In one experiment the reaction mixture was adjusted to 0.10% moisture and allowed to equilibrate for two hours at 90°C. The mixture was then cycled through the evaporator for one hour. In the second experiment the anhydrous reaction mixture was first cycled through the evaporator for two hours. The moisture content was then adjusted to 0.10%, and it was allowed to equilibrate for one hour. The pot temperature was maintained at 90°C. Comparison of the results in Table IV reveals that a high ratio of monoester to diester is more readily obtained by equilibrating with water present, prior to stripping of product methanol.

Purification

After completion of the alcoholysis reaction and stripping of the solvent, the sugar ester is separated from unreacted sucrose, which is then recycled. Any one of a large number of solvents can be used to dissolve the sucrose ester without dissolving the sugar. However the sugar recovered by distillation of the reaction solvent is finely divided. Even with the aid of diatomaceous earth, filtration is difficult and occlusion of the sugar ester is excessive. The problem was resolved by the use of a water-insoluble organic solvent in combination with a relatively small amount of water. The quantity of water used is such as to give a sugar solution containing 50 to 60% sugar. At this concentration of sugar the sugar ester is almost completely extracted by the organic solvent. When xylene is employed to take up the sugar ester, the two phases layer rapidly. The xylene is then removed by steam distillation to recover the sugar ester.

Discussion

Pilot plant studies have demonstrated that the sugar esters can be prepared economically, with good yield and purity, using a batch operation. Our pilot plant equipment is presently being modified for the preparation of the sugar esters on a continuous basis. In essence, the equipment will then consist of a series of surge tanks and evaporators. Make-up water will be fed into the surge tanks to maintain the water level at 0.10%. The bulk of the solvent will be removed in the final evaporator, after which the product stream will be blended with xylene and water. This mixture will then be led into a liquid-liquid separator. The xylene and water layers will be fed to separate stills for the recovery of product and unreacted sugar. The latter will be recycled.

Summary

Improvements in the method of manufacture of the sugar esters are described. The use of a turbulent-film evaporator for removal of product methanol reduces reaction time in batch operation from 15 to 3 hrs. The presence of trace quantities of water inhibits diester formation and permits recovery of better than 90% monoester without extensive purification.

Acknowledgment

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Ampholytic Surface-Active Agents[1]

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CLASSICALLY, SYNTHETIC DETERGENTS have been categorized electrochemically as anionic, cationic, or nonionic according to whether the surface-active portion (in aqueous solution) is present as an anion, a cation, or an unionized molecule. Only recently has the term ampholytic surfactant been employed to characterize those surface-active agents containing both anionic and cationic groups.

The technology of amphoteric (used interchangeably with ampholytic) surfactants is not new. Products of this type have been known for many years. However, until recently, little practical use has been made of this general class of products. And, until recently, ampholytic surfactants were not commercially available.

With the tremendous technological advances in the utilization of synthetic detergents, competition has increased markedly in the surfactant field. Much more is known about surface-active phenomena such as wetting, detergency, and foaming. Application of existing products is advancing rapidly. The relatively unknown and untried ampholytic surfactants are attempting to keep pace. The technology of these products has advanced to the point where several amphoteric detergents are available commercially. Research and development are directed toward seeking out specific areas where ampholytic products may have a definite advantage over other types. Currently amphoteric surfactants are finding application in such divers fields as the shampoo and cosmetic fields, water emulsion paints, the textile industry, corrosion inhibition, industrial cleaning, and many others.

Chemistry of the Ampholytic Functional Groups

Fundamentally an ampholytic surfactant contains both basic (cationic) and acidic (anionic) groups. These products may be "balanced," *i.e.,* the number of acidic and basic groups are equal, or the product may be "unbalanced," in which case either the acidic or the basic groups are in excess. Typical balanced ampholytics are:

N-alkyl β-aminopropionic acid,
$RNHCH_2CH_2COOH$

N,N-dialkyl ethylene diamine diacetic acid,
$R(CH_2COOH)NCH_2CH_2N(CH_2COOH)R$

Typical unbalanced ampholytic detergents are:

N-alkyl β-iminodiacetic acid,
$RN(CH_2COOH)_2$

N-alkyl N′-carboxymethyl ethylenediamine,
$RNHCH_2CH_2NHCH_2COOH$

In practice the basic (cationic) group of an ampholyte is limited almost exclusively to basic nitrogen derivatives, either quaternary or non-quaternary. It is possible to prepare derivatives containing a cationic sulfonium group by the reaction of an alkyl methyl sulfide and chloroacetic acid. However this type of product does not appear to be commercially significant at this time. Typical cationic groups comprising many of the general family of ampholytes are primary, secondary, and tertiary amines, quaternary ammonium compounds, pyridinium group, and the imidazoline group.

