

THE ORIENTED WEDGE THEORY OF EMULSIONS

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Introduction.—Dilute emulsions in which two, and possibly even four, per cent of oil is emulsified in water may be formed without the addition of an emulsifying agent, of which a soap may be cited as a typical example. If a soap is added the amount of oil may be increased to ninety-nine times the volume of the water. According to the orientation theory the molecules of soap orient themselves in the interface between oil and water with the hydrocarbon radicle toward the oil, and the $-\text{COO}^- \text{Na}^+$ toward the water. Thus the oil-like or non-polar end turns toward the oil, and the polar end toward the polar liquid. The oriented wedge theory of emulsions indicates that if the non-polar end of the molecule of the emulsifying agent is the smaller, the emulsion will be one of oil in water—or of the ordinary type—while if the polar end is the smaller, the droplets will be of water.

The theory of molecular orientation in surfaces is thus of prime importance in connection with a theory of emulsions. The orientation theory was suggested by Hardy,¹ but his suggestion was in general unnoticed. The theory was developed and different types of evidence for it presented by Harkins and his associates² and by Langmuir.³ Hardy's suggestion was given in the following words:

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.

Langmuir describes the effect of a base upon a monomolecular film of oleic acid on the surface of water.

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 between 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.

The idea that the shape of the molecules in the film determines whether the emulsion shall be one of oil in water or of water in oil was advanced by Harkins, Davies and Clark.

1. The molecules in the surfaces of liquids seem to be oriented, and in such a way

that the least active or least polar groups are oriented toward the vapor phase. The general law for surfaces seems to be as follows: *If we suppose the structure of the surface of a liquid to be at first the same as that of the interior of the liquid, then the actual surface is always formed by the orientation of the least active portion of the molecule toward the vapor phase, AND AT ANY SURFACE OR INTERFACE THE CHANGE WHICH OCCURS IS SUCH AS TO MAKE THE TRANSITION TO THE ADJACENT PHASE LESS ABRUPT.* This last statement expresses a general law, of which the adsorption law is only a special case. If the molecules are monatomic and symmetrical, then the orientation will consist in a displacement of the electromagnetic fields of the atom. This molecular orientation sets up what is commonly called a "double electrical layer" at the surfaces of liquids and also of solids.

This law if applied to special cases indicates for a few pure liquids the following orientation: In water the hydrogen atoms turn toward the vapor phase and the oxygen atoms toward the liquid. With organic paraffin derivatives the CH_3 groups turn outward, and the more active groups, such as NO_2 , CN , COOH , COOM , COOR , NH_2 , NHCH_3 , NCS , COR , CHO , I , OH , or groups which contain N , S , O , I , or double bonds, turn toward the interior of the liquid.

If any of these organic compounds are dissolved in water, their orientation in the water surface is the same as that just given, with the active groups inward.

At interfaces between two pure liquids the molecules turn so that their *like* parts come together in conformity with the general law. With solutions, the solute molecules orient so that the ends of the molecules toward the liquid A are as much like A as possible and the ends toward B are as much like B as possible. So at interfaces between organic liquids and water, for example, the organic radical sets toward the organic liquid and the polar group toward the water.

