North America and over 870 species are known to occur in Connecticut. In number of species, the order is exceeded, at least in Connecticut, only by the Coleoptera (beetles) Lepidoptera (butterflies and moths), Hymenoptera (ants, bees and wasps), and possibly by the Diptera (flies).

Obviously, a work contributed by so many workers can not be entirely uniform in treatment. But as a rule the various families are provided with keys to the genera and to the species. The keys are usually followed by brief descriptions of the species with host plants together with records of distribution. While most of the descriptions are clear and concise, they are somewhat brief for present-day purposes. Nevertheless, one must concede something to the limits of time and space, and the high cost of printing paper; and acknowledge that it would be somewhat difficult to crowd more into the 700 odd pages.

Such a publication, of course, has a much wider application than to the state of Connecticut alone. In general, it may be said that this work applies to most of the northern states east of the Mississippi River. The treatment of the family Cercopidae by Stearns covers the entire United States. The treatment of the family Meridae by Knight is a practical revision of the forms from eastern North America. The treatment of the Cicadellidae by DeLong, the Membracidae by Funkhouser, the Psyllidae and Aphididae by Miss Patch, the Aleyrodidae and Coccidae by Britton, the Lygaeidae by Barber and the Pentatomidae by Parshley, seem to be especially full and complete.

Beginning students and others will welcome numerous illustrations, especially the figures illustrating anatomical details of the various families where the nomenclature has not been standardized. The plates of typical Hemiptera, chiefly by B. L. Walden, are beautiful examples of what may be done in illustrating small insects by photography.

An extended use of the keys in several families has revealed no errors save very minor ones, and the whole work shows many unmistakable evidences of careful attention to details. Zoologists who seem to be inclined to ignore taxonomy or to condemn all working systematists might do well to consider carefully such a volume as the Hemiptera of Connecticut, for here we have the joint work of sixteen authors put in such form as to be readily available to any serious student. Here one will find marshalled a vast array of suborders, families, subfamilies, tribes, genera and species in a manner to commend respect.

Students of Hemiptera will owe a debt to Dr. Britton and his collaborators for many years to come for the excellent manner in which they have carried a difficult task to a successful conclusion.

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North Carolina State College

## SPECIAL ARTICLES

### THE ORIENTED WEDGE THEORY OF EMULSIONS AND THE INVERSION OF EMULSIONS[1]

For the formation of an emulsion the presence of an emulsifying agent is essential, except in the case in which the emulsion is very dilute. Of the typical soluble emulsifying agents sodium oleate may be cited as an example. At the interface between water and benzol the surface tension is about 35 dynes per cm. If sodium oleate is added to the aqueous phase to give a concentration of 0.01 normal or more, the interfacial tension is reduced to about two dynes per cm. According to the theory that the molecules in surfaces are oriented in such a way as to give the maximum lowering of surface energy, it is to be expected that the sodium ions, and the $COO^-$ groups to which they are attracted, are turned toward the water, while the hydrocarbon chains are oriented toward the oil (benzol).

If the two phases are now intimately mixed, as by an egg beater at high speed, a concentrated emulsion of benzol in water is formed. While the drops of benzol have different sizes, about 20 per cent. are found to be close to 1.94 microns in diameter. Each of these drops is, according to the theory, surrounded by a film of oriented molecules of sodium oleate, and this film serves to stabilize the drops. The orientation theory was applied to emulsions in a paper from this laboratory (Harkins, Davies and Clark, *J. Am. Chem. Soc.*, 39, 592–4 and 587 (1917)), and evidence in its favor has recently been obtained by Griffin, who finds the amount of sodium oleate adsorbed at the surface of the drops to correspond to a monomolecular film, within the limits of the experimental error.

It is to be expected that the sodium oleate in the film will ionize to a certain extent, thus leaving a film which consists of some negatively charged oleate ions in addition to the salt. This leads to the idea that the oil drops should be negatively charged, and cataphoresis experiments indicate that their potential is about — 0.060 volts with respect to the aqueous phase when any paraffin oil is emulsified by sodium, potassium or caesium oleate. The charge upon the droplets of oil is undoubtedly of great importance in giving stability to the emulsion.

