A Test Method for Analyzing Anionic or Cationic Surfactants in Industrial Water

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ABSTRACT

A general 2-phase titration method is introduced for the quantitative identification of either anionic or cationic surface active agents commonly used in the domestic and industrial applications. Initially, an appropriate amount of quaternary ammonium compound is added to an unknown water sample to be analyzed and to ensure the treated sample contains excess amount of quaternary ammonium compound, and thus, is cationic in nature. The amount of excess quaternary ammonium compound is then quantitatively determined by titration with a standard anionic surfactant in the presence of methyl orange dye, buffer reagent, and chloroform. If the original surfactant in the tested sample is anionic, the anionic surfactant content (μM) is equal to the known amount (μM) of the added cationic quaternary ammonium compound minus the amount (μM) of standard anionic titrant spent in the neutralization reaction. If the original surfactant in the tested sample is cationic, the cationic surfactant content (μM) is equal to the amount (μM) of standard anionic titrant spent in the titration minus the known amount (μM) of the added cationic quaternary ammonium compound. The test procedure is simple and can be successfully completed within 5-7 min by a laboratory technician. For research or industrial application, a specific anionic or cationic surfactant to be used should be selected for the surfactant calibration. For the water quality control of unknown samples, the most common anionic surfactant, linear alkylate sulfonate, and the most common cationic surfactant, quaternary ammonium chloride, are selected as surfactant standards. The anionic surfactant concentration of a sample can be reported to be mg/liter as linear alkylate sulfonate while the cationic surfactant concentration of a sample can be reported to be mg/liter as cetyldimethylbenzylammonium chloride. Other alternatives for the use of the proposed general 2-phase titration method are suggested. Effective elimination of the interference caused by the presence of oil in an industrial water is also discussed. The proposed method is limited in application to the measurement of free ionic surface active agents only.

INTRODUCTION

The active agent in synthetic detergents that possesses a high cleaning ability is generally termed surfactant or surface active agent. These agents in solution exhibit special characteristics that include concentration at air-water interfaces, the lowering of surface tension, formation of micelles, and the increased penetration of the liquid in which they are dissolved (1).

A variety of synthetic surfactants, such as linear alkalyte sulfonate, ethylene oxide, etc., have been widely accepted since the end of World War II as active ingredients of detergent to substitute for soap (2,3). Most of the synthetic detergents contain 20-30% surface active agent and 70-80% builders that enhance the detergent properties of the active ingredients (4,5).

Surfactants can be used not only as the active ingredients of the synthetic detergents, but also as flotation agents (6-12), primary coagulants or coagulant aids (13-14), softening agents, dyeing aids, metal strippers, corrosion inhibitors (15), sanitizers (16), and algicides (17). They are important substances for both domestic and industrial uses. The synthetic surfactants are of major types: anionic, nonionic, and cationic.

Most anionic surfactants are sodium salts, which ionize to yield a sodium ion plus a negatively charged, surface active ion. Common anionic surfactants are sulfates (such as sodium lauryl sulfate), and sulfonates (such as alkylbenzene sulfonate, and linear alkylate sulfonate). In general, anionic surface active agents can be quantitatively measured by the methylene blue method (18-20), carbon absorption method (18), azure A method (21), and 2-phase titration method (22-25).

The nonionic surfactants do not ionize, and have to depend upon groups in the molecule to render them soluble. Most of nonionic surfactants depend upon polymers of ethylene oxide to give them this property (5). Burttschell (26) has developed a sensitive analytical method to measure the ethylene oxide based nonionic surfactants in sewage. Other works for analyzing the polyoxyethylene nonionic surfactants have been done by Crabb and Persinger (27) and Patterson, et al., (28).

Cationic quaternary ammonium compounds and amine compounds are the most common cationic surfactants being used today. In a quaternary ammonium salt, the hydrogens of the ammonium ion all have been replaced with alkyl groups, and its surface active properties are contained in the cation. For a cationic amine compound, such as dodecylamine hydrochloride, only 1 of the hydrogens in the ammonium ion is replaced with an alkyl group, i.e., $CH_3(CH_2)_{11}$-. The chemical characteristic of a cationic amine compound is very similar to that of a quaternary ammonium compound. Cross (29) has developed an analytical method to identify and determine cationic surface active agents with sodium tetraphenylboron. His method has been simplified and used by many researchers. Such simplified analytical method for measuring cationic surfactants can be found from 2 recent publications (17,30).

