

bulk of water, thus holding fluctuations in temperature to a minimum, is desirable, but not essential. If this type of bath is employed, the pycnometers should rest on a false bottom of wire mesh or perforated metal and at a depth such that immersion of the pycnometer will be to the neck of the instrument. Any suitable thermometer, graduated to 0.1° or 0.2°C., and accurately calibrated, may be used to register the temperature of the bath.

3. A sensitive analytical balance and set of weights accurately calibrated. Weighings must be made to nearest milligram.

B. Procedure

1. Calibration of Pycnometer—Clean and dry the pycnometer assembly thoroughly and obtain its weight to nearest 0.001 gram. Fill it with freshly boiled distilled water which has been cooled to about 20°C. Insert the thermometer and place in bath with cap of side arm removed. Allow the temperature to rise until the temperature of the pycnometer thermometer and that of the bath are identical, i.e. 25.0°±0.1°C. This may require from 20 to 30 minutes. When this condition has been obtained, remove excess water from the tip of side arm and replace cap. Remove pycnometer from bath and dry thoroughly with a clean towel, avoiding too brisk rubbing which tends to induce a static charge. Weigh pycnometer and contents, dry again with towel and reweigh to nearest milligram.

Weight of pycnometer + water — weight of pycnometer
= weight of water in pycnometer at 25.0°C.

2. Determination of Glycerine Specific Gravity—The glycerine sample must be free from air bubbles. If not, they may be removed by warming and allowing them to rise to the surface, or this action may be hastened by centrifuging. During all of these operations precautions must be taken against loss of moisture from the sample by

evaporation or gain in moisture because of its well known hygroscopic nature. Cool the glycerine to about 20°C. and fill the cleaned, dried and tared pycnometer by pouring the sample carefully down the side of the neck until both side arm and neck overflow. Insert the thermometer carefully and examine for air bubbles. If none are visible, place the assembly, with side arm cap removed, in the bath and bring to 25°C. temperature exactly as in B-1. Carefully remove excess glycerine from tip of side arm, replace cap, dry and weigh as described in B-1.

Weight of pycnometer + sample — weight of pycnometer = weight of sample in pycnometer at 25°C.

C. Calculation

Apparent specific gravity at 25°/25°C.=

$$\frac{\text{Weight of sample in pycnometer at 25°C.}}{\text{Weight of water in pycnometer at 25°C.}}$$

Notes

1. For a given pycnometer, once the water weight is accurately established, the calibration need not be repeated unless some change in the weight of the pycnometer assembly occurs. It is strongly recommended that the weight of each pycnometer, dry and empty, be taken before each determination. This precaution is an insurance against change in weight by chipping or accidental interchange of caps, etc.
2. For conversion of apparent specific gravity of distilled glycerines from 25°/25°C. to other temperatures and for translation of specific gravity into percent glycerine, the tables prepared by Bosart and Snoddy, Ind. & Eng. Chem., 19, pp. 506 at seq. (April, 1927) shall be employed. These tables also permit calculation of true specific gravity and density from apparent specific gravity. It is obvious that these tables are applicable only to solutions of glycerol in which water is the only impurity.

The Effect of Some Inorganic Salts in Dilute Solution on the Formation of Calcium and Magnesium Soaps¹

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BUILDERS, in the jargon of the soap technologist, are materials which are considered to aid detergent action and foaming properties of soap solutions. Alkali carbonates, phosphates, and silicates of various complexity are commonly used as builders.

The most direct means of aiding the detergency of soaps in hard water is the prevention of the formation of calcium or magnesium soaps. This paper is concerned with this function of builders. No attempt has been made to measure the influence builders have on detergency except insofar as can be surmised from their effectiveness in preventing direct loss of soluble soaps to form calcium and magnesium soaps.

The reaction mixture from calcium and magnesium salts, builders, and a commercial soap or even a relatively pure soap, is a complex colloidal system. As long as excess soap is present as a surface active agent, complete precipitation from these dilute solutions has not been possible. Consequently, any direct analysis of the reaction products has not been permissible, and indirect evidence must be resorted to.

Using an indirect method based on the foam stability of the total soluble soap present, we have attempted to interpret these reactions on the basis of solubility products.