It is known that sodium oleate is somewhat hydrolyzed in aqueous solution, so some free oleic acid and also some acid oleate (McBain) are present. They may be expected to influence the interfacial tension and also the size of the drops in the emulsion. One

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[1] A paper which gave some of the data of this paper in preliminary form was presented at the Milwaukee meeting of the American Chemical Society, September, 1923.

effect upon surface tension may be illustrated by an experiment carried out in this laboratory by George L. Clark. In order to avoid the complications due to the partly colloid nature of an aqueous solution of sodium oleate a shorter hydrocarbon chain was used, and the surface tension of 0.1 molar sodium nonylate was determined to be 20 dynes per cm, a remarkably low value for an interfacial tension between an aqueous solution and air. Upon the addition of sodium hydroxide to repress the hydrolysis the surface tension rose with extreme rapidity, as is shown in Fig. A. When the sodium hydroxide concentration had reached 0.008 normal the surface tension had risen nearly to 50 dynes per cm, a most remarkable increase. Strangely enough, and presumably by repression of ionization, further addition of sodium hydroxide caused a decrease of surface tension which is linear with the concentration of the base which was added.

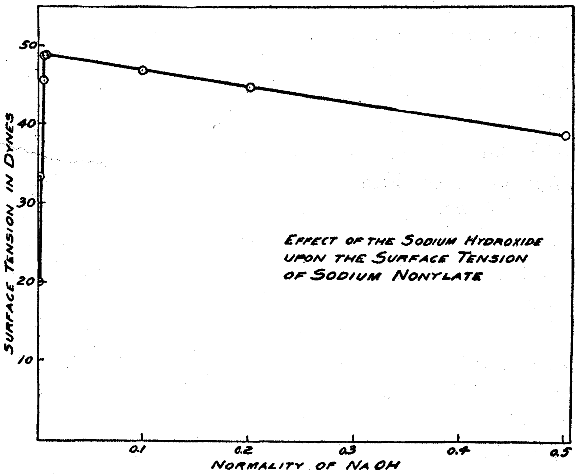

FIG. A

The interfacial tension of dilute aqueous sodium oleate solutions against benzol is greatly *decreased* by the addition of sodium hydroxide and also to a considerable extent by the addition of sodium chloride.

The effect of the addition of such a base upon an emulsion is to decrease the size of the drops of oil, and to lower the P. D. at the oil-water interface to about 0.045 volts.

That the phenomenon of the spreading of oleic acid on water is of importance in connection with a study of the theory of emulsions has been recognized for many years in the work of this laboratory. For example, the lecture notes of George L. Clark for March, 1914, illustrate the change of surface tension which occurs when a film of oleic acid is compressed, and give expression to the fundamental idea of the modern theory of orientation in the short statement: *"COOH of acid down, because both acid and water associated and polar."* The idea that there is some sort of orientation in surfaces was first expressed by Hardy, who, however, made no applications of the idea and did not give the way in which any specific molecule would be oriented, so the above statement is the first record which gives the actual direction of orientation of any specific type of molecule. Hardy (*Proc. Roy. Soc.*, A 86, 634 (1911–12)) says:

> If the stray field of a molecule, that is, of a complex of these atomic systems, be unsymmetrical, the surface layer of fluids and solids, which are closely packed states of matter, must differ from the interior mass in the orientation of the axes of the fields with respect surface of a pure substance having all the molecules oriented in the same way instead of purely in random ways.

The effect of a base upon a film of oleic acid is described by Langmuir (*Chem. and Met. Eng.*, 15, 468 (1916)) as follows:

> If a film of closely packed oleic molecules covers the surface to which sodium hydroxide has been added, OH groups are adsorbed by the COOH radicals, causing an expansion of the lower side of the film without a corresponding expansion of the upper side. This results in the bulging of the film downwards in spots so that it finally detaches itself in the form of particles, the outer surfaces of which consist of COOH groups together with adsorbed OH, while the interior consists of the long hydrocarbon chains.
>
> The size of the colloidal particles is determined by the difference in size betwen the two ends of the molecules, just as the size of the arch is dependent upon the relative sizes of the two ends of the stones of which the arch is constructed.