The objective of this research was to develop a general analytical method which can be used to analyze either anionic or cationic surfactants. Lovell and Sebba (31) have developed a general ion flotation method for analysis of some cationic and anionic surfactants below critical micelle concentration. However, the flotation method is nonstoichiometric, requires precise control of conditions, and is very susceptible to interference from dissolved inorganic ions. The general analytical method present in this paper is termed 2-phase titration, which is stoichiometric, and can be performed easily by a laboratory technician within a very short period of time. Additionally, no instrumentation is required.

The general 2-phase titration method was initially developed by Calspan Corporation. The method is primarily a combination of the analytical procedures for anionic surfactants (22) and the analytical procedures for cationic surfactants (30). It is termed 2-phase titration because water insoluble chloroform is employed as an extractant for reagent separation from the water sample. This water-chloroform, 2-phase mixture is then titrated with a standard sodium tetraphenylboron reagent with intermittent shaking to insure equilibrium between the chloroform and the aqueous phases. The method will enable a chemist or an operator to define whether the dissolved surfactants in the water are cationic, anionic, or nonionic in nature. A single titration test can determine the charge conditions (cationic or anionic) and the concentration of an ionic surfactant sequentially.

EXPERIMENTAL PROCEDURES

Material

The following surfactants were selected for evaluation and discussion.

Linear alkylate sulfonate (LAS): The reference sample was supplied in liquid form by the Analytical Quality Control Laboratory (Environmental Protection Agency, Cincinnati, OH), and has an average mol wt of 316. The sample contained ca. 0.4% free sulfuric acid, in addition to the linear alkylate sulfonic acids. In utilizing the reference sample for analytical purposes, the weighed contents of the ampul were diluted with freshly distilled water to 0.3-0.35% active LAS acids. The ampuls were protected from light and stored under refrigeration, and were warmed to 20 C before use. The diluted stock solution (0.30-0.35% active LAS acids) had a shelf life of 6 months.

Cetyldimethylbenzylammonium chloride (CDBAC): CDBAC was manufactured by Fine Organics Inc. (Lodi, NJ). The reagent was supplied as a 100% active material, and was very soluble in water and alcohol. Its molecular formula is $[(C_{16}H_{33})(CH_3)_2(C_6H_5CH_2)N]^+Cl^-\cdot H_2O$ and mol wt is 413.

Laundry detergent: Cold power was supplied in powder form by Colgate-Palmolive Company (New York, NY), is biodegradable, and contained sodium sulfate, sodium silicate, alkylbenzene sulfonate, soap, ethoxylated alcohol, moisture, carboxymethyl cellulose, cold water brighteners, aluminum silicates, colorant, and perfume.

Dishwashing detergent: Ahoy detergent, supplied in liquid form by the Great Atlantic & Pacific Tea Co., Inc. (New York, NY) can be used for washing dishes, glassware, pots and pans, fabrics, and automobiles. It contained the following: 68.5% water; 16.0% sodium dodecylbenzene sulfonate; 4.0% sodium xylene; 2.5% sodium sulfate; 1.7% carbamide; 1.7% alcohol ether sulfate; 1.0% alcohol ethoxylate; 1.0% coconut diethanolamide; 0.3% sodium citrate, and 3.3% opacifier, preservative and perfume.

Chiffon Lemon Dishwashing Lotion: Chiffon is a product of Armour-Dial, Inc. (Phoenix, AR). The ingredients of the lotion are: 23.0% linear alkylbenzene sulfonate; 5.0% ethoxylated alkyl sulfate; 5.0% ammonium xylene sulfonate; 3.0% alkyl diethanolamide; 1.9% opacifier, ethyl alcohol, perfume and dye; and 62.1% water.