In a previous paper (1) it was shown that the foam stability of solutions of soaps of pure fatty acids is a function of concentration and pH, and for each concentration of each pure soap there was a pH range within which the foam stability was at a maximum. It was also observed that for the soaps of the straight chain saturated fatty acids studied, the presence of dispersed calcium or magnesium soaps in the solutions did not affect the foam stability of the remaining soap. This was not the case for all the soaps of unsaturated fatty acids. For example, sodium oleate solutions showed reduced foam stability in the presence of the corresponding calcium soap.

These observations have been utilized in the method followed in the present investigation. For each pure soap, we have selected a concentration which is sufficiently critical with respect to foam stability in the pH range for maximum foam so that the pour foam test used (2) permits the measurement of a reduction in soap concentration of about 10 per cent. When

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the pH and temperature of these solutions is controlled, any measured loss in foam stability should be due to a loss in soluble sodium soap. This loss in sodium soap is therefore assumed to be due to the formation of calcium or magnesium soap. Salt effects of inorganic reagents on foam stability were disregarded and it should be noted that any such effects would favor the apparent efficiency of the builders.

Materials. The soaps used were purified samples prepared as described previously (1) and their estimated purity with respect to surface active contaminants is indicated in Table I. The various inorganic chemicals used were as pure as could be obtained commercially.

TABLE I.

| Soap Used | Concentration | Estimated Purity* | Ppm. Calcium Equiv. to Soap | pH for Test Solution @ 50°C. |
|-------------------------|---------------|-------------------|-----------------------------|------------------------------|
| | Per cent | Per cent | | |
| Sodium Laurate..... | 0.1 | 98 | 225 | 7.2 |
| Sodium Myristate..... | 0.05 | 98 | 100 | 8.2 |
| Sodium Palmitate..... | 0.015 | 98 | 27 | 10.4 |
| Sodium Oleate..... | 0.05 | 95** | 83 | 10.3 |
| Sodium Elaidate..... | 0.05 | 95 | 83 | 10.5 |
| Sodium Ricinoleate..... | 0.10 | 95** | 158 | 10.5 |

*Purity with regard to organic contaminants.

**Approximately.

Procedure. In preparing the solutions for this study, care was exercised in avoiding variations in temperature or composition after the soap had been added. Therefore all adjustments of pH were made on the builder-hardness mixture with a view to attaining the proper pH when the soap was added. If after making the foam test it was found that the pH was not at the proper level, this solution was discarded and a fresh one prepared. The pH determinations were made with the Model G Beckman pH meter equipped with a Type E glass electrode designed to be relatively free from sodium ion errors at high pH. The pH value was read with the solution at 50°C. with the temperature compensator of the meter set for 40°C. It is assumed that the pH values recorded at 50°C. would be adequate for comparative purposes for solutions used at 57°C.²

The builders or inorganic salts were dissolved in 400 ml. of 100 parts per million hard water. The pH was adjusted, the solution was heated to 57°C. and the proper weight of anhydrous soap was added. The mixture was stirred for five minutes and the relative foam stability measured by the Pour Foam Test method. During the aging period the solution was kept in a water bath to maintain the temperature at 57°C. ± 1°C. After the foam stability was measured, the pH was checked. This procedure was used to determine the relative effectiveness of the various build-

² These values for pH are not rigorously correct because proper allowance has not been made for temperature effects. The values given are probably too high by 0.1 to 0.4 pH units. However, for the purposes of the paper the scale readings as measured are considered adequate.

ers in turn towards prevention of the formation of calcium or magnesium soaps of various fatty acids. The soap concentration was selected so that reductions in concentration of the order of 10 per cent would be detected by the Pour Foam Test of measuring relative foam stability. These concentrations are listed in Table I.

From the foam stability data, the selection of the mole ratio of builder to hardness required for the prevention of calcium or magnesium soap formation was made on the basis of the lowest mole ratio required to give optimum foam height. In most cases this corresponds to the foam height obtained for an equivalent soap concentration in appropriately buffered solution.

Results

Tables III and IV show the mole ratio of builder to hardness required for complete protection of the various soaps under these conditions.