According to Harkins, Davies and Clark (*loc. cit.*), it is *the shape of the molecule of sodium oleate,* and not that of oleic acid with hydroxyl adsorbed on the COOH group, which determines the curvature of the film around the drop in an emulsion produced by oleic acid with sodium hydroxide added. They explain the inversion of an emulsion to a water in oil type which occurs when the salt of a bivalent metal, such as magnesium, calcium or aluminium, is added

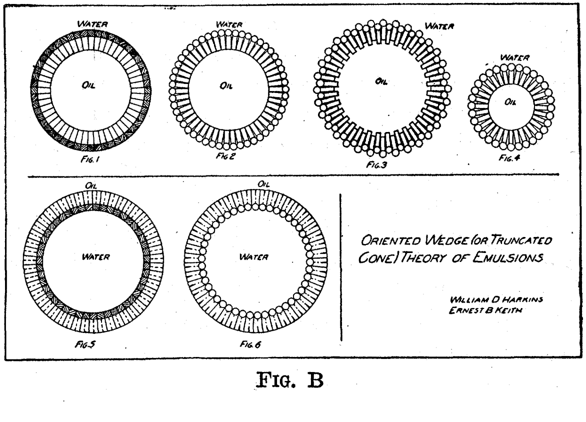

FIG. B

to an oil in water emulsion, as due to the great increase in the cross-section of the oil-like end which results when the soap of a bi- or tri-valent metal is formed. Thus, the cross-section of the two hydrocarbon chains of a magnesium oleate molecule is twice that of the single chain of sodium oleate (or even more on account of motion of the chains). This is illustrated in a highly conventionalized way in Fig. B. Here Figs. 1 and 2 illustrate the oil in water emulsion, which is changed to the water in oil type (Figs. 5 and 6) by the increase in the number of hydrocarbon chains from 1 to 2. Fig. 4 shows how an increase in the size of the polar end of the molecule causes the decrease in the size of the oil drop from that shown in Fig. 2. The size of the drop may be increased by a staggering of the molecules, as in Fig. 3. A more important cause of the increase in size of the oil drops is the penetration of the oil molecules into the spaces between the ends of the hydrocarbon chains.

