The Action of Various Lime Soap Dispersants

N. SCHÖNFELDT, Mölndal, Sweden

Abstract

The course of the lime soap-dispersing action of various surfactants has been examined by use of a titrimetric method. Two types of dispersants can be distinguished. With the addition of a surfactant of the first type, the concentration of the dispersed fatty acid increases gradually. If a surfactant of the second type is used, a definite increase of the fatty acid concentration first occurs after the addition of considerable amounts of the dispersant.

Ethylene oxide adducts and sodium triethylene glycol monolauryl ether sulfate behave like dispersants of the first type whereas sodium dodecylbenzenesulphonate and sodium lauryl sulfate belong to those of the second type. The dispersing action of both types of surfactants is discussed.

Introduction

SEVERAL METHODS ARE KNOWN to evaluate the lime soap-dispersing power of surfactants (1–4). In these tests the minimum amount of dispersant is evaluated by the aid of nephelometry, titrimetry, or simple visual methods to prevent the deposition of the lime soap under defined conditions. Common to these methods is a determination of the point at which the lime soap is completely dispersed. In general, no information is obtained with regard to the course of the dispersion up to this point.

In an earlier paper (5) the author has published a method according to which previously precipitated lime soap is peptized by the addition of increasing amounts of a surfactant. After each addition the fatty acid concentration in the stable dispersion is determined titrimetrically upon removal of the deposited lime soap. At the end-point of the test, the actual concentration of the stable dispersion will be equal to the known fatty acid concentration of the sodium oleate solution which is employed. Not only the minimum amount of dispersant which is required for the complete dispersion of the lime soap is evaluated, but also the course of the dispersing action is followed. This method, altered in a few details, is described in this paper.

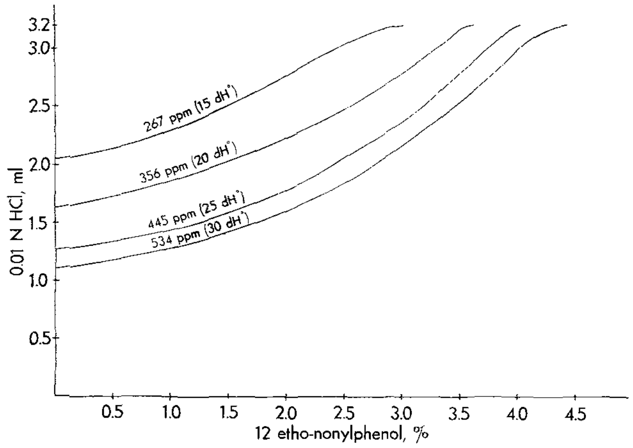

FIG. 1. Dispersion of lime soap by 12 etho-nonylphenol.

Experimental Section

Reagents

Sodium oleate purum, 20 g per liter of solution
Surfactants, 1 g or 10 g of active matter per liter of solution; all surfactants of commercial grade
Hydrochloric acid, 0.01 N
Bromocresolgreen, 1 g per liter of solution
Hard water containing 3,560 ppm $CaCO_3$ (equal to 200° German hardness)

Procedure

Five milliliters of the sodium oleate solution are added to each of six 100-ml graduated tubes together with increasing amounts of the surfactant solution. Then distilled water is added until the volume of the solution is brought up to 100-a ml, where *a* denotes the number of ml of hard water which must be added to obtain the required hardness.

Before addition of the hard water, the test tubes are stoppered and inverted five times in order and in the same way, also are returned to the starting position each time. The stoppers are then removed, hard water is pipetted into each test tube, and these are allowed to stand for 2 to 5 min. Thereafter they are inverted and returned to the starting position five times again, then are placed immediately into a heating bath at 95C. After 30 min, when the lime soap has flocculated on top of the solution, a 10-ml pipette is introduced into each test tube. Each pipette is provided with a device to keep the orifice of the pipette 1 cm above the bottom of the tube. The upper end of the pipette is held closed with a rubber tube and a screw clip.

After 5 min the screw clip is removed, and 10-ml samples are pipetted into six 50-ml beakers. To each sample four drops of the bromocresolgreen solution are added, and the samples are titrated with 0.01 N hydrochloric acid at about 40–50C until the color of the solution turns to a stable yellow-green.

