The Synthesis and Surface Active Properties of Certain Amphoteric Compounds

W. M. LINFIELD, P. G. ABEND, and G. A. DAVIS, Research Department,
Grocery Products Division, Armour and Company, Chicago, Illinois

Abstract

In order to gain some insight into the correlation between chemical structure and surface active properties, a number of amphoteric surface active agents were synthesized. All of these compounds possessed both a quaternary ammonium group and an anionic functional group. The anionic functional group was either a carboxylate, sulfonate, or a sulfate group. The molecules possessed either one or two fat-derived long chains.

In general, the detergency of the single chain compounds was superior to that of the double chain compounds. On the other hand, the double chain compounds showed better fabric softening than single chain compounds. The compatibility with anionic and non-ionic detergents and soap was also studied. It was observed that there were considerable variations in the degree of compatibility with respect to detergency. In general, anionics of the alkylaryl sulfonate type and soap are incompatible with these amphoterics, while non-ionics appear to be more compatible.

Introduction

AMPHOTERIC surface active agents are of considerable interest since they combine a positive as well as a negative charge in one molecule. Such compounds thus can be expected to show some of the characteristics of cationic and anionic surface active agents. Not too much is known about the behavior of such compounds even though amphoterics have been synthesized by various workers in the field and are included in monographs on the subject (1). In this particular study we have synthesized six different amphoterics. Figure 1 shows the molecular structures of these compounds. In all cases R stands for a fat derived straight chain of 16–18 carbon atoms. Because of the awkwardness of naming these compounds a simplified nomenclature was adopted. The first letter denotes the number of long chains, S standing for a single chain and D for two chains. The second letter denotes either a simple quaternary ammonium compound A or an imidazoline I. Lastly the anionic functional group was designated as sulfate, sulfonate, or carboxylate.

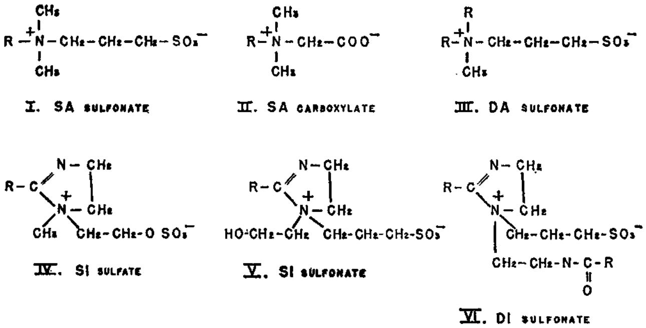
I. SA SULFONATE
II. SA CARBOXYLATE
III. DA SULFONATE
IV. SI SULFATE
V. SI SULFONATE
VI. DI SULFONATE

FIG. 1. Structural formulas of amphoterics.

In order to obtain some correlation between surface active properties and molecular structure we determined the detergency behavior of these six compounds by themselves and in binary mixtures with a nonionic detergent, an alkylarylsulfonate or soap. Lastly the textile softening properties of the six compounds were determined.

Experimental

A Synthesis. A schematic summary of the synthesis is given in Figure 2.

S A Sulfonate

The sulfopropylation of amines with propane sultone to form the corresponding sultaines was by a modification of the procedure of Helberger et al. (2).

To dimethyloctadecylamine (0.61 m 187 g) dissolved in 250 ml of ethylene dichloride, propane sultone (Deutsche Hydrier Werke G.m.b.H.) (0.616 m, 75.6 g) was added dropwise in 45 min at 50C. After addition, the mixture was refluxed (82C) for 15 min and then added, with stirring, to one liter of acetone. The solid product was filtered and dried. Yield: 220 g, 86% of theory. S. anal.: calcd. 7.64%, found 7.35%.

S A Carboxylate

Quaternization. A mixture of commercial dimethyl soya amine (8.2 moles, 2442 g), ethyl chloroacetate (8.2 moles, 1000 g) and methanol (3442 g) was charged to a 3-necked 12-liter flask fitted with a stirrer, condenser, and a thermometer and heated with stirring at the reflux temp (69C) for 6 hr. A sample gave the following analysis: 4.21% free tertiary amine, 44.81% quaternary ammonium ester. The methods of analysis used for these compounds are those of Pifer and Wollish (3) for the quaternary ammonium compounds and of Siggia, Hanna, and Kervenski (4) for the mixture of amines.