Algicide No. 5: This reagent was supplied by Virginia Chemicals Inc. (Portsmouth, VA) in liquid form. The formation of the algicide is: 25% alkyldimethylbenzylammonium chloride; 5% bistributyl tinoxide (1% Sn); 2% trisodium ethylene diamine triacidic acid; and 68% inerts.

Lysol Deodorizing Cleaner II: Lysol was manufactured by Lehn & Fink Products (Montvale, NJ), and was supplied in liquid form. Its formulation is listed below: 2.7% alkyl dimethylbenzylammonium chloride (50% C_{14}, 40% C_{12}, 10% C_{16}); 1.0% tetrasodium ethylenediamine tetra acetate; 0.34% ethyl alcohol; and 95.9% water and inert ingredients.

Downy fabric softener: Downy was manufactured by Procter & Gample (Cincinnati, Ohio). Downy is an aqueous dispersion containing a fabric-softening agent (cationic-type) and perfume, fabric whitener, bluing, and quality control agents in small amounts.

REAGENTS, APPARATUS, AND PROCEDURES OF GENERAL 2-PHASE TITRATION

Reagents

Twelve chemical reagents to be used in conjunction with the 2-phase titration method are listed.

(1) Stock sodium tetraphenyl boron solution: Dissolve 3.42 g sodium tetraphenylboron in 1 liter distilled water; adjust pH value to 9-10 with sodium hydroxide; and store the solution in an amber glass bottle. This stock solution is adequately stable at pH 9-10.

(2) Standard Sodium tetraphenylboron solution: Dilute 10 ml stock sodium tetraphenylboron solution into 1 liter of distilled water; this gives a sodium tetraphenylboron concentration of 34.2 mg/liter which is the suggested titrant concentration for the titration of cationic surfactant of concentration range 0-30 mg/liter. Other proper sodium tetraphenylboron concentrations can be prepared, depending on the concentration range of cationic surfactant.

(3) Stock linear alkylate sulfonate (LAS) solution: Weigh an amount of the reference material equal to 1 g LAS on a 100% active basis. Dissolve in distilled water and dilute to 1 liter; 1 ml = 1 mg LAS.

(4) Standard linear alkylate sulfonate (LAS) solution: Dilute 50 ml stock LAS solution to 1 liter with distilled water; 1 ml = 50 μg LAS.

(5) Stock cetyldimethylbenzylammonium chloride (CDBAC) solution: Weigh an amount of the reference material (Fine Organics, Inc.) equal to 1 g CDBAC on a 100% active basis. Dissolve in distilled water and dilute to 1 liter; 1 ml = 1 mg CDBAC.

(6) Standard cetylcimethylbenzylammonium chloride (CDBAC) solution: Dilute 50 ml stock CDBAC solution to 1 liter with distilled water; 1 ml = 50 μg CDBAC.

(7) Citric acid: 0.5 M.

(8) Disodium hydrogen orthophosphate: 0.2 M.

(9) Methyl orange solution: 0.10%.

(10) Chloroform

(11) Buffer solution: Mix 200 ml 0.5 M citric acid and 200 ml 0.2 M disodium hydrogen orthosphosphate together.

(12) Azure A reagent: Dissolve 100 mg Azure A, 24.8 g $Na_2HPO_4 \cdot 7H_2O$, and 52.5 g citric acid in 400 ml distilled water. Add 4 ml concentrated sulfuric acid to the 400 ml mixture, and shake until dissolution is complete. Dilute the solution to 500 ml.

Among the twelve chemical reagents listed above, the stock and standard linear alkylate sulfonate solution (reagents 3 and 4) are not needed if a calibration curve for linear alkylate sulfonate is preprepared.

Apparatus

The following apparatus should be provided in a water quality laboratory for routine analysis of surfactants in water: (1) separatory funnels, 250 ml, preferably with inert Teflon stopcocks; (2) titration burette, 50 ml; (3) graduated cylinders, 50 ml and 100 ml; and (4) pipettes. A field test kit, including all necessary apparatus, reagents, and calibration curves, is proposed in the Appendix for field use.