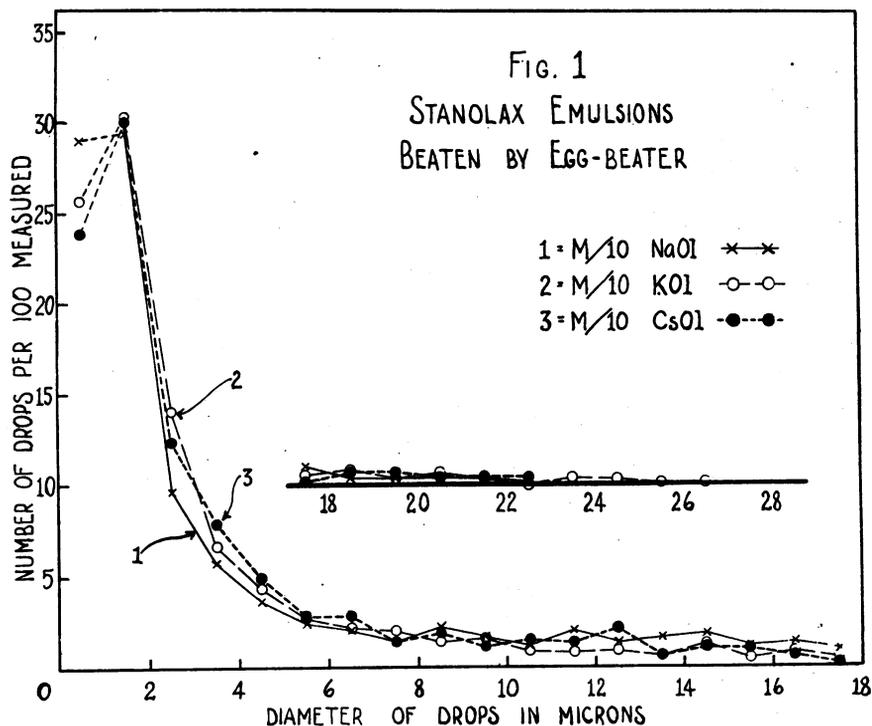
2. If at an interface the transition from a liquid A to the liquid B is made by a saturated film of solute molecules which we may call A-B, that is, they have one end like A and the other like B, then the free surface energy is greatly reduced. For example, with water and benzene with sodium oleate as the solute, the free energy falls as low as 2 ergs per cm^2 .

3. If the solvent is polar, such as water, then solutes will in general be positively adsorbed in the surface if they are less polar than water, and the least polar end of the molecule will be turned outward. Solutes more polar than water are negatively adsorbed.

When Newman, working with Bancroft in 1914, found that while sodium oleate in solution will give emulsions of benzene in water, and the oleate salts of a metal with a valence higher than one will give emulsions of water in benzene, we were working experimentally in this laboratory on the adsorption of these long hydrocarbon chains. Now while Bancroft seemed to think that this work indicated that the liquid with the higher surface tension forms the inner phase, it seemed to us that the only apparent relation was that to the *number of oleate radicals* in the molecule of the protective colloid (sodium oleate, or magnesium oleate). Therefore, it quite possibly may be the orientation and the form of the molecules together with adsorbed ions in the interface between the dispersoid particles (or small drops), and the dispersion medium which determine the surface energy relations, and therefore the size of the drop at which it becomes stable. In other words, this idea is that the drop would be stable whenever the molecules, together with adsorbed ions, etc., in the interface, fit the curvature of the drop. The molecules in the curved surface would not need to be all of the same kind. If the molecules do not fit in the curved surface, the drop will not be perfectly stable and will either decrease or increase in size if given time.

This "oriented wedge theory" of emulsions was, seemingly, given strong support by the experimental results of Finkle, Draper and Hildebrand,⁴

who determined the distribution of the number of drops according to their diameters in solutions of sodium, potassium and caesium palmitate, which were used as emulsifying agents. Thus they kept the negative ion constant, but varied the positive ion and the latter is, presumably, turned toward the outside of the drop, that is, toward the aqueous phase. Now it is known that the *atoms*, sodium, potassium and caesium, increase in diameter in the order given, so if the atoms are effective in the sense of the wedge theory, the outer part of the wedge increases in size in the same order and this would increase the curvature in just this order. Thus the droplets of oil should decrease in diameter as the emulsifying agent is