It will be noted that because of the various pH values of the solutions used, some of these tests are not comparable. Thus sodium laurate solutions were studied with sodium carbonate at a pH 7 where most of the salt is present as bicarbonate and not as carbonate, as in the case of tests using sodium oleate (pH 10.3). To illustrate the typical results obtained which form the basis for Tables III and IV the data for sodium palmitate are shown in Table V.

Reaction Time. Two tests were made in which the soap was dissolved in a portion of the water at 57°C. and this solution added to the builder hardness solution at 57°C. The foam stability measurements were completed at five minutes and at one-half minute after mixing these solutions.

In each case the foam is approximately zero, showing that conversion of sodium soap into calcium soap is complete even in the presence of builder, one-half minute after mixing the solutions.

TABLE II.

| | Hardness | Mole Ratio Builder Hardness | Foam | |
|-------------------------|-------------|-----------------------------|--------------|--------|
| | | | After 5 Min. | ½ Min. |
| .015% Na Palmitate..... | 100 ppm. Ca | 5 Calgon | 15 mm. | 10 mm. |
| Na Oleate..... | 100 ppm. Ca | 5 TSP | 20 mm. | 20 mm. |

These mole ratios are a simple and convenient manner of comparing our observations. It should be noted that where protection is complete the controlling factor is the ratio of the concentrations (activities) of soap and builder anions in the solution.

Mixed Soaps. Using mixtures of sodium palmitate and sodium laurate, several experiments were made to determine as far as possible the distribution of the calcium between the various possible combinations. These two soaps were chosen because they offered an opportunity of distinguishing the separate surface

TABLE III.

Figures Indicate the Mole Ratio of Builder to Hardness Required for Effective Soap Protection at 57°C.

| | Magnesium Hardness | | | | | | |
|------------------|---|--|--|--|--|---|---------------------------------|
| | Na ₆ P ₄ O ₁₈ Quadrafos | Na ₂ P ₃ O ₁₀ Polyfos. | Na ₂ P ₆ O ₁₈ Calgon | Na ₂ P ₂ O ₇ TSP | Na ₃ PO ₄ TSP | Na ₂ O 3.2 SiO ₂ | Na ₂ CO ₃ |
| Oleate..... | 1 | 1 | 1 | 1 | 5 | 4 | > 5 |
| Laurate..... | 1 | 1 | 1 | 2 | 5 | > 5 | > 5 |
| Ricinoleate..... | 1 | 2 | 2 | 3 | 5 | 5 | 5 |
| Myristate..... | 2 | 2 | 1 | 3 | 5 | > 5 | 5 |
| Elaidate..... | 2 | 2 | 2 | 4 | 5 | 5 | 5 |
| Palmitate..... | 2 | 3 | 3 | > 5 | 5 | 5 | > 5 |

TABLE IV.

Figures Indicate the Mole Ratio of Builder to Hardness Required for Effective Soap Protection at 57°C.

| | Calcium Hardness | | | | | | |
|------------------|---|--|--|---|--|---|---------------------------------|
| | Na ₂ P ₄ O ₁₃ Quadrafos | Na ₂ P ₃ O ₁₀ Polyfos. | Na ₂ P ₆ O ₁₈ Calgon | Na ₂ P ₂ O ₇ TSPP | Na ₃ PO ₄ TSP | Na ₂ O 3.2 SiO ₂ | Na ₂ CO ₃ |
| Oleate..... | 2 | > 5 | 2 | > 5 | 1 | > 5 | 3 |
| Laurate..... | 2 | > 5 | 2 | > 5 | > 5 | > 5 | > 5 |
| Ricinoleate..... | 3 | > 5 | 3 | > 5 | > 5 | > 5 | > 5 |
| Myristate..... | 3 | > 5 | 2 | > 5 | > 5 | > 5 | > 5 |
| Elaidate..... | > 5 | > 5 | > 5 | > 5 | > 5 | > 5 | 2 |
| Palmitate..... | > 5 | > 5 | > 5 | > 5 | > 5 | > 5 | > 5 |

active components since they exhibit maximum foam stability at widely different levels of pH. Figure I summarizes these results.

Sodium Oxalate and Sodium Fluoride as Builders.