Reaction 338 g of powdered 97% NaOH (8.2 moles) was added in portions with extreme caution to the well-stirred quaternary-ester solution of 45–50C over a 1 hr period. This initial reaction is quite violent. The reaction mixture was refluxed for 3 additional hr and allowed to settle overnight to help the separation of the NaCl. After filtering to remove the salt, an analysis showed 1.4% free tertiary amine, 0.8% quaternary amine, 1.3% NaCl and 42.0% betaine; the total solids were 45.5%. The methanol solution was used in all subsequent evaluations.

D A Sulfonate

Propane sultone (0.505 m, 62 g) was added to a solution of methyl dioctadecylamine (0.50 m, 275 g) in 125 ml of ethylene dichloride. No rise in temp was

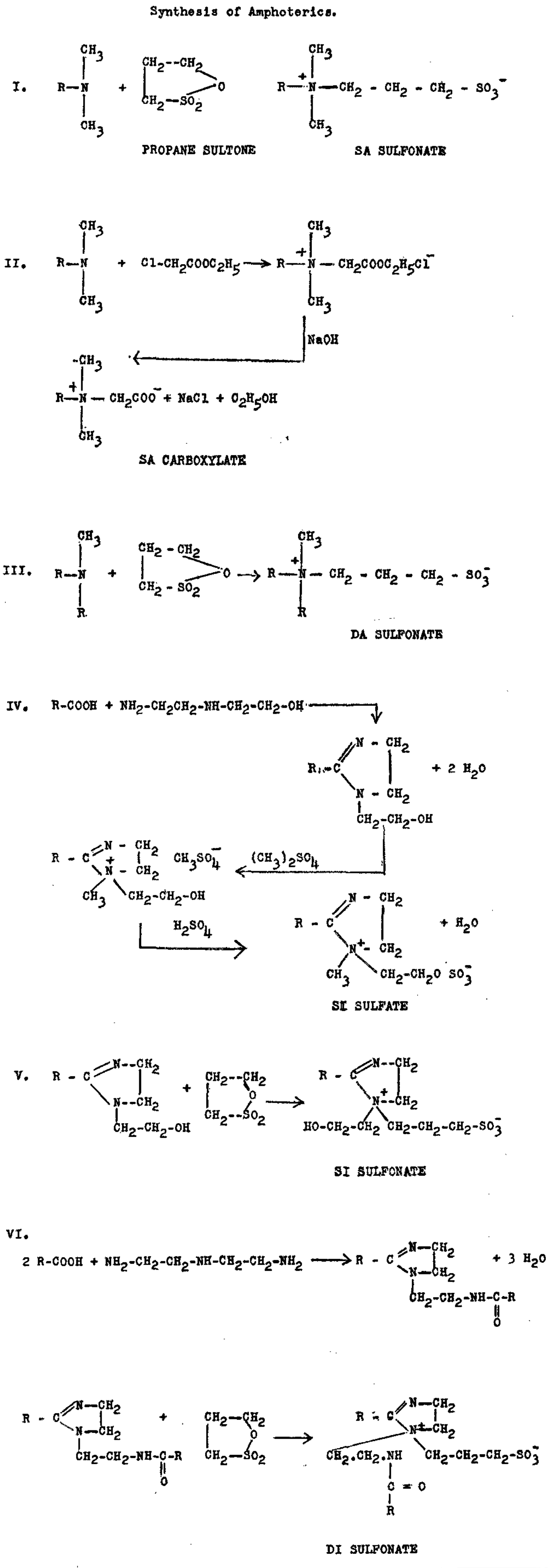

FIG. 2. Synthesis of amphoterics.

observed. The mixture was refluxed for 1.5 hr (99C). The hot mixture was poured into one liter of acetone, left in the freezer overnight and the product (a white precipitate) was filtered and then air-dried.

Yield: 270 g, 81% of theory. S. anal.: calcd. 4.77%, found 4.63%.

S I Sulfate

This type of compound is mentioned by Schwartz and Perry (5).

Synthesis of the Imidazoline. A commercial eutectic mixture of stearic and palmitic acids (630 g, 2.29 m) was melted and charged into a 3-liter, 4-neck reaction flask equipped for vacuum distillation using a Vigreux column, with agitator and nitrogen inlet.

With nitrogen bubbled slowly through the fatty acid, a solution of sodium hypophosphite (7 g in 10 ml of water) was added, and the temp was raised to 100C where aminoethylethanolamine (298 g, 2.86 m) was added through a dropping funnel over a 15 min period. After addition of the amine, the mixture was heated to 190C. Distillation started when the temp reached 160C. The temp of the mixture was increased to 210C. When the vapor temp (at the top of the column) dropped below 100C, vacuum was applied gradually so that the vapor temp remained between 80 and 85C. The final pressure should be 25 mm Hg or less. The reaction is then continued at 210C for another 2 hr.