Procedures

The analytical procedures presented below are particularly useful for environmental engineers who analyze the industrial water samples containing unknown surfactants. The most common anionic surfactant, LAS, has been selected as reference standard of anionic surfactants by the American Public Health Association, American Water Works Association, Water Polution Control Federation (18), and Environmental Protection Agency (32). This paper also suggests the use of LAS as reference standard of anionic surfactant(s) for general water quality control of unknown samples. The anionic surfactant concentration of a sample can be reported to be "mg/liter as LAS." For research or industrial applications, the specific anionic surfactant(s) to be used in the chemical process also can be selected for the anionic surfactant's calibration.

According to R.C. Kroner, Chief of Physical & Chemical Methods, Environmental Protection Agency, Cincinnati, OH, so far there is no generally accepted primary standard for cationic surfactants (R.C. Kroner, personal communication, 1972). Because the quaternary ammonium compounds are now the most common cationic surfactants being used in the country (33), Wang (17) has proposed the use of a 100% pure quaternary ammonium compound, cetyldimethylbenzylammonium chloride (CDBAC), as the reference standard of cationic surfactants for general water quality control. The cationic surfactant concentration of a sample can be reported to be "mg/liter as CDBAC." Similarly, for research or industrial applications, the specific cationic surfactant(s) to be used in the process can also be selected for the cationic surfactant's calibration.

Preparation of Calibration Curve A for Analyzing Anionic Surfactant

Prepare a series of 10 250-ml separatory funnels with 0, 2, 4, 6, 8, 10, 15, 20, 25, and 30 ml amounts of the standard LAS solution. Add 30 ml of the standard CDBAC solution to each funnel, and add sufficient distilled water to make the total volume 60 ml in each separatory funnel.

Add 5 ml buffer solution, 5 drops methyl orange solution, and 30 ml chloroform to the separatory funnel. Stopper and shake vigorously for 30 sec.

Titrate this solution in the separatory funnel with standard sodium tetraphenylboron solution by adding small amounts, restoppering, and shaking.

Continue titration until the yellow color in the chloroform layer becomes completely colorless. Record the ml of standard sodium tetraphenylboron solution required for titration.

Plot a calibration curve of μg LAS versus ml standard sodium tetraphenylboron titrant (calibration curve A in Figure 1).

Preparation of Calibration Curve B for Analyzing Cationic Surfactant

Prepare a series of 10 250-ml separatory funnels with 0, 2, 4, 6, 8, 10, 15, 20, 25, and 30 ml amounts of the standard CDBAC solution to each funnel. Add 30 ml of the standard CDBAC solution to each funnel and add sufficient distilled water to make the total volume 60 ml in each separatory funnel.

Add 5 ml buffer solution, 5 drops methyl orange solution, and 30 ml chloroform to the separatory funnel. Stopper and shake vigorously for 30 sec.

Titrate this solution in the separatory funnel with standard sodium tetraphenylboron (STPB) solution by adding small amounts, restopper, and shake.

Continue titration until the yellow color in the chloroform layer becomes completely colorless. Record the ml of standard sodium tetraphenylboron solution required for titration.

Plot a calibration curve of μg CDBAC (counting initially added standard CDBAC from 0, 2, 4, 6, . . . 30 ml only) versus ml standard sodium tetraphenylboron titrant (calibration curve B in Figure 1).

Analysis of Surfactants for Unknown Samples

Calibration curves A and B shown in Figure 1 can be used for analysis of ionic surfactants in water or wastewater sample. Calibration curves A and B should be provided in a water quality laboratory or in the field test kit described in the Appendix.

The analytical procedures using the general method are presented below.