In order to estimate the concentration of builders necessary to prevent the formation of calcium soap on the basis of solubility products, calcium oxalate and calcium fluoride were taken as examples since these salts show sufficiently low solubility among those for which data are available. These comparisons were made disregarding the known limitations of applying solubility products due to the salt concentrations involved and the presence of soap which may influence the apparent solubility of the calcium compounds. The results for sodium laurate and sodium myristate are summarized in Table V.

TABLE V.

The Foam Stability of 0.015% Sodium Palmitate as a Function of Builder to Hardness Ratio in 100 PPM Hard Water 57°C.

| A Builder Used | B Hardness | Foam mm. | Mole Ratio A to B | Protective Mole Ratio |
|--|---------------|-------------|-------------------------|-----------------------------|
| None..... | None | 230 | | |
| Na ₂ PO ₄ | Calcium | 0 | 5 | > 5 |
| Na ₂ P ₂ O ₇ | Calcium | 0 | 5 | > 5 |
| Na ₂ P ₄ O ₁₃ | Calcium | 0 | 5 | > 5 |
| Na ₂ P ₆ O ₁₈ | Calcium | 0 | 5 | > 5 |
| Na ₂ P ₃ O ₁₀ | Calcium | 0 | 5 | > 5 |
| Na ₂ CO ₃ | Calcium | 0 | 5 | > 5 |
| Na ₂ O 3.2 SiO ₂ | Calcium | 0 | 5 | > 5 |
| Na ₂ PO ₄ | Magnesium | 30 | 5 | > 5 |
| Na ₂ P ₂ O ₇ | Magnesium | 70 | 5 | > 5 |
| Na ₂ P ₄ O ₁₃ | Magnesium | 230 | 3 | |
| Na ₂ P ₄ O ₁₃ | Magnesium | 220 | 2 | 2 |
| Na ₂ P ₄ O ₁₃ | Magnesium | 0 | 1 | |
| Na ₂ P ₆ O ₁₈ | Magnesium | 220 | 3 | |
| Na ₂ P ₃ O ₁₀ | Magnesium | 180 | 2 | 3 |
| Na ₂ P ₃ O ₁₀ | Magnesium | 220 | 4 | |
| Na ₂ P ₃ O ₁₀ | Magnesium | 220 | 3 | |
| Na ₂ P ₃ O ₁₀ | Magnesium | 80 | 2 | |
| Na ₂ CO ₃ | Magnesium | 0 | 5 | > 5 |
| Na ₂ O 3.2 SiO ₂ | Magnesium | 200 | 4 | 4 |
| Na ₂ O 3.2 SiO ₂ | Magnesium | 160 | 3 | |

A 0.1% solution of sodium laurate in 0.03 molar KCl at 40° (pH 7.4) gave 210 mm. of foam. To a solution 0.03 molar KCl and 0.001 molar CaCl₂ (100 ppm. Ca hardness) to which a known amount of sodium oxalate was added and the pH adjusted to 7.4 at 40°C., sodium laurate was added to make it 0.1% sodium laurate (4.5 × 10⁻³ molar), the solution aged 5 minutes and the pour foam test carried out. It was found from several experiments varying the amount of sodium oxalate added, that a mole ratio of $\frac{Na_2C_2O_4}{CaCl_2} = 3$ was required for protection. A ratio of 2.5 did not give protection.

The solubility of CaC₂O₄ (interpolated) in 0.0425 normal salt solution is 0.0159 gm. per liter at 40° (3). In the following calculations parentheses indicate concentrations:

(a) The solubility product of CaC₂O₄ at 60° at a salt concentration of 0.0425 normal $K_1 = (Ca^{++})(C_2O_4^{--}) =$

$$\left(\frac{0.0159}{128}\right)^2 = 15.5 \times 10^{-9}$$

(b) (Ca⁺⁺) initial = 10⁻³ moles per liter

(c) Mole ratio $\frac{(C_2O_4^{--})}{(Ca^{++})} = 3$ to protect sodium laurate solution by experiment.

