Alkaline Earth Stearate Emulsions

A Study of Some Properties of Water in Oil Emulsions Formed by Soaps of the Alkaline Earths

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Introduction: It is well known [1;2] that soaps of the alkaline earths give rise to emulsions of water and oil in which the oil is the continuous phase and water the disperse or discontinuous phase.

This investigation was planned in order to study some of the properties of the alkaline earth stearates in relation to their respective positions in the periodic arrangement of the elements according to Mendeleef. At the outset, the authors believed that the properties of the alkaline earth stearates as emulsifiers would show a continuous variation from Mg. to Ba. The investigation was undertaken, therefore, to prove that continuous variations do occur, and to determine what were the amounts of some of these variations.

Theory

All emulsions consist of a disperse phase in a dispersion medium. Various theories [3;4] have been advanced concerning the mechanism by which emulsions come into being, and what factors determine which phase is disperse and which continuous. The character and amount of the peptizing agent, as well as the character and amounts of the two compounds of the system, determine the kind of emulsion which will be produced as well as its properties. The type of emulsion with which we are dealing can be illustrated very well as in Fig. 1.

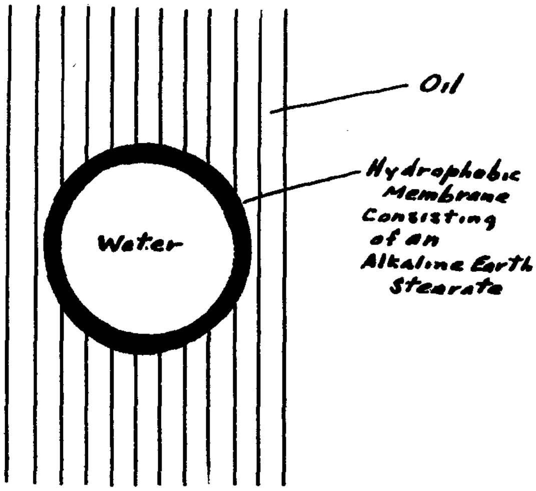

Fig. I

Graphic Structure of Water in Oil Emulsion.

The alkaline earth stearates, being more easily wetted by oil than by water, form the hydrophobic membrane shown in Figure 1. This hydrophobic membrane may consist of discrete particles or of a tough elastic film[5].

Experimental

The emulsions to be described in this paper are of water in a high grade of refined cottonseed oil (Wesson Oil). Cottonseed oil was chosen in order to extend the study of water in oil emulsions to vegetable oils. Wesson Oil was chosen as a typical highly refined and deodorized oil, so that we might make the results of the study as free as possible from the influence of non-fatty materials, such as coloring matter, albuminous material, resinous and mucilaginous matter.

The alkaline earth stearates were all prepared from a large sample of sodium stearate by double decomposition with the pure chlorides of the alkaline earths. The stearic acid from which the sodium soap was prepared was U. S. P. material.

In order to avoid entrainment of sodium soap in our alkaline earth soaps, the sodium stearate was dissolved in water, the solution brought to a boil and solutions of the alkaline earth chlorides added in excess to separate portions of the sodium stearate solution. Each alkaline earth stearate, after a period of sedimentation, was separated by filtration, thoroughly washed with warm water, and completely dried in a hot air bath. All emulsions herein described were prepared by identical methods, and under the same conditions. Each portion of alkaline earth stearate was added at 25°C. to fifty grams of Wesson oil from a freshly opened tin. Each emulsion was prepared in a 400 ml. beaker, under the following procedure: the Wesson oil, to which the desired quantity of alkaline earth stearate had been added, was placed in the beaker, after which fifty millilitres of water at 25°C. was added. The beaker was placed in a definite position under a high-speed agitator of the soda-mixer type, and the system agitated for three minutes as timed by a stop-watch.

A set of five emulsions containing respectively 0.001, 0.002, 0.004, 0.005, and 0.006 gram-molecules of magnesium stearate was prepared by the method above-described, for the purpose of studying the variation of stability in relation to the quantity of peptizing agent. A fifty millilitre portion of each of these emulsions was placed in a 50 ml. Erlenmeyer flask and stored, tightly corked, on the laboratory bench, for observation.

