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.

Ampholytic Surface-Active Agents

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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 amphoterics (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 untired ampholytic surfactants are attempting to keep pace. The technology of these products has advanced to the point where several amphoterics 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 amphoterics surfactants are finding application in such diverse 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 ampholytes are:

- N-alkyl β-aminopropionic acid, RNHCH2CH2COOH
- N,N-dialkyl ethylene diamine dicarboxylic acid, R(CH2COOH)N(CH2CH2N(CH2COOH)R

Typical unbalanced ampholytic detergents are:

- N-alkyl β-iminodiacetic acid, RN(CH2COOH)2
- N-alkyl N'-carboxymethyl ethylenediamine, RNHCH2CH2NHCH2COOH

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

The investigation described herein was supported by the Sugar Research Foundation Inc., New York, N.Y.

REFERENCES


[Received September 26, 1956]
In practice the basic (cationic) group of an amphotolyte 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>
<thead>
<tr>
<th>Relation of pH to Properties in a Typical Ampholytic System</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acidic range ≈ isoelectric range ≈ basic range</td>
</tr>
<tr>
<td>+ R₂N⁺CH₂CH₂COO⁻ ≈ R₂N⁺CH₂CH₂COO⁻ ≈ R₂N⁺CH₂CH₂COO⁻</td>
</tr>
<tr>
<td>Cationic properties = non-ionic properties = anionic properties</td>
</tr>
</tbody>
</table>

In the case of unbalanced ampholytic 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 ampholytes 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, ampholytes 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.

\[
\text{RNH}_2 + \text{CH}_2 = \text{CHCOOCH}_3 \quad \rightarrow \quad \text{RNHCH}_2\text{CH}_2\text{COOCH}_3
\]

\[
\text{RNHCH}_2\text{CH}_2\text{COOCH}_3 \quad \rightarrow \quad \text{RNHCH}_2\text{CH}_2\text{COO}^- + \text{CH}_3\text{COO}^-
\]

**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 lyophilic group) also plays an important role in determining the over-all physical and performance properties.