(d) For this mole ratio assuming precipitation of only calcium oxalate
(C₂O₄⁻⁻) = (3 - 1)10⁻³ = 2 × 10⁻³ moles per liter

(e) After calcium oxalate is precipitated

$$(Ca^{++}) = \frac{K_1}{(C_2O_4^{--})} = \frac{15.5 \times 10^{-9}}{2 \times 10^{-3}} = 7.75 \times 10^{-6}$$

Suitable data of the salt effect on the solubility of sodium fluoride are not available. Assuming the same influence on its solubility as that given for calcium oxalate in 0.0425 normal salt solution, a value of 0.0328 gm. CaF₂ per liter was taken.

(f) Solubility product of CaF₂ at 40° in 0.0425 molar salt solution

$$K_2 = (Ca^{++})(F')^2 = 4 \left(\frac{0.0328}{78.1}\right)^2 = 29.6 \times 10^{-11}$$

(g) To satisfy (Ca) = 7.75 × 10⁻⁶ moles per liter ---- from (e)

$$(F') = \left(\frac{K_2}{Ca^{++}}\right)^{\frac{1}{2}} = \left(\frac{29.6 \times 10^{-11}}{7.75 \times 10^{-6}}\right)^{\frac{1}{2}} = 6.2 \times 10^{-3}$$

(h) The total (F') = (6.2 + 2) × 10⁻³ = 8.2 × 10⁻³ and therefore to protect laurate with fluoride in 100 ppm. calcium hard water at 40°C. in 0.03 molar KCl requires a mole ratio of fluoride to calcium of 8.2. In Table VI it is seen that the experimental value was 8.

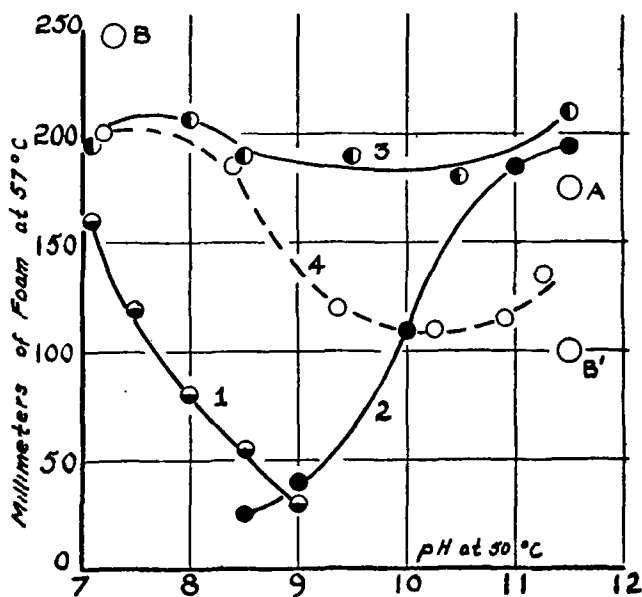


FIG. I. Foam stability of solutions of single and mixed soaps vs. pH

- (1) 0.1% sodium laurate
- (2) 0.01% sodium palmitate
- (3) Mixture containing 0.1% sodium laurate and 0.01% sodium palmitate
- (4) Mixture containing 0.1% sodium laurate, 0.05% sodium palmitate and calcium hardness equivalent to palmitate.
- (A) Foam stability of 0.005% sodium palmitate at pH 11.5
- (B)(B') Foam stability of solution containing 0.1% sodium laurate, 0.015% sodium palmitate, 100 ppm. calcium hardness and 5 moles quadrafos (Na₂P₄O₁₃) at pH 7.3 and 11.5.

A similar experiment and calculation was made using sodium myristate and it is seen that the calculated values agree well with the experimental values in Table VI.

Discussion

In the mixture of soaps in hard water plus builder, it appears that the least soluble components are selectively precipitated or dispersed. The calcium or magnesium soaps of the higher fatty acids appear less soluble than the calcium or magnesium salts of the builders.

The data summarized in Tables III and IV indicate that in general to prevent calcium soap formation, higher builder concentrations are required than is necessary for the prevention of magnesium soap formation. It also appears that for the majority of cases no single builder among those studied is more efficient as a water softener than soap itself on a weight for weight basis in hard water containing both magnesium and calcium salts.

The results of the reaction time tests show that the reactions involved proceed rapidly enough to equilibrium so that time effects can be neglected under these conditions.