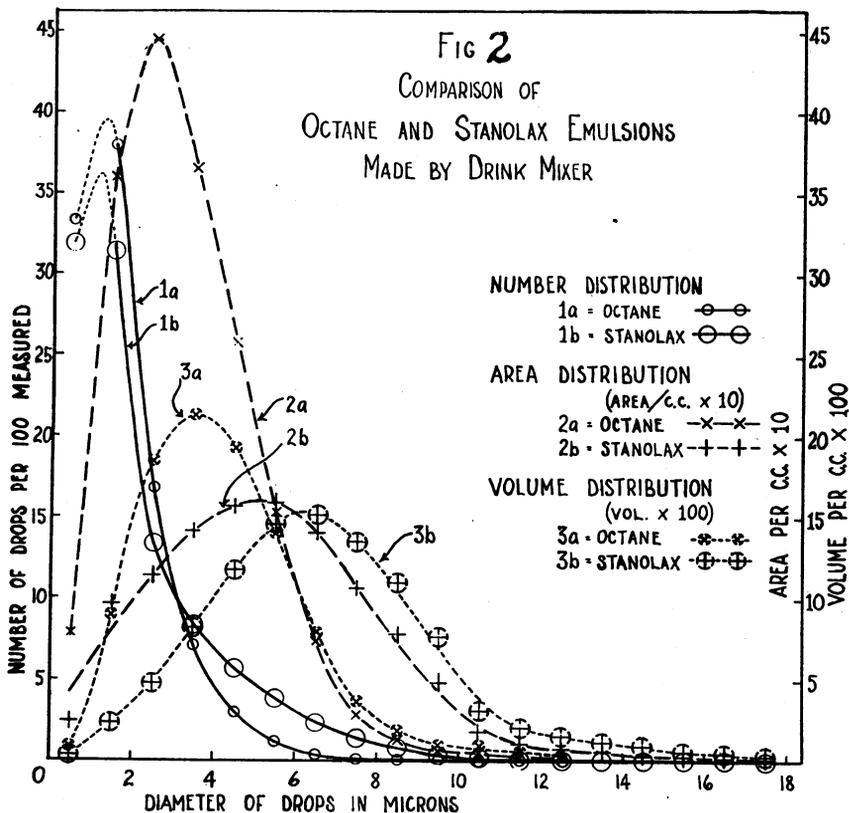


changed from sodium to potassium, and to caesium oleate, and this is just what was found in the experiments of Finkle, Draper and Hildebrand. Preliminary results obtained by Harkins and Keith⁵ also seemed to agree entirely with theirs, but later, upon the more careful elimination of all factors which might cause some type of segregation and the use of a more suitable optical system, the results presented below were obtained.

It is found that the distribution curve is the same, within the limits of error, of the work for sodium, potassium or caesium soaps used as emulsifying agents. Figure 1 illustrates this in a case in which a heavy paraffin

oil was emulsified by oleate (O1) soaps. Each curve represents the measurement of about 800 drops.