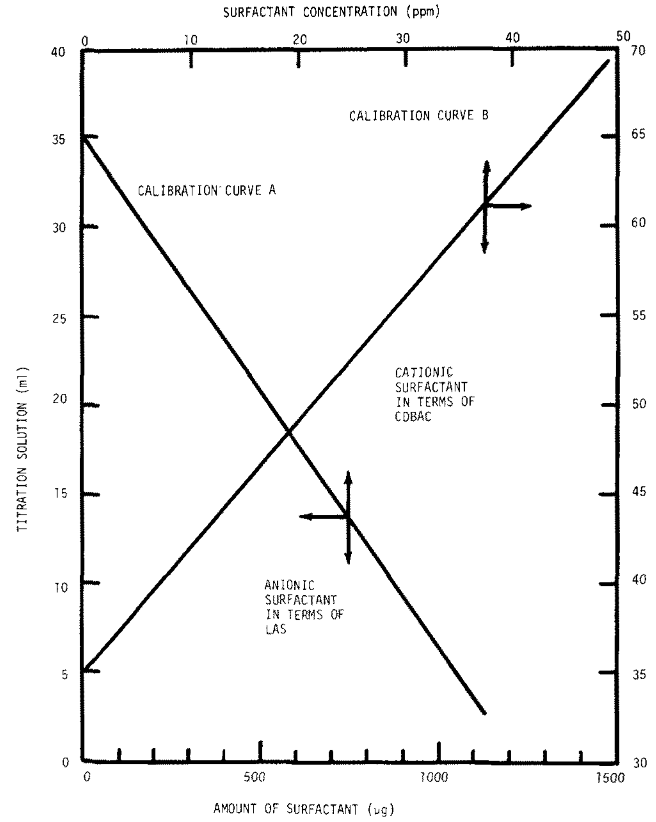

FIG. 1. Calibration curves A and B of surfactant concentration versus titration solution. The ordinate on the right hand side also indicates the ml of standard sodium tetraphenylboron (STPB) solution spent in titration. LAS = Linear alkylate sulfonate; CDBAC = cetyldimethylbenzylammonium chloride.

Pipette 30 ml detergent sample, 30 ml standard CDBAC solution, 5 ml buffer solution, 5 drops methyl orange solution, and 30 ml chloroform to a 100-ml graduated cylinder.

Pour this solution from the graduated cylinder to a separatory funnel. Titrate the solution in the separatory funnel with standard STPB solution by adding small amounts, restoppering, and shaking. Continue titration until the yellow chloroform layer becomes completely colorless. Record the ml standard STPB solution required for titration.

The reference sample containing 30 ml distilled water, 30 ml standard CDBAC solution, 5 ml buffer solution, 30 ml chloroform, and 5 drops methyl orange, will require 35 ml standard STPB titrant (Figure 1). There are 4 possibilities for unknown samples: (1) If the amount of standard STPB solution required for titrating the unknown sample is less than 35 ml, the unknown sample is known to contain anionic surfactant. Read mg/liter surfactant as LAS present in the unknown sample from calibration curve A. (2) If the amount of standard STPB solution required for titrating the unknown sample is more than 35 ml, the unknown sample contains cationic surfactant. Read mg/liter surfactant as CDBAC present in the unknown sample from calibration curve B (Figure 1). (3) If the ml of standard STPB solution required for titrating the unknown sample is equal to 35 ml, the sample contains nonionic surfactant, undetectable surfactant, or no surfactant. (4) If the ml of standard STPB solution required for titrating the unknown sample is zero, the concentration of anionic surfactant in the sample is too high to be analyzed. The sample should be diluted and analyzed again.

Interferences and Limitations

A most serious limitation is one analogous to that associated with the methylene blue method (18,19) in that the suggested 2-phase titration method is incapable of resolving