Typical anionic groups are limited by practical considerations to carboxylic acids, sulfonic acids, or sulfuric or phosphoric esters.

The chemistry of the functional groups comprising the majority of amphoteric detergents is simple. However the chemistry of the syntheses of the myriad of compounds possible through all the permutations and combinations is exceedingly complex and is far outside the scope of this paper. Schwartz and Perry in their book "Surface-Active Agents" (Interscience Publishers Inc., 1949) give a rather complete account of the more important syntheses.

Electrochemistry of the Ampholytes

Surface-active agents, in general, derive the bulk of their physical and performance characteristics from their electrochemical nature. The properties of ampholytic surfactants are to an even greater extent dependent on electrochemical factors. Not only does the ionic environment exert a marked force on the measurable properties, but pH actually determines the type of property (cationic, non-ionic, or anionic) to be manifested. In the simple, monoamino, monocarboxylic (balanced) ampholyte, the relationship between pH and physical properties is relatively straightforward, as shown in Table I.

TABLE I

Relation of pH to Properties in a Typical Ampholytic System

Acidic range ⇌ isoelectric range ⇌ basic range
$R\overset{+}{N}H_2CH_2CH_2COOH \rightleftharpoons R\overset{+}{N}H_2CH_2CH_2COO^- \rightleftharpoons RNHCH_2CH_2COO^-$
Cationic properties ⇌ non-ionic properties ⇌ anionic properties

In the case of unbalanced amphoteric surfactants the picture becomes somewhat more complex, but the same general conditions prevail, that is, anionic properties dominate in the basic pH range and cationic properties in the acidic range.

It is in the exaggerated electrochemical nature of the ampholytic surface-active agent that the molecule becomes interesting in its potential application to specific problems. Poly-functionality offers an intriguing possibility. For example, anionic performance as a sodium salt in the basic pH range, then cationic softening in the acidic pH range. Certain of the ampholytics by virtue of their basic nitrogen atom offer corrosion-inhibiting properties. Schmitz (Fette u. Seifen, *55*, 10 [1953]) reports on an unbalanced ampholytic surfactant, possessing high bactericidal properties even in the presence of serum proteins and at the same time exhibiting a lower toxicity to higher animals than the usual quaternary ammonium disinfectants. Metal chelation and resistance to hard water are typical properties of ampholytic surfactants based on their electrochemical nature. By virtue of their amphoteric nature these products offer a very wide range of compatibility with anionic, nonionic, and cationic surfactants.

In general, the electrochemical nature of the ampholytic surfactants leads to a class of compounds exhibiting a high degree of versatility, both within individual members of the class and within the class as a whole to meet varying end-use demands. However certain limitations of the ampholytics in general must be realized. Primary among these is the limitation of cost. By virtue of the substituents and of the relatively complicated synthetic processes, ampholytics are by nature relatively costly to produce. As such, it can be seen that they cannot compete successfully with the petroleum-based products except in specific areas wherein performance excellence overrides the economics.

Physical and Performance Properties

It is nearly impossible to separate performance properties from electrochemical properties. It is almost always the electrochemical nature of the product which controls any given performance property. Physical and performance characteristics are simply measurable manifestations of the much more complex interplay of electrochemical forces.

Mainly as a means of simplification, the remainder of the discussion about typical physical and performance characteristics will be limited to a relatively simple family of amphoteric surface-active agents, the N-fatty β-aminopropionic acids. This family of compounds represents an almost classically simple, balanced monoamino-monocarboxylic ampholyte. As such, it is felt that many of its properties will be typical of ampholytic products in general and will serve to illustrate the important characteristics.