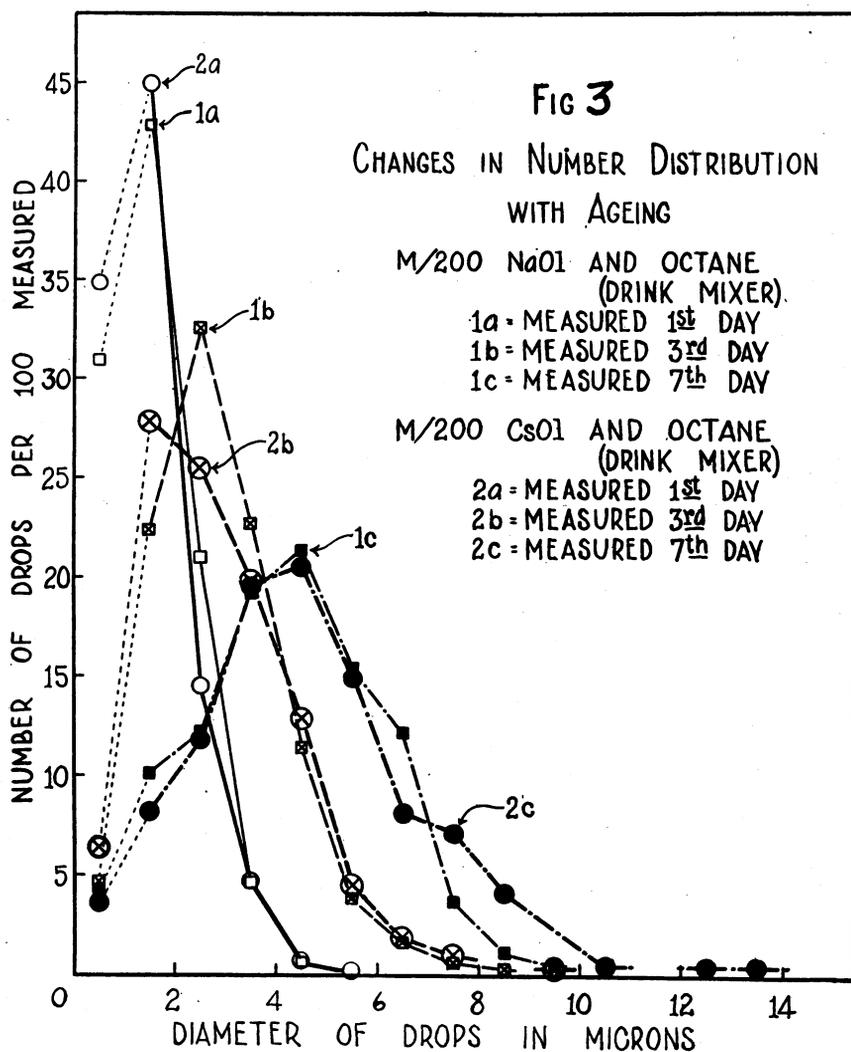
While the greatest number of drops have diameters of about 1.5 microns, so that the peak in the number curve is independent both of the positive alkali ion of the soap and also of the oil, there are many more large drops if a viscous oil like stanolax is used than are found with a very fluid oil like octane. Figure 2 shows the number, area and volume distributions for emulsions of octane and of stanolax, respectively. In order to obtain



smooth curves about ten thousand drops were measured with each oil. It is apparent that while the peak in the number distribution curve falls at 1.5 microns with either oil, that for the area and volume distributions lies in each case in a larger size and is also lower for the more viscous oil.

The use of magnesium or aluminium oleates, that is, of oleates of bi- or trivalent metals gave water in oil emulsions, as is well known. What is of interest is that the number distribution curve was practically the same as that found for the oil in water emulsions, and the curves of figure 1 serve

well to represent the results in such a case. The same result was obtained when an oil in water emulsion produced by the use of a soap of a univalent metal is inverted to the type water in oil by the addition of a salt of a bi- or trivalent metal.



A water in oil emulsion was produced by dissolving a large amount of soap in the oil and beating this up with water. This inverted to the ordinary oil in water type on the addition of more water.

The method of mixing has an effect upon the distribution. Thus when

emulsions produced by a high speed drink mixer were compared with those made by a motor driven egg beater, it was found that while the curves had the same form for the smaller sizes the size of the largest drop found was much less for the former than with the latter. In general, the number of large drops decreases with the time of stirring, rapidly at first and more slowly later.

A new method of determining the stability of an emulsion was tried. This consisted of determining the distribution curve on different days, that is, the change of distribution with time. As an example of the results it was found that in the case of an emulsion produced by tenth molal soap that months of standing did not change the curve. On the other hand the curve changed rapidly if the soap was one two-hundredth molal, as is exhibited by figure 3, which gives the curves for the first, third and seventh days.

