Some typical results obtained by the colorimetric method are given in Table VIII.

The results of Table VIII are seen to be entirely satisfactory except in the instance in which an attempt was made to compare the depths of color of a tube containing 5 mg. of sodium with a standard tube containing 4 mg. More experience with the method will undoubtedly remove such discrepancies.

Summary

1. A method for the direct determination of sodium by precipitating it as magnesium sodium uranyl acetate has been presented.

2. Both gravimetric and colorimetric measurements have been used.

COLUMBUS, OHIO

[CONTRIBUTION FROM THE KENT CHEMICAL LABORATORY OF THE UNIVERSITY OF CHICAGO]

EMULSIONS: STABILITY, AREA PER MOLECULE IN THE INTERFACIAL FILM, DISTRIBUTION OF SIZES AND THE ORIENTED WEDGE THEORY[1]

BY WILLIAM D. HARKINS AND NORVIL BEEMAN

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1. Introduction

When this work was begun no accurate determination had been made of the distribution of sizes of the droplets in emulsions. If such determinations could be made they would give a basis for a decision with respect to three of the most important fundamental problems of this branch of colloid science. These are: (1) the number of molecules of the emulsifying agent per unit area of the oil-water interface, (2) the stability of emulsions and the effect of aging and (3) the oriented wedge theory of emulsions.

While the requirements of the last two problems might be met by large-scale methods, the demands of the first problem seemed to necessitate the use of a fine-scale, or microscopic method, since with large-scale methods there is considerable uncertainty in the theory which is used to translate the scattering of light or the speed of sedimentation into the sizes of the drops.

2. Experimental Methods

1. Apparatus

1. **Microscopic Equipment.**—An image of the highly diluted emulsion was projected on a screen by the use of a microscope fitted with a 61x, 3-mm. apochromatic oil immersion objective, 1.40 N.A.; an aplanatic condenser 12-mm., 1.40 N.A.; and a 25x, compensating ocular.

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[1] A preliminary version of this article was received August 31, 1925.

2. **The Cell.**—An important part of the equipment was the microscope slide, which was made of thin glass and contained a cell of 4-mm. diameter with a depth of 0.10 mm. which was covered by a thin cover glass. The bottom of this cell was ruled in squares and it was surrounded by a circular depression 0.5 mm. deep and 3 mm. wide. Two small grooves leading from this depression allow any excess of solution to flow away when the cover glass is put in place. The use of a drop of the emulsion suspended from the bottom of a cover glass gives poor results since the surface forces cause a considerable segregation of the droplets according to their sizes.

2. Preparation of Emulsions

1. **Materials.** Oils.—The octane was the synthetic substance obtained from the Eastman Laboratories, Rochester, N. Y. The "Stanolax" was a heavy paraffin oil sold by the Standard Oil Company of Indiana. Kahlbaum's benzol, thiophene-free, was also used.

Water.—The water used for making the emulsions and for cleaning the slide and cover glasses was distilled water examined periodically to assure freedom from suspended particles of microscopic size.

Soaps.—The oleate soaps were made from oleic acid, U. S. P., after extensive purification by both the lead salt and barium salt treatments[2] and finally by a vacuum distillation.

The sodium and potassium oleates were made by dissolving the solid alkali metal in absolute alcohol, filtering to remove any carbonate, adding oleic acid and evaporating to dryness. The residue was then dissolved in absolute alcohol and refluxed for a half hour. (The amount of oleic acid was arbitrarily determined according to the method used by Laing[3] in which the acid was added until the alcoholic solution after dilution with a recently boiled mixture of alcohol and water (3:1) was found by repeated tests to give a neutral reaction with neutral alcoholic solution of phenolphthalein.) The hot solution was now filtered through a hot-water funnel and the soap allowed to crystallize out. It was then drained, washed with absolute alcohol and ether and dried.

For the cesium oleate, cesium nitrate was converted into cesium carbonate by fusion with oxalic acid. An excess of the carbonate was dissolved in a small volume of water, the oleic acid dissolved in 95% alcohol, the two solutions were mixed and evaporated to dryness. The residue was dissolved in absolute alcohol, the exact amount of oleic acid being determined as before. The solution was filtered and again evaporated to dryness. After redissolving in absolute alcohol the procedure was the same as for sodium and potassium oleates. Cesium oleate is a fairly "soft" soap and does not crystallize out readily even in the cold.