Next a set of four emulsions was prepared, using equimolar quantities of the stearates of calcium, magnesium, strontium and barium. After preparation each emulsion was allowed to stand for exactly fifteen minutes, and its viscosity immediately determined. The emulsions were prepared under constant temperature conditions, so that the viscosity could be measured at the same temperature for each, in order that comparative results could be obtained. The viscosimeter was a simple pipette, which was clamped in a vertical position. The volume between the two working marks of the pipette was 20 ml. The emulsions were drawn into the pipette and the time of outflow between the two marks was recorded.

General Observations

A phase examination[6] by the method of T. R. Briggs showed that each of the emulsions herein described was of the water in oil type. The interface: cottonseed oil—water, was found to be convex toward the water. The soaps with which we dealt were found to concentrate at the interface of the two liquids.

The solubility of the magnesium and strontium stearates in the cottonseed oil used in these experiments were found to be nil at 25°C. Spectroscopic traces of the metals were observed, however, in the oil which had been used for the solubility tests.

It was found that the greater the amount of magnesium stearate used to peptize the water into the oil, the greater was the stability of the emulsion thus formed, (see Table I and Curve I). This variation as measured by the amount of oil found above the emulsion cream after fifteen days has been plotted against the number of gram mols of soap used.

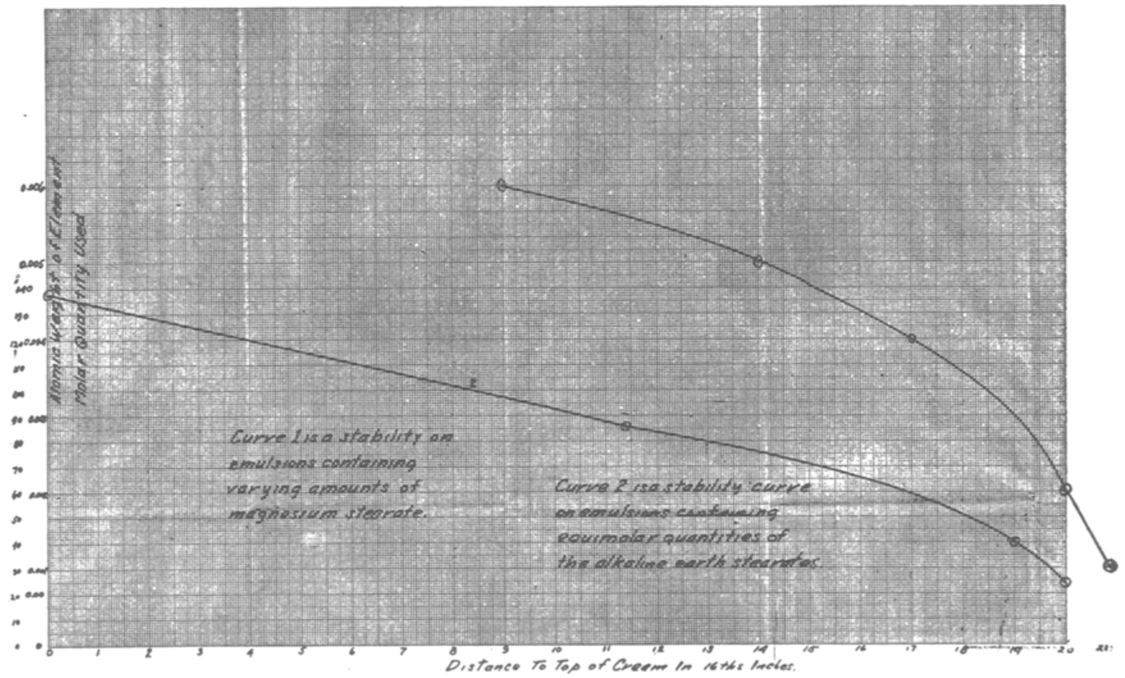

Fig. II
Curves 1 *and* 2.