Preparation. Commercially these products are offered under the trade name of Deriphats by General Mills Inc. (Chemical Division, Kankakee, Ill.) and are prepared by the reaction of a fatty primary amine and methyl acrylate to give the N-fatty β-aminopropionic ester, which is saponified to give the water-soluble salts thereof.

$$RNH_2 + CH_2 = CHCOOCH_3 \longrightarrow$$
$$RNHCH_2CH_2COOCH_3 \longrightarrow$$
$$RNHCH_2CH_2COO^-M^+$$

Physical Properties. Primary commercial production yields these products as a 98% active flaked form, more or less readily soluble in water (depending to a marked degree on the nature of the alkyl group derived from the parent amine) and definitely alkaline in reaction. However, by virtue of their water solubility and amphoteric nature, most of these products can be obtained as concentrated solutions and at nearly neutral pH's.

Performance Characteristics. There are two keys to the performance of an ampholytic surfactant: pH and chain length of the fatty portion.

The pH of a formulation determines the solubility, viscosity, and ionic character. At use concentrations the pH controls or modifies the performance characteristics. Likewise the chain length of the fatty portion of the molecule (the hydrophobic or lypophilic group) also plays an important role in determining the over-all physical and performance properties.

Other factors such as the ampholytic balance, the nature of the substituents, both cationic and anionic, do determine the general properties of a given family of ampholytic compounds. However, within that family, factors, such as pH and chain length of the fatty group, can and do often alter the properties so drastically as to cause considerable overlapping of functionality and application.

pH Versus Solubility. As a family, the N-alkyl β-aminopropionates are relatively water-soluble, but the fatty chain determines solubility to a considerable extent, as does pH.

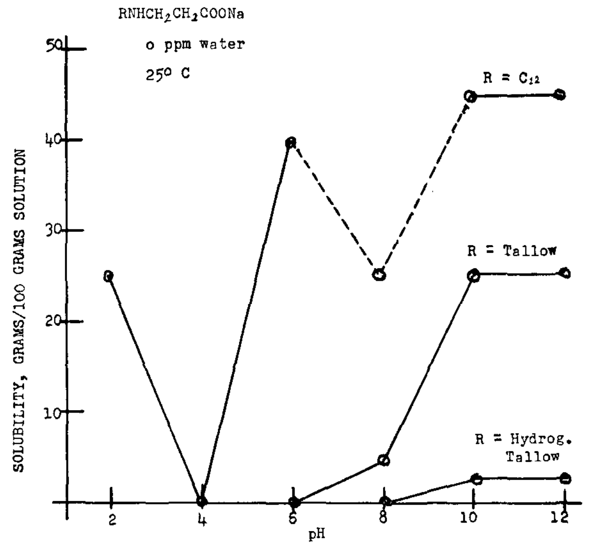

FIG. 1. Solubility *vs.* pH of typical N-alkyl β-aminoproprionates.

Viscosity as a Function of pH. Because of their highly electrochemical nature, many ampholytics exhibit rather marked pH-viscosity curves. It is postulated that this is caused by micellular formation in certain specific electrochemical environment which is conducive to extremely stable micele structures.

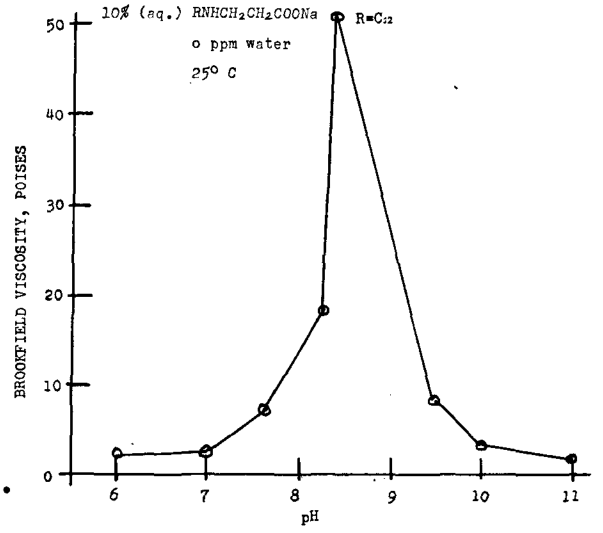

FIG. 2. pH viscosity relationship for sodium N-dodecyl β-aminopropionate.

Foam (Ross-Miles) Versus pH and Chain Length. Foam volume of a surface-active agent is both beneficial and deleterious, depending on the end-use. A product for use in shampoos must of necessity exhibit a high foam volume, and often a product used as an emulsifier or a wetting agent must be very low foaming. Ampholytic materials, in addition to the normal range of foaming tendencies governed by the fatty chain length, have an additional control on foam, that of pH. As a result of their amphoterism these products almost always exhibit a marked decrease in foaming in the isoelectric range, and, in general, the foam level is higher in either the basic or acidic pH ranges if solubility permits.