The reaction mixture is cooled to 100C, and the vacuum is broken with nitrogen.

Anal.: Total amine, 2.90 meq/g; tertiary amine, 2.50 meq/g.

Quaternization. A modification of the procedure of Groenewould and Robinson (6).

Ethylene dichloride (786 g) was added to the imidazoline (786 g, 2.29 m) and the mixture was cooled to 45C.

Sodium bicarbonate (32 g, 4% of the imidazoline by wt) was added with agitation. Dimethyl sulfate (306 g, 2.43 m) was then added dropwise (with cooling) in 1 hr. The temp was maintained between 45 and 55C.

Sulfation (7). 20% oleum (431 g, 4.6 m total SO_3) was added dropwise to the quaternized material in one and one-half hr at 30–40C. Slight cooling was necessary. After the oleum addition, the reaction mixture was transferred to a separatory funnel.

Neutralization. Sodium carbonate (477 g, 9.0 eq.) is dissolved in 2360 ml of water in a five-liter flask equipped with stirrer, thermometer, and an air condenser. Isopropyl alcohol (315 ml) is added to the solution. Then the sulfonated mixture is added to the carbonate solution in one and one-half hr. Addition of the sulfated mixture should proceed at such a rate that little foam develops on the surface. In case of slurry formation (which may happen at temp below 40C or by excessive foaming), 50–100 ml of isopropyl alcohol may be added.

Toward the end of addition, the pH of the mixture was checked frequently with pH paper. (More sodium carbonate should be added if the pH is below 5).

After the addition was completed, the agitation was interrupted and the layers allowed to separate. The lower aqueous layer, which consisted mainly of a concentrated sodium sulfate solution, was drawn off and discarded.

Removal of Solvent. The organic layer obtained after the neutralization step was placed in a reaction flask equipped for vacuum distillation and heated to 45C with agitation. The pressure was reduced to 150–200 mm Hg and controlled so that a rapid and even flow of distillate was obtained, with min foaming. After most of the ethylene dichloride had been removed (in about 30–45 min) foaming became excessive. The distillation was interrupted and 275 ml of water and 200 ml of isopropyl alcohol were added. The distillation was then continued as before, starting at 40C. The temp was increased gradually to 75C (max). The vacuum was simultaneously increased such that the vapor and flask temp differed only by 2–3C. Yield: 1600g (99%). Anal. Solids: 62.5%; S. calcd., 7.32%, found 7.0%.

S I Sulfonate

To the imidazoline as described under S I Sulfate (1.21 m, 411 g) dissolved in 239 g of ethanol, propane sultone (1.22 m, 150 g) was added dropwise in 1 hr. The temp rose from 35 to 42C. After addition, the mixture was heated to 60C and the reaction continued for 45 min more. The product contains 70% solids. Yield 800 g of solution. The solution was used as is in the evaluation tests.

D I Sulfonate

A mixture of 564 g (2 moles) of commercial stearic acid and 103 g of diethylene triamine was heated in an atmosphere of nitrogen to a temp of 180C. Vacuum was then applied gradually until a pressure of 15 mm was attained. Heating at 180 C under vacuum was continued for another 4 hr. The product was allowed to cool to 80C and 250 ml of methylene chloride were added cautiously (reflux) in 15–20 min to the molten 2-heptadecyl-1-methyl-1-(2-stearoylamido) ethyl-imidazoline.

To a portion (0.560 eq., 350 g) of this imidazoline solution propane sultone (0.566 mole, 69.5 g) was added dropwise in 15 min and the mixture was refluxed for 45 min more (48–50C). 100 ml of methylene chloride was distilled off and the viscous mixture dropped into 2 liters of acetone. The solid product was filtered and dried. Yield: 370 g, 88.5% of theory. S. anal. calcd.: 3.78%, found 3.74%.

Detergency Studies. The detergency studies were carried out in a Tergotometer and the soil used for the study was the standard cotton soil cloth of U.S. Testing Co.

The tests were run at 150 rpm for a period of 15 min at 120F. The solution to fabric ratio was held approximately at 25:1.