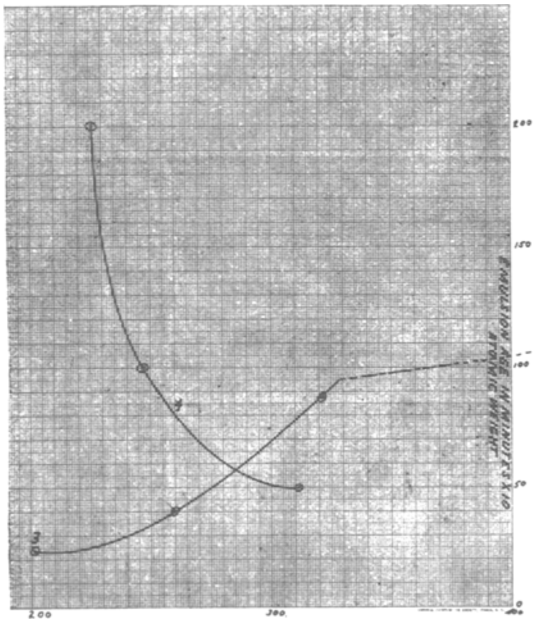

Fig. 3

Curves 3 and 4.

When these emulsions creamed a two layer system was formed. The upper layer consisted of cottonseed oil which apparently contained colloidally dispersed metallic stearate. The lower layer was found to consist of a coarse emulsion of water in oil.

Table I.

Stearate	No. gm. mols.	Distance to top of cream in ins./16
Mg	0.001	21
Mg	0.002	20
Mg	0.004	17
Mg	0.005	14
Mg	0.006	9

Since the curve plotted from this data shows a tendency to flatten out, it appears as if there is a concentration of magnesium stearate above which the stability of the emulsion is not increased by increase of the soap concentration. It is questionable whether or not the emulsion stability will decrease after this point is passed. In other words, will an excess of the peptizing agent cause the drops of water to coalesce?

The emulsions formed by the use of the different alkaline earth stearates showed an increasing relative viscosity in passing downward in the second group of the periodic table.

Table II.

Stearate	Atomic wgt. of metal	Time of flow in seconds
Mg	24.31	201.6
Ca	40.07	259.8
Sr	87.63	321.0
Ba	137.37	5756.0

In curve 3 the above data is plotted using the atomic weights of the metal as abscissae and the times of flow in seconds as ordinates. The curve shows a more or less regular variation for the first three metals, but the barium stearate emulsion was found to have a relative viscosity out of all proportion to the atomic weight of the metal. A possible explanation of this is that the peptizing ability of the barium stearate may become specific. It appears to be much greater than that of the other stearates tested, for the only truly stable emulsion over a period of fiften days, of all prepared in these experiments, was that in which the peptizing agent was the barium stearate.

The stabilities of the emulsions made with the aid of the different alkaline earth stearates were found to vary progressively with the increase in atomic weight of the metal, as illustrated in Table III, following.

Table III.

Stearate	Atomic wgt. of metal	Molar quantity	Distance to top of cream in ins./16
Mg	24.32	0.004	20
Ca	40.07	0.004	19
Sr	87.63	0.004	11
Ba	137.37	0.004	0

It is thus apparent that magnesium and calcium stearates peptize water into water in oil emulsions which are less stable than those formed by the use of strontium and barium stearates. This of course, does not necessarily occur under conditions other than those under which these experiments were conducted.

The varying stability of the emulsions prepared with the different alkaline earths as peptizing agents is shown in Curve 2, in which the atomic weights of the metals are plotted against the distances to the tops of the creams.

Experiments have shown that the relative viscosity of each of at least two of these emulsions varies continuously for a short time after preparation. Some preliminary data has been taken on this point in the case of one emulsion containing strontium stearate. The following Table IV illustrates this point.

Table IV

Temp. °C.	Stearate	Gm. mols. taken for emulsion	Age	Time of Flow
19.5	Sr	0.004	5 min.	311.4 sec.
19.5	Sr	0.004	10 min.	247.2 sec.
19.5	Sr	0.004	20 min.	226.8 sec.