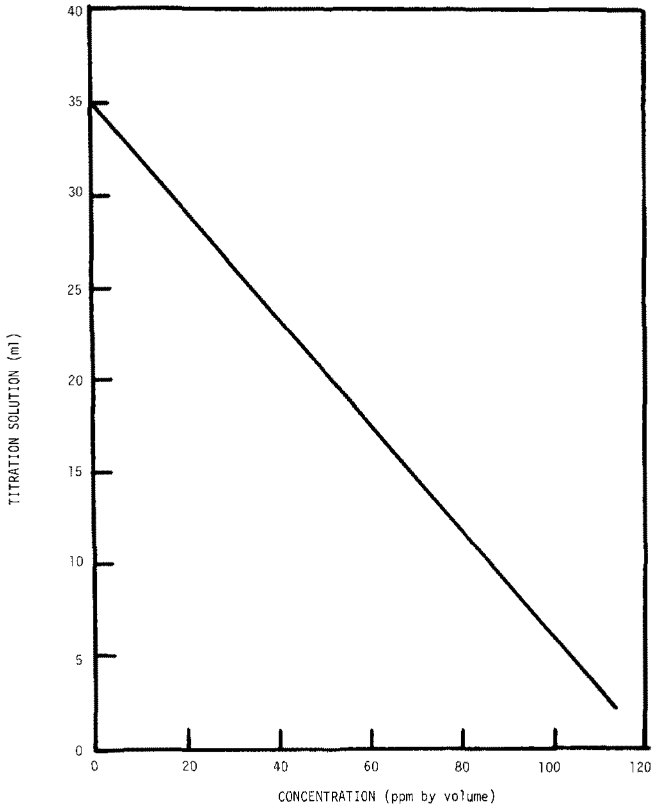

FIG. 2. Concentration of Chiffon Lemon dishwashing lotion versus titration solution. Sample size = 30 ml. Read the concentration of linear alkylate sulfonate from Figure 1.

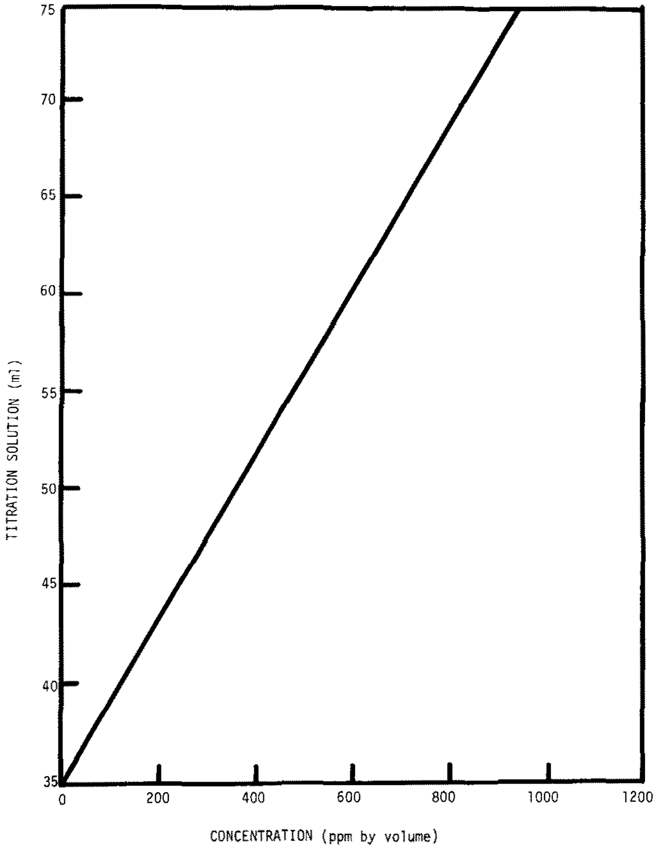

FIG. 3. Concentration of Downy Fabric Softener versus titration solution. Sample size = 30 ml.

and identifying the different types of surfactants being analyzed. The analysis data of cationic surfactant can be expressed grossly as methyl orange active substances (MOAS), and of anionic surfactant can be expressed grossly as CDBAC active substances.

A second limitation of the 2-phase titration method is that it cannot be used for analysis of water or wastewater samples with relatively high potassium content. A water soluble salt is formed by reaction of potassium ions with the STPB reagent. This tends to increase the STPB reagent demand, thus, giving lower values for the anionic surfactant content, and high values for the cationic surfactant content.

RESULTS AND DISCUSSION

General Discussion

Figure 1 shows the calibration curves of standard anionic surfactant LAS (Curve A) and standard cationic surfactant CDBAC (Curve B). For general environmental water quality control, Figure 1 can be adopted for use. The surfactant contents of a water or wastewater sample can be quantitatively measured by the simple procedures outlined previously. If the surfactant present in the sample is anionic in nature, use Curve A in Figure 1 and report the surfactant concentration to be mg/liter as LAS. If the surfactant in the sample is cationic, use Curve B and report the surfactant concentration to be mg/liter as CDBAC.