The titration value of the blank is determined in the following way. Five milliliters of the sodium oleate

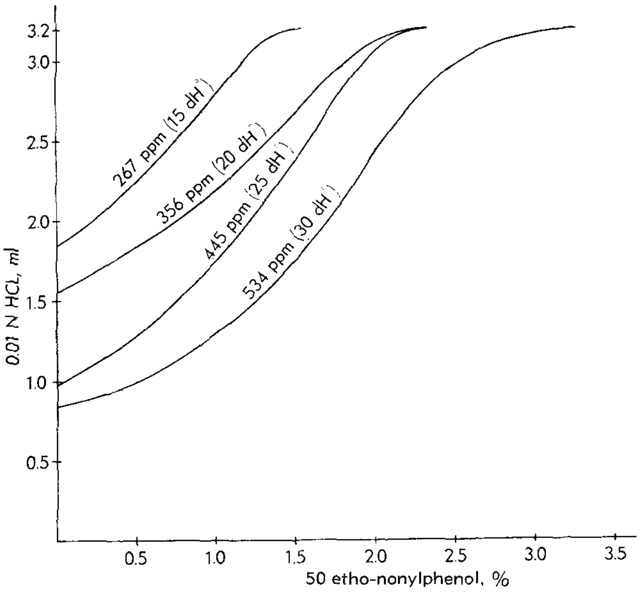

FIG. 2. Dispersion of lime soap by 50 etho-nonylphenol.

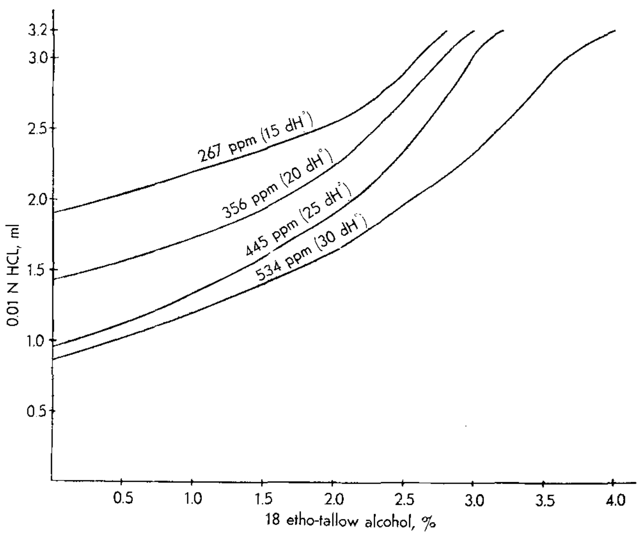

FIG. 3. Dispersion of lime soap by 18-etho-tallow alcohol.

solution containing 0.1 g of sodium oleate are pipetted into a 100-ml graduated tube, diluted to 100 ml with distilled water, and thereafter inverted and returned to the starting position five times. Then to a 10-ml sample four drops of the bromocresolgreen solution are added, and the sample is titrated with 0.01 N hydrochloric acid. The consumption is 3.2 ml. (If the dispersant also consumes hydrochloric acid, the titration value will be higher, as seen in the dotted line in Fig. 5.) The amount of dispersant is expressed as percentage of the weight of sodium oleate.

The surfactants tested were four ethylene oxide adducts (Fig. 1–4), sodium dodecylbenzenesulphonate (Fig. 5), sodium lauryl sulphate (Fig. 6), and sodium triethylene glycol monolauryl ether sulphate (3 etho-lauryl sulfate, sodium salt) (Fig. 7). The amount of dispersant, in percentage, corresponding to the titration value of the blank (3.2 ml in all figures with the exception of Fig. 5) denotes the point at which the lime soap is completely dispersed.

The curves in Fig. 1 to 4 show a similar course. With the increasing length of the ethylene oxide chain, the amounts of dispersant required for a complete dispersion of the lime soap show a tendency to decrease. These amounts are between 1.5 and 4.5%; 50 etho-nonylphenol shows the lowest values.

