Alkaline Methylene Blue Method for Determination of Anionic Surfactants and for Amine Oxides in Detergents

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Abstract

The concen of anionic surfactants in alkaline media has been determined by modification of the methylene blue titration. The method is based on the oxidation of methylene blue chloride to dimethyldihydroxyindoline, a red dye, in the presence of chloroform and sodium hydroxide. This method in conjunction with the acid methylene blue titration, also may be used to determine the amon of amine oxides in formulated products. For concens of less than 100 ppm a spectrophotometric method was used.

Introduction

Anionic surfactants in alkaline solutions are used industrially in applications such as textile processing, metal cleaning, bottle washing, and fruit and vegetable peeling. In order to maintain the concen of surfactant in the cleaning bath, a quick method of analysis is desirable. The total anionic surfactant historically has been determined by titration with quaternary surfactant using methylene blue as an indicator (2), in an acidic system. Longwell and Maneese (4) reported that with aqueous solutions about pH 7 the chloroform layer turned various shades of pink and blue interfering with the end point. To destroy these colors successive extractions with buffered salt and neutral methylene blue indicator (1,4) were required. A spectrophotometric technique using methyl green (5) as the indicator also required the surfactant solution to be acidic. A titrimetric method using bromoresol green (3) as an indicator for the measurement of anionic surfactants in alkaline media has been published.

An investigation of methods for determining the amon of anionic surfactant in highly alkaline systems led to a modification of the methylene blue titration. The method proposed has been extended to include an analysis for amine oxides in formulated products, based on the cationic nature of amine oxides at low pH and nonionic nature at high pH. Concens investigated titrimetrically were 10 to 0.01% actives. Spectrophotometrically the procedure appears sensitive to 10 ppm.

Experimental

Reagents

Methylene Blue Indicator. Dissolve 0.03 g methylene blue chloride (methylthionine chloride) in 50 ml water. Add 6.6 ml 96% sulfuric acid and mix. Add 20.0 g sodium sulfate (anhydrous) and dissolve. Add water to make up to 1 liter.

Hyamine 1622 Solution (ca. 0.0040 N). Dissolve 1.814 g Hyamine 1622, di-isobutyl phenoxy ethoxy ethyl dimethylbenzy ammonium chloride (Rohn and Haas), in water and dilute to 1 liter. Standardize

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solution against 0.0040 N Aerosol OT, 100%, sodium di-2-ethylhexylsulfosuccinate (American Cyanamid) (2).

Procedure

The weighed sample is dissolved and diluted to 250 ml with water. A 10 ml aliquot is pipetted into a 100 ml glass stoppered graduate containing 15 ml chloroform and 25 ml methylene blue indicator. The stoppered graduate is shaken vigorously. A 15 ml volume of 15% sodium hydroxide solution is added and the stoppered graduate is shaken again. The mixture is then titrated with Hyamine 1622. After each addition of titrant, the graduate is shaken vigorously. The separation of the chloroform-in-water emulsion is no blue hue. As the end point is approached, the titration proceeds, the water layer becomes colorless and the chloroform layer goes from blue, blue-violet, to red violet. The end point is reached when the chloroform layer is a clear red or pink containing no blue hue. As the end point is approached, the separation of the chloroform-in-water emulsion is rapid. To give a reasonable titer, it may be necessary to vary the concn of the Hyamine 1622 solution or increase the size of the aliquot of detergent solution.

Calculation

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\text{% Anionic} = \frac{H \times N_H}{W'} \times 100
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H = \text{ml Hyamine 1622 solution}
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\[
N_H = \text{normality Hyamine 1622 solution}
\]

\[
\text{meq} = \text{milliequivalent weight of anionic}
\]

\[
W' = \frac{\text{ml in aliquot} \times \text{sample weight (W)}}{\text{solution volume}}
\]

\[
\text{W} = \frac{\text{W}}{\text{solution volume}}
\]

\[
\text{Eq} = \text{equivalent weight of anionic}
\]

Discussion and Results

The basis for the determination of the amount of anionic surfactant by the acid methylene blue titration is the solubility of the anionic-cationic complex in chloroform. Initially, acidic methylene blue reacts with the anionic surfactant to give a chloroform soluble complex. Titration with a stronger cationic releases the methylene blue to the water layer, to complex with more anionic. This process is repeated until an end point is reached, which is defined as the even distribution of the blue color between the water and chloroform layers.

In discussing the behavior of methylene blue, D. C. Abbott (1) reported that in the presence of alkaline solutions (above pH 9.5) and chloroform, methylene blue chloride is readily oxidized to dimethylthionoline giving bright red solutions. In this investigation when 15% sodium hydroxide, methylene blue and chloroform were shaken, an immediate red color developed in the chloroform layer. When surfactant solution, methylene blue, chloroform and 15% sodium hydroxide were shaken, the chloroform layer was blue indicating that the anionic surfactant had complexed with the methylene blue preventing its oxidation to dimethylthionoline. The complexing of the methylene blue and anionic appeared to be preferential to the oxidation of the indicator. Therefore, the titration for the determination of anionic surfactant was carried out in alkaline solution using the formation of the red color as the end point.

Table I gives the results of the analyses of surfactant solutions (calculated as 0.2% anionic) by methylene blue titrations. With increasing percentages of sodium hydroxide (i.e., 2, 5, 10, 15%) the end point in the chloroform layer changed from matching blue colors for 2%, to red-violet for 5%, to red for 15%. With 5% sodium hydroxide, the water layer was blue, with 10% light blue, and with 15% almost colorless. For a theoretical concn of 0.200% anionic the range of experimental values was 0.189 to 0.211 (Table I). Since the red color of the end point depends on the demethylation-oxidation of the methylene blue, the higher levels of sodium hydroxide provide a more rapid titration and a more definitive end point. Some surfactants cause the chloroform layer to retain a milky appearance throughout the acid methylene blue titration making the matching of blue colors difficult. Using the alkaline titration provides a means to obtain a sharper end point. This analysis was found to be applicable for compounds of high surface activity as well as those of borderline surface activity.

The alkaline methylene blue titration was employed over a wide concn range for sodium 2-ethylhexyl sulfate (Tergitol Anionic 08). For the concns other than 0.05 to 0.2%, the concn of the quaternary solution and/or the volume of detergent solution was adjusted to obtain a reasonable titer. The results are given in Table II. The precision for 100 ppm and below was not good. Deviation from the theoretical concn was 9% for 100 ppm; for the higher concns 4% or less.

By using both the alkaline methylene blue titration and the acid methylene blue titration, detergent formulations containing amine oxides were analyzed. Based on the behavior of alkyl dimethylamine oxides