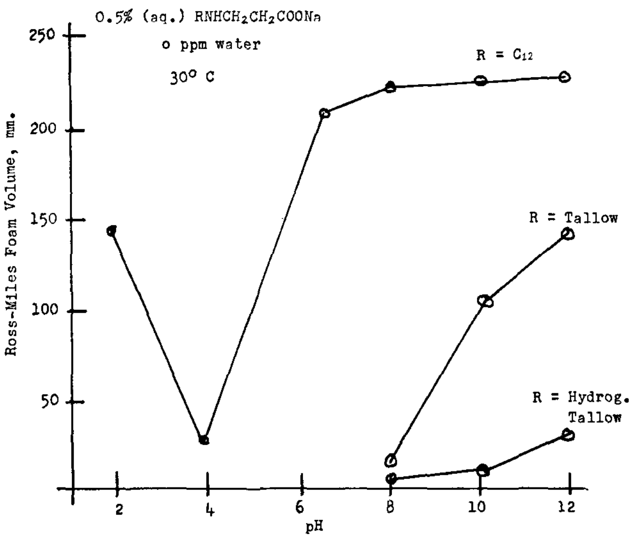

FIG. 3. Foam volume of ampholytics as a function of fatty chain length and pH.

Detergency as a Function of pH and Fatty Chain Length. It is in the realm of detergency, or cleaning power, that the ampholytics usually cannot compete with the inexpensive and very effective petroleum-based products. As the main ingredient of formulations wherein heavy-duty cleaning power is the major function, ampholytics, in general, are not feasible. However in their use as additives to formulations comprised mainly of less expensive surfactants the detergency of a given ampholyte can be considered as a definite "plus" feature. The ampholyte, in addition to performing some specific function, such as foam stabilization, also contributes to the overall detergency of the formulation.

There is considerable controversy over detergency, the factors producing good (or bad) detergency, the relationship of cotton, wool, and hard-surface cleaning, and the means of quantitatively measuring detergency as a specific property of a surfactant. In the areas of specialized detergency problems the amphoterics by virtue of their versatility and pH functionality may well offer promise. The removal of soil by a detergent is, in part at least, considered to be electrochemical in nature. Hence the correct balance of cationic and anionic character might be found whereby the ionic nature of the ampholytic detergent matches or exactly opposes the ionic nature of the substrate and/or soil, thereby greatly facilitating the removal of the soil.

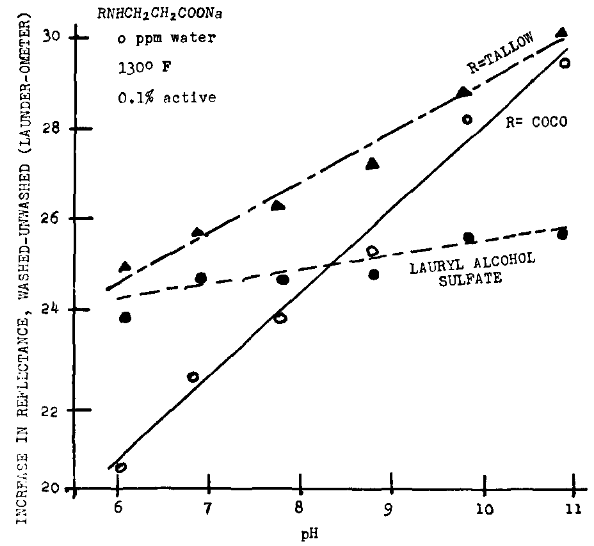

FIG. 4. Detergency of typical ampholytics as a function of fatty chain length and pH.

Wetting as a Function of pH and Chain Length. Wetting action is another area in which ampholytics, as such, probably cannot compete directly with less expensive products. However, in conjunction with other properties for a specific application, wetting becomes a definite plus feature. In general, wetting action of an ampholytic follows the typical pattern of being quite specific as regards chain length with the optimum for the N-fatty β-aminopropionates occurring at a chain length of about C_{12}, at which chain length is exhibited an almost instantaneous wetting time. The pH functionality of wetting action follows the general trend of that of the majority of the other performance characteristics, going through a minimum in the isoelectric range.