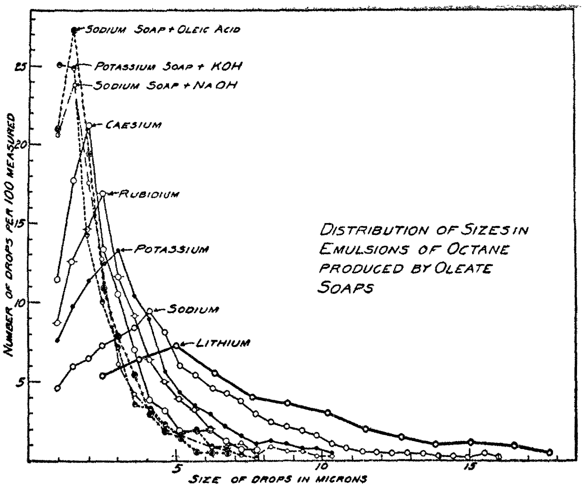

FIG. C

Definite support for the theory of Harkins, Davies and Clark, that *the shape of the molecule of soap is of importance in determining the size of the drop*, is contained in the recent work of Finkle, Draper and Hildebrand. They find that the size of the oil drops decreases as the theory demands, as the size of the water-like end of the soap molecule is increased by changing from a sodium to a potassium, and still further to a caesium soap. However, their work indicates the diameter of the drops to be about $5 \times 10^{-4}$ cm, or 50,000 A. U., as the most frequent size in an emulsion produced by sodium oleate. Now a sodium oleate molecule is probably not longer than $30 \times 10^{-8}$ cm (30 A. U.), or less than one eight hundredth the radius of the drop. Thus, with such fitting as is shown in B, Figs. 1 or 2, the cross-section of the polar end of the sodium oleate molecule could have a diameter not more than 1/800 greater than the homopolar or oil-like end. Now Adam, from his measurements upon films of organic acids, comes to the conclusion that the cross-section of the hydrocarbon chain is 21.0 $A.^2$ U., while that of the carboxyl group is 25.1 $A.^2$ U., and even this latter value would be considerably increased by the addition of sodium. It is therefore evident that the molecule as a truncated cone has a shape such that a close fitting such as that illustrated in Fig. B, 1 to 4, should give a drop about 100 times smaller in diameter than that actually found. Thus the shape of the molecule of soap does not *uniquely* determine the size of the drops, but in spite of this it seems that it is nevertheless one of the most important factors in the determination. As has been stated, there are a number of factors which may result in giving drops much larger than the size predicted by the idea of "close fitting." Among these are the staggering and bending of molecules in the film; the presence of oil between the hydrocarbon chains; the presence of acid or acid salt, and of oleate ions in the film.

If the film at the surface of the drops contains any considerable proportion of oleic acid and oleate ions, then the addition of sodium hydroxide should repress the hydrolysis and the ionization of the sodium soap and give a larger amount of sodium oleate in the film. Whether this is or is not the true explanation, Fig. C shows that the size of the drops is greatly decreased by the addition of sodium hydroxide, and that the same effect occurs when potassium hydroxide is added to the potassium soap. We find:

(1) The size of the drops is highly dependent upon the nature of the oil which is emulsified. Thus the diameter in microns of the drops at the peak of the distribution curves as produced by tenth molar sodium oleate are: 2.03 in benzol and in mesitylene, 4.12 in octane, and 9.2 in stanolax, an oil which contains the higher liquid paraffins.

(2) When any specific oil is used the diameter of the drops decreases as the atom of the metal becomes larger. Thus the sizes for the drops of octane as emulsified by oleate soaps are: lithium 4.60, sodium 4.12, potassium 3.09, rubidium 2.57 and caesium 2.03. In stanolax: sodium 9.2, potassium 6.9, caesium 4.6.

(3) The addition of the corresponding base to a concentration of tenth molar decreases the diameter to 1.54 for the sodium, and to 1.27 for the potassium soap. Thus in the presence of the base the drops grow smaller as the size of the atom of the metal increases.

(4) The addition of oleic acid to the oil to give a concentration of 0.1 molar also increases the dispersion greatly. For the sodium soap this decreases the diameter at the peak from 4.2 for the neutral soap to 1.54. With stanolax the corresponding decrease is from 9.2 to 4.6.

(5) The addition of either sodium chloride or potassium iodide (0.1 M) to the 0.1 molar solution of the sodium soap decreases the surface tension at the interface, and also decreases the size of the drops.

(6) Figure 3 gives the points which correspond to the measurements. It may be seen that the shape of the distribution curve is similar to that of the Maxwell distribution curve of velocities. The sharpness of the peak is due to the method of measurement, since all the drops within a quarter of a micron of a certain diameter are estimated as of that diameter.

(7) The peaks lie almost upon an equilateral hyperbola, which indicates that all the distribution curves are of the same form. Thus, as the drops grow smaller the peaks rise higher. The caesium oleate distribution curve in octane (Fig. C) is almost exactly the same as the curves for sodium oleate in both benzol and mesitylene. The peaks for stanolax lie on the same hyperbola as those in octane in Fig. C. Thus the sodium oleate peak lies at 9.2 microns at a height of 3.7 per cent.

(8) The work of Harkins and W. A. Thomas gives the interfacial tension between water and purified stanolax as 31 dynes per cm. The addition of 0.001 molar oleic acid to the oil and 0.001 molar sodium hydroxide to the water lowers this value to 7.2. The remarkable effect of the addition of sodium chloride (0.15 M) to the solution of the base is to lower the interfacial tension to almost zero, the nearest approximation to the value being about 0.01 to 0.02 dynes per cm. If both this sodium chloride and 0.0015 molar calcium chloride are present in the 0.001 normal sodium hydroxide solution, the interfacial tension is 7.4. Clowes found that calcium and sodium chlorides have such effects, but did not obtain surface tension values.