Age of the emulsion here refers to elapsed time from the end of agitation to the time of starting the relative viscosity test. Plotting ages as ordinates against times of flow as abscissae we obtain Curve 4, which appears to be asymptotic to an ordinate. This must be caused by the system not having reached equilibrium at the time the readings were made. In other words, the disintegrating action of the strontium stearate is less than that of the agitator. It is planned to study this point further in the future.

Conclusions

Considering the conditions under which these emulsions were prepared and from the facts brought out about them, we believe, with Bancroft and others, that the peptizing action of these soaps is due to their concentration at the liquid-liquid interface and to the subsequent formation of a tough elastic film of particles of the soap around the drops of water. From the character of the soaps dealt with, it appears to us that the hydrophobic film consists of discrete particles. The variations found in viscosities can be explained upon the assumption that there is difference in the water particle size under the different conditions. The solubility of the soap in the oil can take but little, if any, part in determining the character of these emulsions, for the work was done with concentrations far in excess of the solubilities of the several soaps at the temperatures employed.

References

[1] Newman, J. Phys. Chem., 18, 40(1914).

[2] Bancroft, "Applied Colloid Chemistry."

[3] See Freundlich, "Colloid and Capillary Chemistry," for an extensive list of references.

[4] See Holmes, "Laboratory Manual of Colloid Chemistry" for a concise explanation of several of these theories.

[5] Pickering, Kolloid Zeit. 7, 11(1910).

[6] Newman, J. Phys. Chem. 18, 40(1914).

Committee Hearing on Codliver Oil

During the past week the Ways and Means Committee of the House of Representatives has continued consideration of the arguments for and against increased duties on animal and vegetable oils and related products. The proposal to place a duty of 45 percent ad valorem on codliver oil and cod oil, first made during the hearings on schedule I, came up again during consideration of the free list and was argued at length by domestic producers and by importers. Dr. H. F. Taylor, speaking for the Atlantic Coast Fisheries Company and for the United States Fisheries Association, was the principal speaker in behalf of the 45 percent rate. The discovery of vitamins some three years ago started the cod liver oil industry in this country, he said, describing the American industry as an infant needing protection. With adequate protection, Dr. Taylor said, the American fisheries could produce 20 percent of the domestic demands with the present catch of cod and haddock, and could greatly increase this through development of fisheries in the cod banks of the Pacific and of Alaska. The price of a dose of cod liver oil to the consumer, he said, is largely the same, regardless of wide fluctuation in the wholesale price of the oil, declaring that the proposed duty would not be a burden on consumers. Dan Sutherland, Delegate in Congress from Alaska, also supported the proposed duty on cod liver oil, declaring that it would develop the now untouched cod banks of the North Pacific American waters, which, he said, are more extensive than those of any other nation.

Opposition to a duty on codliver oil was expressed chiefly by James Campbell Lewis, for E. R. Squibb & Sons. Mr. Lewis stated that because of the enormous increase in the demand for cod oil and codliver oil, his company went all over the world and put in extracting plants in every fishing port where enough cod were brought in to make a plant pay, but he is still doubtful that the needs of the United States, which already uses three-fourths of the world's production, can be supplied. Mr. Lewis offered, on behalf of his company, to buy the entire codliver oil output of all who asked the imposition of the duty, and he also expressed willingness to enter negotiations for developing cod fisheries in Alaska as a future supply for oil. He asserted that American producers of codliver oil are now receiving a price 100 percent greater than their production cost. Mr. Lewis was supported in his arguments by C. P. Gulick, for National Oil Products Co., Harrison, New Jersey, who declared that the greatest annual domestic production of codliver oil was only 6 percent of domestic consumption and that the potential capacity of the domestic industry is only 3 percent of the potential domestic demands for poultry feeding alone.

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Final briefs in the linseed oil investigation were filed recently with United States Tariff Commission by John B. Gordon, Bureau of Raw Materials for the American Vegetable Oils and Fats Industries, seeking a reduction in the duty, and by C. T. Nolan, for the domestic linseed crushers, seeking a retention of the present duty of 3.3c on linseed oil.