Surface and Interfacial Tension Data. The N-fatty β-aminopropionates exhibit a very high degree of surface and interfacial tension lowering. When the fatty group is essentially 12 carbons in length, interfacial tensions are well below 2 dynes per cm. at concentrations of 0.1% active. Likewise, at 0.1% active concentration, this product (sodium N-dodecyl β-aminopropionate) will exhibit a surface tension of about 25 dynes per cm. As with wetting, these values are more or less independent of pH except in the isoelectric range.

Compatibility with Other Surfactants. In the complex realm of multi-component formulations, ampholytic surfactants have very interesting possibilities. In general, ampholytics are compatible over wide ranges of detergent ratios and with anionic, non-ionic, and cationic surfactants. Cationic surfactant compatibility is probably the most interesting. Virtually all anionic surfactants will almost quantitatively precipitate or inactivate cationic detergents, especially quaternary ammonium compounds. However, even in ratios as high as 16 parts of sodium N-alkyl β-aminopropionate and 1 part quaternary, the germicidal effectiveness of the quaternary is virtually unaffected. Hence it is possible to formulate a quaternary with an ampholytic in its anionic form and enjoy the advantages of both cationic and anionic behavior.

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Analytical Test Methods for Organic Detergents

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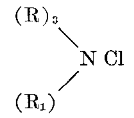
THE AMERICAN SOCIETY FOR TESTING MATERIALS has defined a detergent as a composition that cleans. A synthetic detergent, it is further stated, is produced by chemical synthesis and comprises an organic composition other than soap. This paper will attempt to summarize some of the current analytical methods employed to isolate, identify, and measure the most important detergents being manufactured today.

Versatility is a word that might be used to keynote the problem of analyzing these organic substances. Surface-active agents (detergents, in particular) are versatile performers. Versatility (plus complexity) is evidenced by the organic chemist in the way he tailors the "detergent molecule" to fit a given set of requirements. Dexterity is also displayed by the formulator in creating balance within a product so that it adequately performs its task. Finally the adept analyst employs a diversity of tools and methods to enable him to keep abreast of the changing scene.

In order to control production of syndets, rapid analytical procedures are necessary each step of the way. These methods must have a reasonable degree of accuracy in order to yield material balance and supply accounting figures. The analyst must also concern himself with the composition of competitive products and the nature of his own organic synthesis. There is no one analytical scheme, nor is there one method for a given classification of surfactants, that will work with all the compositions the chemist will encounter. The detergents known as anionics and nonionics comprise the bulk of the market, and the methods reported for the analyses of these are of the most importance to the analytical chemist.

Classification

The molecules of surface-active agents are characterized by a water-loving portion (hydrophilic) and a water-hating portion (hydrophobic). In dilute aqueous solutions they lower the surface tension of water considerably, and phase boundaries are easily broken. The properties (wetting, foaming, detergency, etc.) can be varied by changing the shape and size of the hydrocarbon group or by modifying the nature of the solubilizing group or a combination of both. The surface-active agents are most commonly classified on the basis of the charge on the colloidal particles dispersed in water. The anionic has an active portion which carries a negative electrical charge, whereas the effective portion of the cationic has a positive charge. The nonionics are electrically neutral in solution and may be classified with the ester and ether compounds. Sometimes the molecule contains both anionic and cationic groups, and these are said to be amphoteric or ampholytic. They are usually anionic in alkaline medium and cationic in acid medium. Typical examples of each class are given herewith:

Anionics	
a. Alkyl aryl sulfonates	R aryl SO_3Na
b. Alkyl sulfates	$ROSO_3Na$
Nonionics	
a. Alkyl phenol ethylene oxide derivatives	R phenol $(C_2H_4O)_n$
Cationics	
a. Quaternary ammonium compounds	 $(R)_3(R_1)NCl$
Ampholytic	
a. Salts of alkyl amino acids	R NH $CH_2CH_2COON_a$

Sampling

Although the literature contains many references in regard to the analysis of syndets, very little has been written about sampling. Discrepancies in results are probably as frequently caused by inadequate sampling practices as by poor analytical procedures. There are few official sampling methods for detergent products. Spray-dried built detergents are mixtures of varying particle size and usually require adequate blending and riffling, followed by rapid grinding, if small samples are to be representative. Liquid detergent mixtures containing volatile constituents must be sampled carefully if the volatile constituents are to be determined quantitatively and subsequent samples used for analysis are to give results that can be