(9) An interesting result was obtained with a sodium oleate emulsion of heptane. Upon the addition of oleic acid (0.1 M) to the heptane the emulsion was inverted to the water in oil type.

(10) The size of the drops in an emulsion depends upon the method of preparation, so the above results were obtained only because a carefully standardized method was used. Certain factors, among them the shape of the molecular truncated cone, influence greatly the effect of the method of shaking, of stirring and of homogenizing upon the size of the drop.

(11) Preliminary measurements upon the effect of dilution indicate that the drops are slightly larger in a 0.01 than in a 0.1 molar solution of the same soap.

(12) The standard method used in preparing the above emulsions was to stir equal parts of the soap solution and of oil for ten minutes by an electrically driven egg beater, and then to put the emulsion through a Briggs's homogenizer five times. When this method was followed carefully it was found that practically any distribution curve in Figure C could be duplicated almost exactly except for any minor irregularity.

(13) When, however, a high speed drink mixer was used for about one hour it was found that all of the drops became much smaller. Thus the stanolax as emulsified by sodium oleate by the use of the egg beater gave a peak at 9.2 microns, while the use of the drink mixer reduced the peak to 4.12 microns. Strangely enough the curve obtained in this way was an almost exact duplicate of the sodium oleate curve for octane (Fig. C). With octane and sodium oleate the use of the drink mixer gave such a fine emulsion that the drop sizes could not be measured by a microscope. Immediately after an hour of mixing it was found that no drop was larger than a micron in diameter, and the Brownian movement was extremely marked. On standing for four days five per cent. of the drops had increased to two microns or more in diameter, but the peak in the distribution curve was apparently below one micron.

(14) When this high speed mixing was used the difference in drop size corresponding to differences in the size of the atoms of the metal was increased. Thus with a sodium oleate emulsion of stanolax the peak occurred at four microns, while with potassium oleate it came at two microns, a much greater difference than that shown in Fig. C.

(15) Benzol and mesitylene are two liquids of the benzol series with about the same viscosity as octane. In fact one of the two liquids has a slightly higher, and the other a slightly lower viscosity than octane, yet when emulsified by 0.1 M. sodium oleate, and by the use of the egg beater, both benzol and mesitylene gave the same distribution curve, and this proved to be exactly the same curve as that given by a caesium oleate emulsion of octane. Thus, without a change in the viscosity of the oil, the peak shifted from 4 to 2 microns, that is to one half the diameter.

(16) As corresponds with the theory of the oriented molecular wedge in the interfacial film, 0.1 normal ferric oleate produced an *emulsion of water in oil* in which the drops were much smaller (peak at 1.5 microns) than those produced by magnesium oleate of the same concentration (peak at 2.5 microns). The oil used was stanolax, and the distribution curves were practically the same as those for the sodium soap plus sodium hydroxide, and for rubidium oleate, respectively, as given in Fig C. The three oleate chains of a ferric oleate molecule give a greater cross section to the oil-like end than the two chains of magnesium oleate. Of additional interest is the fact that the inversion of these emulsions to the water in oil type has not materially affected the shape of the distribution curves.

The experiments, outlined only in part in this note, lead to a theory of emulsion which is more comprehensive than has been developed heretofore, and this will be presented in connection with a series of papers which will include measurements on cataphoresis, on surface energy and on other factors of importance in this connection.

William D. Harkins,
Ernest B. Keith

University of Chicago

## THE MICHIGAN ACADEMY OF SCIENCE, ARTS AND LETTERS

The twenty-ninth annual meeting of the Michigan Academy of Science, Arts and Letters was held in Ann Arbor, April 2-4, 1924. The presidential address, "Science and letters," was delivered by the president, Campbell Bonner. Dr. H. G. Moulton, director of the Institute of Economics, Washington, D. C., addressed the academy on "The European economic situation."

Besides these papers the following program was presented:

### General Session

*A comparison of the Permian of North America with that of Europe*: E. C. Case.

*Glimpses of recent tendencies in British and French psychology*: W. B. Pillsbury.