Discussion.—These results give no proof for nor against the oriented wedge theory, they only indicate that some of the evidence which has seemed to support it is not valid. Soaps are salts and according to recent theories salts are completely ionized in aqueous solutions. If this is true it is hardly to be expected that the shape of the molecule should have an effect upon the shape of the drop unless almost all of the metal ions are held by the electrostatic forces close to the respective negative ions in the film.

Furthermore the diameter of the greatest number of drops is 1.5 microns, or 15,000 Angstrom units. A sodium oleate molecule is probably about 30\AA long, so the radius of the drop is 250 times greater than the thickness of a monomolecular film of soap.

It would be remarkable if such a molecule should uniquely determine the size of so large a drop.

What is needed to test the theory is to use emulsifying agents with molecules in which the polar end is larger and also those whose non-polar end is larger. With bi- or trivalent metals, even although the salt may be considered as ionized, the number of negative ions attached electrostatically somewhat closely to the metal is on the average considerably higher than if the metal is univalent. Thus this has an effect which corresponds to an increase in the non-polar or oil-like end of the molecule, which is in the direction indicated by the theory for a change to the water in oil type of emulsion, as is found experimentally. This is the evidence for the theory cited by Harkins, Davies and Clark.

The effect was tested of potassium chaulmoograte, in which the negative ion has a slightly different shape from the oleate, palmitate and stearate ions used earlier in this work. This emulsifying agent gave many more small drops than any of the others used.

¹ Hardy, *Proc. Roy. Soc.*, **86A**, 634 (1912); **88A**, 303-333 (1913).

² Harkins, Brown and Davies, *J. Amer. Chem. Soc.*, **39**, 354-64 (1917); Harkins, Davies and Clark, *Ibid.* 541-96, and later papers.

³ Langmuir, *Chem. Met. Eng.*, **15**, 468 (1916); *J. Amer. Chem. Soc.*, **39**, 1848 (1917).

⁴ Finkle, Draper and Hildebrand, *J. Amer. Chem. Soc.*, **45**, 2780 (1923).

⁵ Harkins and Keith, *Science*, **59**, 463-7 (1924).

POLYMOLECULAR AND MONOMOLECULAR FILMS

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The work of Harkins and Feldman¹ indicates that pure liquids may spread upon water to give films which are thicker than one molecule, and the writers have been able to find these films with such characteristics that accurate measurements may, and have been made of the variation of the force of compression with a change in area. Lord Rayleigh,² Devaux,³ Marcelin,⁴ Langmuir,⁵ Harkins and King,⁶ Adam,⁷ Harkins and Grafton⁸ and Harkins and McLaughlin⁹ have made measurements upon monomolecular films.

Monomolecular Films.—The thickness of monomolecular films has not been measured, but a "mean" thickness has been calculated from the molecular area. The water film on an aqueous salt solution is thus found to be 4×10^{-8} cm. (4Å) thick for a tenth molal, and 2.4Å for a 5 molal concentration. Langmuir has found that a film of palmitic acid is 25, and of myricyl alcohol, 41Å thick. The molecules of this alcohol are very long, and contain a chain of 30 carbon atoms.

Phenanthrol (Fig. 1), with a polar hydroxyl group in each molecule when spread on an aqueous solution of calcium chloride, exhibits the characteristics of a monomolecular film. This substance and phenyl dibiphenyl methyl amine form films which are thinner than any others which have been measured directly. Both of these films were spread on a concentrated aqueous solution of calcium chloride. As the phenanthrol film is compressed, no force of compression is apparent until the area per molecule is decreased to 36.5×10^{-16} sq. cm. (36.5 A.U.). On further compression the increase of compressive force is linear to the molecular area up to 32 dynes per cm. and 21.5 A.U. molecular area. From this on the increase is again linear, but with a much steeper slope; that is, the film has become stronger. When the force reaches 44 dynes per cm. the film collapses and the force rises only very slightly higher as the film is still further compressed. The mean thickness of the film is 7Å at the point where the force first becomes apparent and 12Å at collapse. The next row in the