The stearates and other soaps were made in much the same manner. Kahlbaum's best stearic acid was used for the stearate soaps. The chaulmoogric acid was obtained from Professor B. H. Nicolet and was a sample sent to this Laboratory for research purposes in connection with the chaulmoogra oil treatment for leprosy. The elaidic acid was purified by Mr. T. C. Poulter in this Laboratory.

Aluminum and magnesium oleates were made by the precipitation of these oleates from sodium oleate solutions followed by purification by recrystallization from absolute alcohol.

Through the kindness of Professor J. H. Hildebrand samples of the sodium and cesium stearates formerly used in work with emulsions at the University of California were also tried.

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[2] Vanino, "Präparative Chemie," Vol. II, p. 120; Lewkowitsch, "Chemical Technology," **1909**, Vol. I, p. 140.

[3] Mary E. Laing, *J. Chem. Soc.*, **119**, 1669 (1921).

2. **Procedure.**—The general method followed for oil in water emulsions was to make a fresh soap solution of the concentration desired, add an equal quantity of oil and then beat or stir to form the emulsion. The beating was done by a motor-driven egg beater, the stirring by an Arnold drink mixer. For the former 7 to 10 cc. of soap solution and an equal volume of oil were most convenient; for the latter 5 cc. or more of each phase was put in a large flat-bottomed test-tube. The time of beating and stirring was varied according to purpose but more commonly emulsions were given twenty minutes' beating by the egg beater or, if stirring was the method, ten minutes' stirring with the drink mixer. A Briggs' homogenizer was used, except in special cases, and the emulsion after beating or stirring was drawn through about five times by suction. The homogenizer was especially of service in removing air bubbles formed during beating. *Unstable emulsions were easily broken by homogenization* and this treatment was omitted in such cases, the air bubbles if found present being removed by subjecting the emulsion to a vacuum treatment.

There seems to be a definite relation between foaming and efficiency of emulsification. This applies particularly to emulsification with dilute soaps. It was noticed that emulsions which did not foam up during the beating—and this was rather characteristic of emulsions made with very dilute soaps—separated more readily than those which did foam, though some very stable emulsions were made which did not foam. It was a common practice in such cases to beat the soap solution to a foam and then add the oil in a thin stream or in portions while beating.

3. **Method of Sampling.**—The emulsion—cream, aqueous phase and all—was mixed by running it back and forth from end to end of the test-tube which contained it. Care was taken to prevent formation of foam during this mixing. From this thoroughly mixed emulsion 3 or 4 drops were pipetted out and diluted in microscopically clear distilled water. The degree of dilution depended upon the emulsion, varying from 1 drop in 300 cc. of water in some octane emulsions, in which the particles were very small and more numerous, to 8 or 9 drops in 300 cc. of water for some Stanolax emulsions, in which the drops were much larger and less numerous. Immediately after dilution the sample was pipetted out, placed upon the slide and covered with a cover glass. Oil contacts between condenser and slide and between cover glass and objective were made with Stanolax since it was more easily cleaned off and does not harden after exposure to the air as cedar oil does.

4. **Cleaning the Slide and Cover Glass.**—The slide and cover glass must be thoroughly clean if good results are to be obtained. Sticking of drops to the cover glass was avoided entirely by the following method. The slide and cover glass were washed in soap solution. Just before use the cover glass and slide were removed from the soap solution and rinsed well with clear, distilled water. This rinse water was shaken off and the sample placed between the *wet* slide and a *wet* cover glass. For water in oil emulsions the slide and cover glass were cleaned as before, dried with alcohol and ether, and then dipped into some of the same oil as that of the continuous phase of the emulsion to be examined.

5. **Measuring the Drops.**—The sample was diluted so that there were about 10 or 12 drops in the field at one time. Measurements were taken upon every drop from the bottom of the cell to the cover glass in a strip across the cell from one edge to the other. This strip was definitely determined by lines drawn in a horizontal direction across the scale on the screen.

The smallest drops up to 1 micron in diameter were recorded and plotted as 0.5 micron, from 1 to 2 as 1.5 micron, from 2 to 3 as 2.5 microns, etc.