The reflectance of the swatches was read on a Hunter Multipurpose Reflectometer using a green filter and the percentage of soil removal was calculated according to the following formula:

$$\% \text{ Soil Removal} = [(R_w - R_s)/(R_o - R_s)] \times 100$$

where R_w = reflectance of washed soil piece
R_s = reflectance of unwashed soil piece
R_o = reflectance of unsoiled cotton (86.5)

The detergency tests (8) were run at 50 and 300 ppm of artificial hardness and the results were plotted as shown in Figures 3 and 4. D A sulfonate showed almost zero soil removal and was not shown in Figures 3 and 4. The concentration of the detergent was varied from .02–0.1% which represents a practical use range. The pH of these tests was approximately 7. In addition one of the compounds, S I Sulfate, was tested at a fixed concentration of 0.04 at various pH values. The results of these are shown graphically in Figure 5.

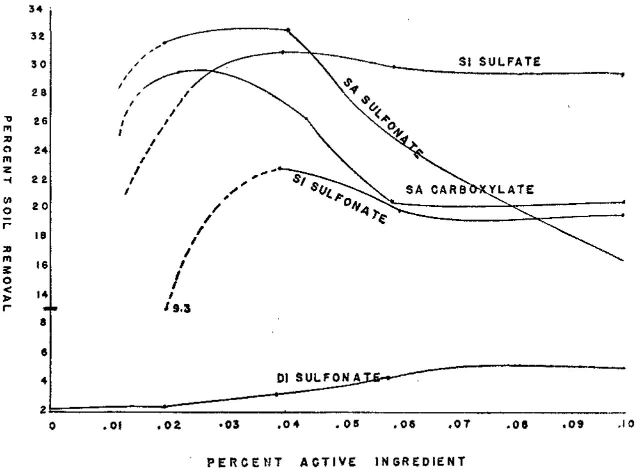

FIG. 3. Detergency (% soil removal) at 50 ppm hardness.

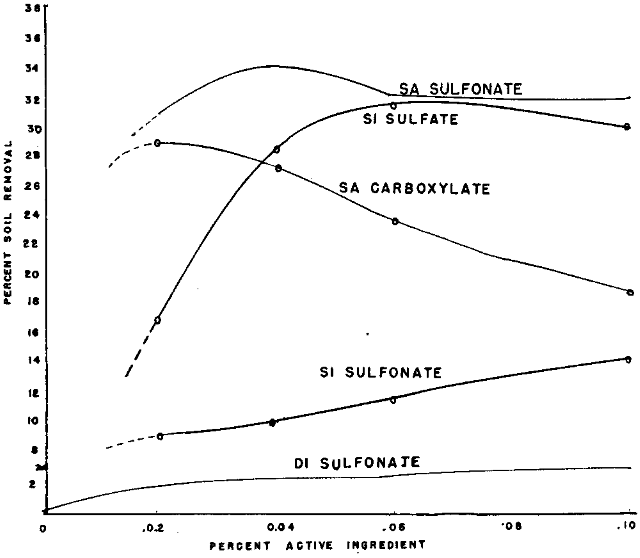

FIG. 4. Detergency (% soil removal) at 300 ppm hardness.

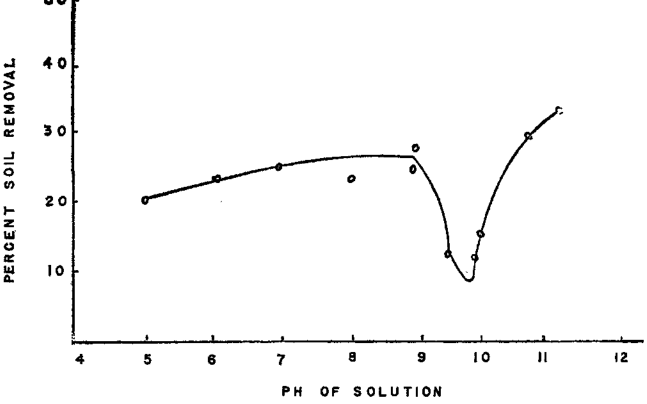

FIG. 5. Variation of detergency of S I sulfate with pH (0.04% active ingredient).

Compatibility Tests. The compatibility tests were run in the Tergotometer very much in the same manner as above except that binary mixtures of the amphoteric with a nonionic detergent-nonylphenol with 9 mols. of ethylene oxide, with an anionic detergent-sodium dodecyl-benzene sulfonate shown in the chart as ABS, and a tallow soap. In these compatibility tests the concentration of the amphoterics was held constant at 0.02% and the concentration of the nonionic and anionic detergents was held const. at .04%. For obvious reasons the concentration of the soap was raised to 0.2 in 50 ppm hardness water and 0.3% at 300 ppm hardness. The purpose of this study was to determine the effect of the amphoteric upon the detergency behavior of a nonionic, an anionic detergent and of soap. The results are shown in chart form in Table I.