The nonbiodegradable alkylbenzene sulfonate (ABS) is still the major ingredient of household detergents in many Asian and European countries, due to its cheap cost. It has been demonstrated by the author that ABS can also be accurately measured by the general 2-phase titration method, provided that ABS is used as the standard anionic surfactant for water quality control. The results can be reported to be mg/liter as ABS.

CDBAC is propsed to be the standard reference cationic surfactant. Other pure quaternary ammonium compounds, i.e., ethylhexadecyldimethylammonium bromide, cetyldimethylethylammonium bromide, cetyltrimethylammonium bromide, stearyldimethylbenzylammonium chloride, and amine compounds, i.e., dodecylamine hydrochloride can also be adopted as standard surfactant for preparing a desired calibration curve for the cationic surfactant determinations.

Evaluation

Figure 2 shows that the water sample containg Chiffon Lemon Dishwashing Lotion can be quantitatively measured by the 2-phase titration method described in this paper. The dishwashing lotion was found to be anionic in nature because the amount of standard STPB solution required for titrating the sample containing the lotion is less than 35 ml. From both Figures 1 and 2, its equivalent LAS concentration can be determined readily. For instance, 100 ppm (by volume) of Chiffon requires 6 ml standard STPB for titration (Figure 2); thus, it is equivalent to 32.4 ppm (or mg/liter) of LAS by wt (Figure 1).

Two other commercial detergents, Cold Power and Ahoy, were also evaluated in this program. Both detergents contain anionic surfactants. It was found that 1 mg/liter Cold Power contained 0.325 ml/liter of anionic surfactant as LAS, and 1 ppm (by volume) of Ahoy contained 0.2 mg/liter (by wt) of anionic surfactant as LAS.

Commercial Downy fabric softener is made of mainly cationic surface active agent(s). When it is present in water or wastewater, Cationic Downy cannot be detected by the standard methylene blue method (18), but can be qualitatively and quantitatively analyzed by the general 2-phase titration method. Figure 3 shows that when the general method is used, the volume of standard STPB solution required for titration will be more than 35 ml if Downy is present in the water sample. Downy's equivalent CDBAC concentration can be read from the curve B of Figure 1.

For example, 350 ppm (by volume) of Downy fabric softener requires 50 ml standard STPB titrant for a stoichiometric reaction (Figure 3); thus, it is equivalent to 21.25 ppm (or mg/liter) of CDBAC by wt.

Two other samples, Lysol Deodorizing Cleaner II and Algicide No. 5, were demonstrated to contain cationic surfactants. One ppm (by volume) of the algicide was found to contain 0.34 mg/liter (by wt) of cationic surfactant as CDBAC. Similarly, Lysol can also be quantitatively measured by titration with STPB.

In summation, the general 2-phase titration method described in this paper has been demonstrated to be feasible for analyzing either anionic or cationic surfactants in water samples.

Remarks

If the oil (or any other chloroform extractable substances) content is high in the water sample, the equilibrium end point cannot be detected easily. In such a case, the color of the separated chloroform layer is lightly foggy instead of crystal clear. A remedy method for the easy detection of the equilibrium end point involves the use of Azure A reagent. When the prepared sample (containing methyl orange solution, buffer, chloroform, wastewater sample, and surfactant, if necessary) shows a yellow color in its shaked and separated chloroform layer, titrating the prepared 2-phase sample with the standard STPB solution is required. When the titration end almost reaches, an additional 1 ml Azure A reagent should be added to the prepared sample. The equilibrium end point is known to be accurately reached when the yellow color in the separated chloroform layer turns to green due to the titration with standard STPB solution.

It should be noted that the method is limited in application to the measurement of free ionic surface active agent (either anionic or cationic). A sample containing equimolar concentrations of anionic and cationic surfactants would show zero by this method because of interaction to form the anionic-cationic surfactant complex. The surfactants are, therefore, still present but in a complexed form. In other words, cationic surfactants present interfere with anionic surfactants and vice versa.