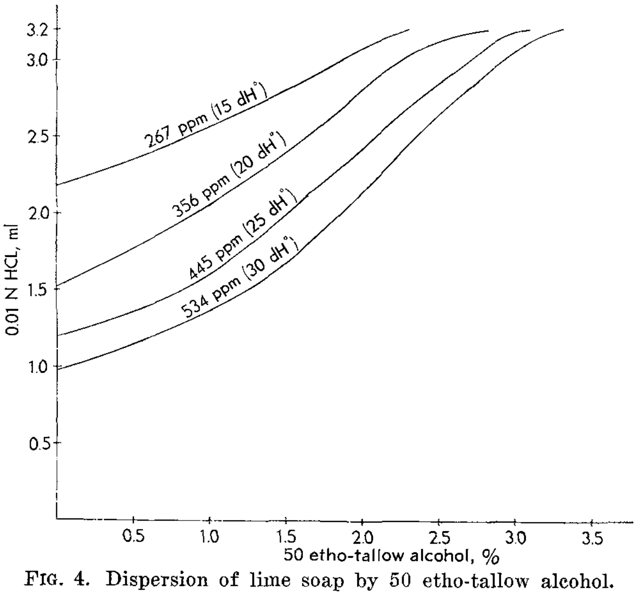

FIG. 4. Dispersion of lime soap by 50 etho-tallow alcohol.

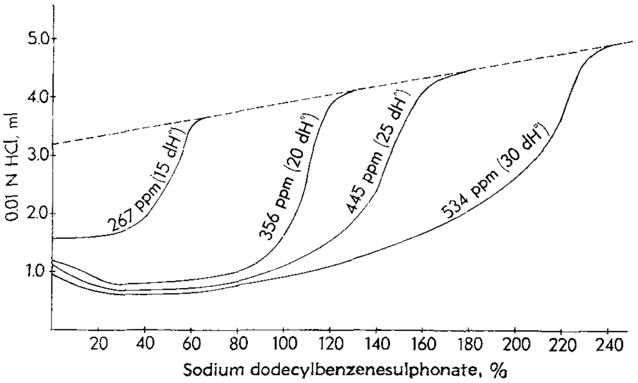

FIG. 5. Dispersion of lime soap by sodium dodecylbenzenesulphonate.

A different course shows the curves of sodium dodecylbenzenesulphonate and of sodium lauryl sulphate. No definite increase of the fatty acid concentration can be observed up to approximately 20% surfactant addition at 267 ppm water hardness, and up to approximately 100% addition at 534 ppm.

The course of the dispersing action changes markedly, if instead of lauryl sulfate, 3 etho-lauryl sulfate is used as dispersant. In this case the curves are similar to those in Fig. 1 to 4; also the amounts required for a complete dispersion of the lime soap are in the same range. Consequently, as a lime soap dispersant, 3 etho-lauryl sulfate behaves like an ethylene oxide adduct and not like a sulphate lauryl alcohol.

Discussion

In Fig. 1 to 4 and in Fig. 7 the curves have a course other than those in Fig. 5 and 6. The mode of the dispersing action can be divided into two types. Surfactants of the Type a) disperse a certain part of the lime soap after the first addition, and this action is extended by further additions until the lime soap is completely dispersed, at surfactant additions not exceeding 6%. Surfactants of the Type b) at first show no definite dispersing action in spite of the addition of considerable amounts. For a complete dispersion of the lime soap between 60 and 240% are required.

In order to obtain a stable dispersion of hydrophobic substances in water, two factors are, in gen-

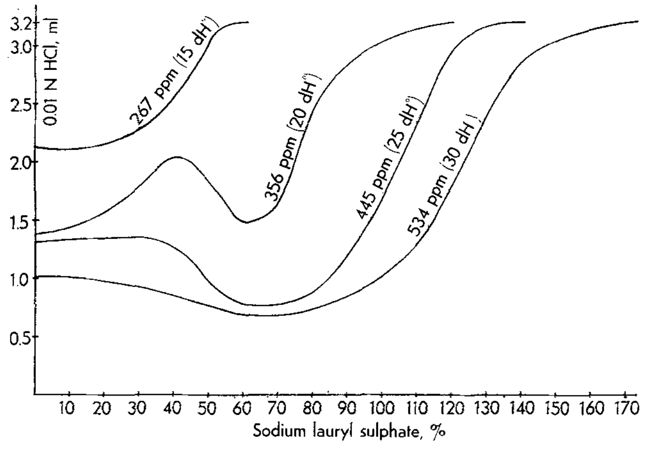

FIG. 6. Dispersion of lime soap by sodium lauryl sulfate.