TABLE I

Compatibility of Amphoterics with Various Surfactants

No.	Compound added (0.02%)	Percentage of Soil Removal of Binary Mixtures					
		50 ppm Hardness			300 ppm Hardness		
		0.04% Non-ionic	0.04% ABS	0.2% Soap	0.04% Non-ionic	0.04% ABS	0.3% Soap
I	S A Sulfonate	34.1	8.1	25.5	31.7	5.9	25.3
II	S A Carboxylate	23.2	4.9	27.9	23.9	7.2	3.0
III	D A Sulfonate	14.1	0.0	14.0	......	......	......
IV	S I Sulfate	28.5	7.8	29.8	26.3	6.6	21.4
V	S I Sulfonate	24.3	13.8	26.1	13.4	12.2	18.8
VI	D I Sulfonate	34.1	5.5	26.9	32.1	4.2	17.8
	Blank	36.1	19.1	24.3	34.4	17.2	20.0

Softening Evaluation. The evaluation of softening, unfortunately, is a highly subjective matter and it is difficult to assign numerical values in this area. Cotton fabric was washed in a conventional washing machine with a household detergent and was treated in the last rinse with the various amphoterics at such a level that the softening was close to that obtained with a typical commercial fabric softener, namely dioctadecyldimethylammonium chloride. The latter was used as a standard of comparison and was applied at a level of 0.1% on the basis of the fabric wt. Softening of the amphoterics was expressed as that concentration required to give softening approximately equal to 0.1% of the standard softener. The results are given in Table II.

TABLE II

Textile Softening Properties

Concentration (basis fabric wt) to give equivalent softening

	Dioctadecyldimethyl Ammonium Chloride (reference compound)	.1%
I	S A Sulfonate	No softening
II	S A Carboxylate	No softening
III	D A Sulfonate	.4%
IV	S I Sulfate	.5%
V	S I Sulfonate	1.0%
VI	D I Sulfonate	.4%

Discussion

It can be noted that the single chain compounds possess considerably better detergency than the double chain compounds. This by itself is not too unusual and merely bears out what is common knowledge in the fiield of surface active agents. Of the six compounds tested only the sulfated single chain imidazoline S I sulfate appears to be a resonably good detergent. Most of the amphoterics show a decrease in detergency with increasing concentration which is a somewhat anomalous behavior. While the detergency tests initially were all run at a neutral pH of 7 it was obviously of interest to determine how detergency would vary with pH. Such a study undertaken with S I sulfate showed a pH range between 9 and 10.5 where there was an unexpected and very dramatic drop in detergency. This is particularly disturbing since most practical detergent formulations would have a pH in that range.

The soft water detergency of S I sulfonate is considerably better than that in hard water. The other compounds do not show such dramatic differences. The betaine S A carboxylate is a fairly poor detergent. Examination of the compatibility data in Table I shows that all of the amphoteric compounds of this study are incompatible with a standard alkylbenzene sulfonate. In other words combination of an amphoteric and an alkylbenzene sulfonate results in a detergency which is lower than that of either compound. By and large compatibility with a nonionic detergent or with soap is fairly good in soft water. While in many cases the detergency is not additive, only in the case of DA sulfonate is there a sharp decrease in the detergency of the substrate. In hard water the amphoterics depress the detergency of the nonionic detergent and with the exception of S A sulfonate they depress the detergency of soap. This behavior of the amphoterics indicates that they are largely cationic in nature and that therefore an anionic detergent, such as ABS, would show marked interference with detergency. A weak anionic detergent like soap shows evidence of some interference and a nonionic detergent shows very little interference. In the area of softening it can be noted in Table II that the single chain compounds show very little or no softening as compared with the reference compound whereas the double chain compounds D A sulfonate and D I sulfonate, show some softening although they are only one-fourth as effective as the reference compound. This would indicate that the presence of an anion in the molecule has a marked effect on the adsorption of the amphoterics on textiles. On the other hand, the performance of S I sulfate, a single chain compound, is fairly close to the two double chain compounds, indicating that proper molecular structure apparently can help to overcome the defect of only a single fatty chain.

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