TABLE VI.

| | Ratio | (F') | (F') |
|--|--------------------|------------------------------|-----------------------------------|
| | Oxalate Calcium | (Ca ⁺⁺) Found | (Ca ⁺⁺) Calculated |
| 0.1% Sodium Laurate @ 40° and pH 7.4..... | 3 | 8 | 8.2 |
| 0.025% Sodium Myristate @ 50° and pH 7.9..... | 5.5 | 12 | 12.5 |

Curves 1 and 2 show foam for 0.1% sodium laurate and 0.01% sodium palmitate respectively. Curve 3 shows the foam for a mixture containing 0.1% sodium laurate and 0.01% sodium palmitate and it is noted that foam height of the mixture is greater than for either soap alone and does not vary much with pH change. Curve 4 shows the foam stability of a solution containing 0.1% sodium laurate and 0.05% sodium palmitate together with 90 ppm. calcium hardness which amount is equivalent to the total palmitate present. It is seen that at low pH the foam stability approaches that obtained in Curve 3. At high pH the curve is lower than at point A which corresponds to 0.005% sodium palmitate, which is 10% of the concentration of palmitate as shown in Curve 4.

A solution was taken containing 0.1% sodium laurate and 0.015% sodium palmitate, 100 ppm. calcium and 5 moles of quadrafos (Na₆P₄O₁₃) per mole of calcium, which was sufficient to protect sodium laurate and insufficient to protect sodium palmitate under the conditions of tests in Table V. Point B shows higher foam stability than Curve 3 for a mixture of laurate and palmitate at low pH and B¹ shows foam stability lower than any of previous solutions which indicates removal of the major portion of palmitate. We interpret the values B and B¹ as indicating that behavior of the builder in the mixture was substantially the same as it was for the corresponding experiments where the soaps were examined separately.

The selective removal of palmitate as shown in Figure I might be expected on the basis of the lower solubility of calcium palmitate compared to calcium laurate as reported by Pohle (4).

The examination of sodium oxalate and sodium fluoride as builders illustrates some of the assumptions involved in attempting to interpret the data on the basis of solubility products. The agreement between experimental and calculated values based upon the experimental figure for protection of sodium laurate and myristate and the known values for solubilities of calcium oxalate and fluoride is surprisingly close. This treatment must be considered an over-simplification of the problem and cannot be accepted as entirely adequate on a quantitative basis.

Previous investigators of this subject have used a procedure derived from the Clark titration of water hardness and we feel that their method and conclusions are open to criticism.

The procedure in general consists of the stepwise addition of soap solutions to hard water until a foam or froth can be produced of sufficient stability to last five minutes. When the relative effectiveness of builders is compared, the practice has been to add these to the hard water and compare the amount of soap required for the titrations when the builder is present, with the titration of the blank using soap alone. Bolton (5) and later Dedrick and Wills (6) used this technique with relatively pure soaps and mixed hardness (1 part magnesium to 2 parts calcium). A great disadvantage in the use of this method is that neither the nature nor concentration of the material responsible for the foam is known. The graphs of Bolton where he plots grams soap required in the titration against grams builder present, suggest that most of the builder was combined with the magnesium hardness and did not prevent calcium soap formation to any appreciable extent, since definite breaks occur at soap concentrations of two-thirds that required for the blank. In our own laboratories a series of such titrations was carried out using a commercial soap, various builders and the effect towards calcium or magnesium hardness was examined separately. Graphical representation of the data obtained (7) did not reveal breaks such as were obtained by Bolton.

Ruff (8) has shown by means of the modified Clark titration technique that the end point for some soaps varies greatly, depending upon the ratio of calcium to magnesium in the hard water. When a builder is used it would be expected that the least soluble compounds would be removed. Therefore, in Bolton's experiments the composition of the hard water with respect to the calcium magnesium ratio was constantly varying in an unknown fashion which would alter the end point in an unknown way. However, from examination of his data it is evident that very high mole ratios of builder to hardness were required to protect the low concentrations of free soap present at the end point.

