0.719	0.741
4	1.29	0.961	0.744
5	1.61	1.21	0.747

[a] No hydrolysis was employed in the analysis of these samples which provided a ratio for $\bar{x}$ of 0.745.

TABLE III

Analysis of CTAB in the Presence of SLS

Sample No.	Absorbance	Mg (CTAB)	Mg CTAB[a] / Absorbance units	Molar $\frac{\text{SLS}}{\text{CTAB}}$ ratio
1	0.271	0.237	0.875	1.05
2	0.548	0.481	0.878	0.52
3	1.18	1.04	0.878	0.24

[a] Hydrolysis was employed in these determinations. The mean ratio $\bar{x}$ for these samples is 0.877.

TABLE IV

Analysis of CTAB in the Absence of SLS

Sample No.	Absorbance	Mg (CTAB)	Mg CTAB[a] / Absorbance units
1	0.213	0.188	0.884
2	0.274	0.243	0.885
3	0.376	0.331	0.882
4	0.430	0.373	0.868
5	0.567	0.494	0.871

[a] No hydrolysis was employed in these analyses which provided a ratio for $\bar{x}$ of 0.878.

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