Exact measurements upon moving spheres of varied sizes are difficult because the sizes seem to change with the change of focus of the microscope, intensity of illumination, direction of the beam of light, condition of the eyes with respect to presence or absence of fatigue, etc. For this reason a finer scale was not used in the classification.

3. Effects of Various Monovalent Cations on the Distribution of Sizes

The distribution of sizes (diameters) of the oil droplets in emulsions produced by oleate soaps is found to be exactly the same, within the experimental limits of accuracy, for any of the three univalent cations, lithium, sodium and cesium. This is shown to be true in emulsions of a very viscous paraffin oil (Fig. 1) and in those in which the oil is extremely fluid, such as octane or hexane (Figs. 2 and 3). According to the method used in plotting, each point gives the number of drops per 100 counted of the size designated. Thus the maximum number found in these figures occurs at 1.5 microns, and for emulsions of Stanolax the number for this size is 30. That is, in the Stanolax emulsion 30% of the droplets have diameters between 1 and 2 microns.

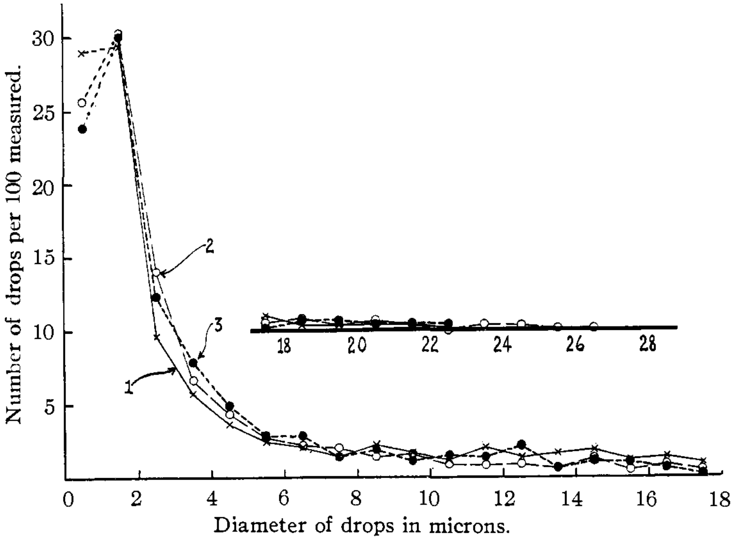

Fig. 1.—Stanolax emulsions beaten by egg beater. 1, $M/10$ sodium oleate, X—X—X; 2, $M/10$ potassium oleate, O--O--O; 3, $M/10$ cesium oleate, ●---●···●.

A forced variation from this general procedure occurs for the points at 0.5 micron, which represent the number of droplets between 1μ as the upper limit and about 0.1μ (the limit of visibility) as the lower limit. Obviously if ultramicroscopic droplets were counted, the number represented at 0.5μ would be greater, but it is improbable that the distribution of area of the interface is greatly affected by this omission.

The results described above have a bearing upon the extent of application of the oriented wedge theory. Langmuir considered that the form of colloidal particles of oleic acid is determined by the *adsorption of hydroxyl* groups: "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 downward in spots so that it finally detaches itself in the form of particles, the outer surfaces of which consists 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."[4]

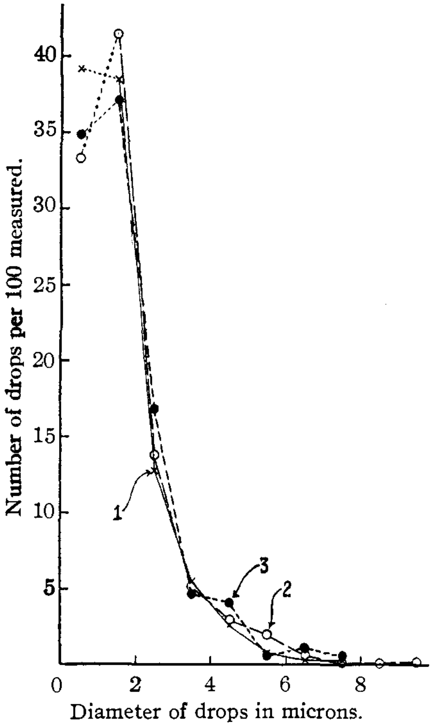

Fig. 2.—Octane emulsions beaten by egg beater: 1, $M/10$ sodium oleate, X—X—X; 2, $M/10$ cesium oleate, O—O—O; 3, $M/10$ cesium oleate, ●—●—●. Curves 2 and 3 show the effect of aging an emulsion produced by 0.1 molal cesium oleate. Curve 2 was obtained on the day of preparation and Curve 3 one month later.