In addition to the above ambiguities the titration method is subject to a serious error of interpretation because it is tacitly assumed that after the end point is reached further additions of soap will result in a corresponding increase in the soap concentration. If pure soap were used this would be true only where the changed soap concentration did not effect the already established equilibrium. Where mixed soaps are used the case is not so simple because the first appearance of persistent foam is probably only associated with the presence of excess amounts of the most soluble soap in the mixture. The selective precipita-

tion of the least soluble compound is demonstrated in Figure I. Accordingly, further addition of soap after the end point has been reached will not necessarily result in a corresponding increase in soap concentration of the same composition as the added soap.

Conclusion. While the authors realize that the procedure in this study does not correspond to that generally employed where soaps and builders are added concomitantly to the hard water, we believe that by prior addition of builder to hard water any soap saving would be favored. On this assumption our results suggest that the builders examined are not efficient in preventing the formation of calcium or magnesium soaps when used with the mixed soaps of commerce.

Summary

1. The reactions in mixtures of dilute solutions of builders, pure soaps and hard water have been examined under conditions for optimum foam stability for the soap solution.

2. An attempt has been made to interpret these reactions on the basis of solubility products.

3. For dilute solutions of soaps of pure fatty acids a minimum mole ratio of builder to calcium or magnesium salts is required to prevent the formation of alkaline earth soaps. These mole ratios are different for each soap studied and vary with the particular calcium or magnesium salt and builder combinations.

4. The procedure used by previous investigators of this subject is discussed.

The authors wish to express their appreciation to C. W. Jakob for performing many of the determinations upon which this paper is based.

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Fixed Oils of Mexico*

I. Oil of Chia-Salvia Hispanica¹

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THE topography and climate of Mexico are such as to enable Mexico to produce oils of all classes.

At the present time substantial quantities of sesame, cottonseed, peanut, coconut, linseed, and castor oils are produced, although in most cases production is insufficient to meet domestic requirements. In addition a number of other oil bearing plants native to Mexico could be grown on a commercial scale. Because of the important position of fixed oils in the industrial development of Mexico a concentrated effort is now being made to expand production to meet the increasing domestic demand for oils and to provide an exportable surplus where possible. In order to determine whether any of the now non-industrial oils of Mexico can share in this program the Banco de Mexico has authorized a study of these oils to be carried out as a cooperative research project between the Armour Research Foundation and the Instituto de Quimica of the National University of Mexico.

Chia oil, from the seeds of *Salvia hispanica* L., family Labiatae, has long been recognized as an excellent drying oil. In 1918 Lomanitz (1) obtained a patent on a process to obtain a drying oil from chia and for the use of the press cake as a cattle feed. In 1920 Gardner and Holdt (2) studied the oil and reported that the raw oil dried slowly and tended to form droplets but that heat treatment at 210° C. for

15 minutes resulted in an oil of superior drying characteristics to linseed. Heat treatment does not cause appreciable darkening of the oil and its use in light colored varnishes was suggested. Gardner (3) compared the properties of chia oils obtained by hot and cold pressing in a paper published in 1926, showing only slight differences in the quality of the oils obtained by these methods. In 1937, Gardner (4) and Stewart (5) suggested the use of oil of chia as a substitute for tung oil. Also in 1937, Rulfo (6) reported on the cultivation and production of chia in Mexico.

Baughman and Jamieson (7), Gardner (8), and Steger, van Loon, and Pennekamp (9) have studied the composition of chia oil. Their results are summarized in Table I.

TABLE I
Composition of Chia Oil

| | B. & J. | Gardner | Steger |
|----------------------|---------|---------|--------|
| Saturated Acids..... | 8.2 | 8.1 | 10.6 |
| Oleic Acid..... | 0.8 | 0.7 | —0.8 |
| Linoleic Acid..... | 48.6 | 45.2 | 32.0 |
| Linolenic Acid..... | 42.2 | 39.3 | 56.2 |

The composition of the unsaturated acid fractions were calculated by the Kaufman method using the theoretical thiocyanogen values. Since no record could be found of a study of chia oil using empirical thiocyanogen values, it was deemed of interest to repeat this work.

The chia plant is a rather large shrub, sometimes reaching a height of six feet. The seeds are quite small, approximately 2 mm. long and 1 mm. wide.

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