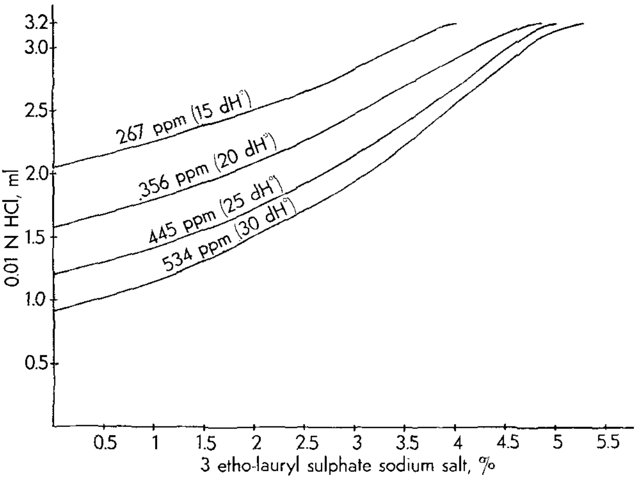

FIG. 7. Dispersion of lime soap by 3 etho-lauryl sulphate, sodium salt.

eral, considered to be of special importance, namely, a low interfacial tension and the formation of a colloid film on the surface of the hydrophobic particles which protects them against coalescence.

The interfacial tension of 0.1% aqueous solutions of 9 etho-isooctylphenol, sodium dodecylbenzenesulphonate, and sodium lauryl sulfate against red oil (oleic acid) at 25 to 26C was reported as 3.9, 1.9, and 0.4 dynes/cm respectively (6). In the lime soap-dispersing tests the major part of oleic acid is present as calcium oleate, and this circumstance may, no doubt, alter the above figures, but this can hardly explain why substances of the Type a) are so much more effective than surfactants of the Type b) at so much lower concentrations. Differences of the protective films on the surface of the lime soap particles must be the reason for the behavior of the two types of surfactants.

As mentioned earlier, each addition of the ethylene oxide adducts caused the dispersion of some part of the lime soap particles which were present. A protective film is probably formed in the presence of a comparatively small amount of surfactant. Hydrogen-bonded water molecules may play an important role, and these molecules are attached to the ether oxygen atoms of the ethylene oxide chain. Thus the protective film consists of ethylene oxide adduct molecules and of a probably considerable number of water molecules.

In the presence of dodecylbenzenesulphonate and lauryl sulfate a protective film is probably formed in another way. Water molecules may not be hydrogen-bonded to the surfactant molecules to the same extent as in the case of the ethylene oxide adduct molecules. This means that the protective film consists mainly of surfactant molecules; consequently, these must be present in a comparatively large amount to permit the building up of the protective film. At lower additions, no appreciable amount of the lime soap will be dispersed.

A protective film of the Type b) seems to be more sensitive to hard water than a film of the Type a). In the case of sodium dodecylbenzenesulphonate and sodium lauryl sulfate, the amounts required for a complete dispersion of the lime soap differ considerably with the hardness of water. With ethylene oxide adducts as dispersants the differences are small.

No attempts are made to explain the irregularities of the curves in Fig. 6; they are probably restricted to the prevailing conditions of the tests. As the irregularities occurred before a definite increase of the fatty acid concentration, they were considered to be irrelevant to this discussion.

The tentative explanation of the dispersant action appears to be supported by the results, especially by the striking difference in the behavior of lauryl ether sulfate and lauryl sulfate as lime soap dispersant. Surfactants of the Type a), however, need not be restricted to substances containing an ethylene oxide chain. A further elucidation of the dispersant mode of action makes a broadening of the experimental basis desirable.

ACKNOWLEDGMENTS

This investigation was carried out in the development laboratory of Berol AB, Gothenburg, Sweden. Thanks are given to K. H. Grunewald, managing director, for his interest as well as to Mrs. Anna Lamm and Miss Ingegerd Friberg for their assistance.

REFERENCES

1. Lindner, K., "Tenside—Textilhilfsmittel—Waschrohstoffe," Wissenschaftliche Verlagsgesellschaft M. B. H., Stuttgart, 1964.
2. Schönfeldt, N., "Oberflächenaktive Anlagerungsprodukte des Äthylenoxyds," Wissenschaftliche Verlagsgesellschaft M. B. H., Stuttgart, 1959.
3. Borghetty, H. C., and C. A. Bergman, JAOCS *27*, 88 (1950).
4. Mayhew, R. L., and L. W. Burnette, Soap Chem. Specialties *38*, No. 8, 55 (1962).
5. Schönfeldt, N., Proc. Intern. Congr. Surface Activity, 4th, Brussels, 1964, Preprint C/I/7.
6. Mankowich, A. M., Ind. Eng. Chem. *45*, 2759 (1953).

[Received September 18, 1967]