Fortunately, anionic surfactants (containing LAS or ABS) represent ca. 90% of all surfactants used in this country. From an environmental engineers' point of view, anionic surfactants are mainly present in nature water which is the source of our water supply. For this reason, the US Public Health Service and the International Specification (WHO) require concentrations of <0.5 mg/liter anionic surfactant (LAS or ABS) in the drinking water (5,34). Cationic surfactant concentration in the nature water or drinking water is not legally controlled because it is so low as considered to be negligible. For routine monitoring of detergent (or surfactant) content in nature waters or domestic sewage, the chemist in charge would not encounter any analytical problems because the detergent would only be anionic in nature.

Certain industrial operations, however, use both anionic surfactants and cationic surfactants. For instance, in the flotation process, only anionic surfactants are effective flotation agents for the separation of positively charged metal colloids. On the contrary, only cationic surfactants can be used for the flotation of negatively charged organic colloids. In either case, the charge conditions of the surfactants are known, and either surfactant concentration can be quantitatively measured and monitored by the 2-phase titration method.

A question would probably arise if the process engineer or chemist would mix one industrial waste stream containing residual cationic surfactant with another containing residual anionic surfactant together. In this case, neither the titration method nor any other existing analytical method will work. For the efficient process monitoring and control, each industrial water stream or waste stream will have to analyzed separately if different charges of surfactants are to be used.

As mentioned earlier, the method described in this paper is feasible for analyzing ionic (either cationic or anionic) surfactants. If 1 mole anionic surfactant is mixed with 2 moles cationic surfactant, the resultant products would be 1 mole cationic surfactant and 1 mole nonionic surfactant. The former (1 mole cationic surfactant) can certainly be measured by the 2-phase titration method, while the latter is no longer ionic, and, thus, cannot be measured. Thorough understanding of the titration method will assist an engineer or a chemist to operate his/her process properly, and interpret the analytical results relative to the ionic surfactant contents accurately.

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APPENDIX: FIELD TEST KIT

A simple field test kit for analyzing ionic surfactants by the 2-phase titration method consists of the following apparatus and reagents.

(1) One separatory funnel: 250 ml, preferably with inert Teflon stopcocks.
(2) One glass graduated cylinder (optional): 100 ml.
(3) One polypropylene titration buret: 25 or 50 ml (VWR Scientific, Bronx, NY).
(4) One bottle of buffer solution: 120 ml (4 oz) solution stored in a bottle (Hach Chemical Co., Ames, IA) with precision calibrated 2.5-ml pipet and bulb.
(5) One bottle of 0.1% methyl orange solution: 30 ml (1 oz.) solution stored in a plastic bottle with dropper or dispenser (U.S. Plastic Corp., Lima, OH).
(6) One bottle of 0.01 M (34.2 mg/liter) sodium tetraphenylboron titrant: 240 ml titrant stored in an Amber Nalgene bottle (U.S. Plastic Corp.).
(7) One bottle of 1 M (3,420 mg/liter) sodium tetraphenylboron solution (optinal): 30 ml (1 oz.) solution stored in an Amber Nalgene bottle (U.S. Plastic Corp.).
(8) One or 2 bottles of chloroform: 240 ml each, stored in the glass or metal bottles.
(9) One bottle of distilled water (optional): 240 ml stored in a polyethylene bottle (U.S. Plastic Corp.).
(10) One bottle of 50-mg/liter cetyldimethylbenzylammonium chloride solution: 240 ml (8 oz.) solution stored in a narrow mouth Nalgene bottle (U.S. Plastic Corp.).
(11) One bottle of 1,000 mg/liter cetyldimethylbenzylammonium chloride solution (optional): 30 ml (1 oz.) solution stored in a Nalgene bottle (U.S. Plastic Corp.).
(12) One calibration curve (Figure 1).
(13) One glass hypodermic syringe: 30 ml capacity.
(14) One plastic hypodermic syringe: 30 ml capacity.
(15) One bottle of Azure A reagent (optional): 30 ml solution stored in a plastic bottle with caibrated dropper.

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