### Section of Anthropology

H. H. Bartlett, *vice-president*

*Modes of cousin marriage in India:* T. C. Hodson.

*Greek and Roman stories of children nursed by animals*: Eugene S. McCartney.

*A trephined Indian skull from Devil River, Michigan*: W. B. Hinsdale.

*Prehistoric "forts" of Michigan, with special reference to the Missaukee Preserve*: W. B. Hinsdale.

*Paleolithic (?) implements from Washtenaw County, Michigan*: J. B. Steere.

*Early musical scales*: Chas. K. Wead.

*The East Indian and Philippine alphabets*: H. H. Bartlett.

*Reincarnation and its relation to the cycle of life customs and to social structure*: T. C. Hodson.

### Section of Botany

R. P. Hibbard, *vice-president*

*An annotated list of the higher plants of the region of Douglas Lake, Michigan*: F. C. Gates and J. H. Ehlers.

*An ecological study of Mud Lake, Cheboygan County*: Elsie E. Erickson, Louis E. Goe and Edith Woollett. Presented by J. H. Ehlers.

*Meteorological data, Douglas Lake, Michigan*: F. C. Gates. Presented by J. H. Ehlers.

*Vegetation of the Douglas Lake region*: F. C. Gates. Presented by J. H. Ehlers.

*The ecological structure of the hardwood forests of North America*: H. A. Gleason (by invitation).

*The flora of the peninsula of Virginia:* Eileen W. Erlanson.

*The flowering plants and ferns of Warren Woods, Berrien County, Michigan*: C. Billington.

*Leaf fall in the monsoon forest (illustrated)*: L. A. Kenoyer.

*Supplement to the "Guide to the literature for the identification of Fungi"*: E. A. Bessey.

*The relationships of the Ascomyceteae, Basidiomyceteae, and Telisporeae* (illustrated): E. A. Bessey.

*Notes on selective action of preservatives on mold spores*: Adelia McCrea.

*The Genus Lepiota in the United States*: C. H. Kauffman.

*Formes fraxineus in culture:* Dow V. Baxter.

*The Pythiomorphaceae and a species of the group from Michigan*: Bessie B. Kanouse.

*The perfect stage of the Valsaceae in culture and the hypothesis of sexual strains in this group*: L. E. Wehmeyer.

*The morphological development of Asterosporium hoffmani Kze*: W. A. Archer.

*Morphology of the seed in Phytolacca* (illustrated): E. F. Woodcock.

*The mung bean* (lantern): H. H. M. Bowman.

*Herbaria—useful and otherwise*: E. E. Watson (by invitation).

*Growth and yield of corn as influenced by the date of planting*: D. A. Seeley (by invitation).

*A comparative study of Lauraceous woods*: W. W. Tupper.

*The inheritance of red bud color in crosses of Oenothera pratincola and related forms*: Frieda Cobb Blanchard and H. H. Bartlett.

*The absence of chromosome pairing during meiosis in Oenothera biennis*: Sterling H. Emerson (by invitation).

*Do balanced lethals explain the Oenothera problem?* Sterling H. Emerson (by invitation).

*Genetic factors for yellow endosperm color in maize*: E. G. Anderson.

*X-rays and the frequency of non-disjunction in Drosophila:* E. G. Anderson (by invitation).

*Experiments with the annual variety of sweet clover (Melilotus alba)*: Hugh B. Smith (by invitation).

*An injurious factor affecting the viability of Phaseolus vulgarus, soaked prior to germination*: Paul Tilford, C. F. Abel and R. P. Hibbard.

*Variability in wheat seedlings in water (solution) cultures:* R. P. Hibbard.

*(Joint session with Section of Zoology)*

*Michigan state parks*: P. J. Hoffmaster.

*Douglass Houghton and the Schoolcraft expeditions of 1831 and 1832*: Lois Smith Ehlers.

*The asmotic properties of living cells:* L. J. Heilbrunn.

*The biological sciences in Albion College*: A. M. Chickering.

*The Idaho white pine forest* (illustrated): W. E. Praeger.