The idea that the number of hydrocarbon groups associated with one ion of a metal determines whether the emulsion shall be one of oil in water (univalent cation) or of water in oil (polyvalent cation) was advanced by Harkins, Davies and Clark,[5] as shown in the following quotation.

"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 seem 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*

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[4] Langmuir, *Chem. Met. Eng.*, **15**, 468 (1916); THIS JOURNAL, **39**, 1848 (1917).

[5] Harkins, Brown and Davies, *ibid.*, **39**, 354–364 (1917); Harkins, Davies and Clark, *ibid.*, **39**, 541–596 (1917); and later papers.

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. . . . .

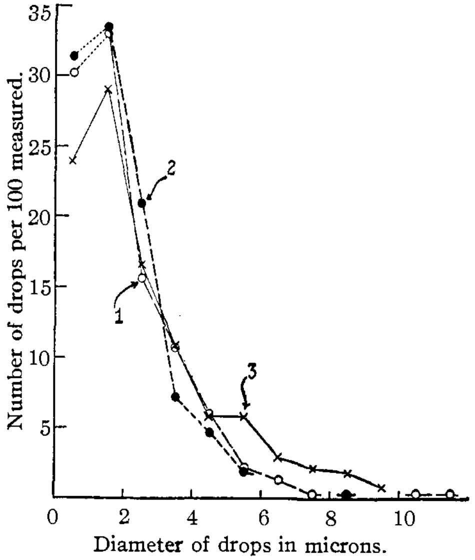

Fig. 3.—Octane emulsions stirred by drink mixer: 1, $M/200$ sodium stearate, ○--○--○; 2, $M/200$ cesium stearate, ●—●—●. Stanolax emulsion beaten by egg beater and inverted: 3, $M/10$ sodium oleate, ×—×—×, after inversion with aluminum nitrate. Curve 3 represents a water in oil emulsion.

"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,[6] who determined the distribution of the number of drops according to their diameters in solutions of sodium, potassium and cesium palmitate, which were used as emulsifying agents. Thus they kept the negative ion constant but varied the positive ion. 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 cesium, 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 cesium oleate, and this is just what was found in the experiments of Finkle, Draper and Hildebrand. Preliminary results obtained by Harkins and Keith[7] 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 result presented above was obtained.

However, there is another more proper point of view according to which *the oriented wedge theory does not indicate any such decrease in size of the droplets in the change from sodium to cesium.* The negative oleate ions are adsorbed at the oil–water interface with the hydrocarbon radical toward the oil and the $-COO^-$ group toward the water. The Na^+ or Cs^+ ions are held to these by electrostatic attractions alone, so the alkali ions form a diffuse but extremely thin positively charged layer, in which the distribution may follow the Boltzmann *e*-theorem. A part of the soap in the film is present as oleic acid formed by hydrolysis. From this point of view it seems improbable that the sizes of the atoms will produce any marked influence upon the sizes of the droplets. It is known too that the smaller the alkali atom, the more highly hydrated is its ion.

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[6] Finkle, Draper and Hildebrand, THIS JOURNAL, **45**, 2780 (1923).

[7] Harkins and Keith, *Science*, **59**, 463–467 (1924).

When, on the other hand, the ion of the metal is bi- or tri-valent, the electrostatic relations are such that in general two $RCOO^-$ ions are held by only one M^{++} ion. Such conditions are favorable to the expansion of that side of the film which is turned toward the oil by the spreading of the hydrocarbon chains. Thus the addition of aluminum nitrate to an emulsion produced by sodium oleate inverts the emulsion and changes it to the water in oil type.

It was found by Harkins and Keith that when a drop of the emulsion is suspended from a cover glass, there is a segregation of the microscopic droplets in the emulsion according to their sizes. This makes it extremely difficult to obtain a correct determination of the distribution of sizes, and is undoubtedly the cause of the discrepancy between the earlier work and that presented here.

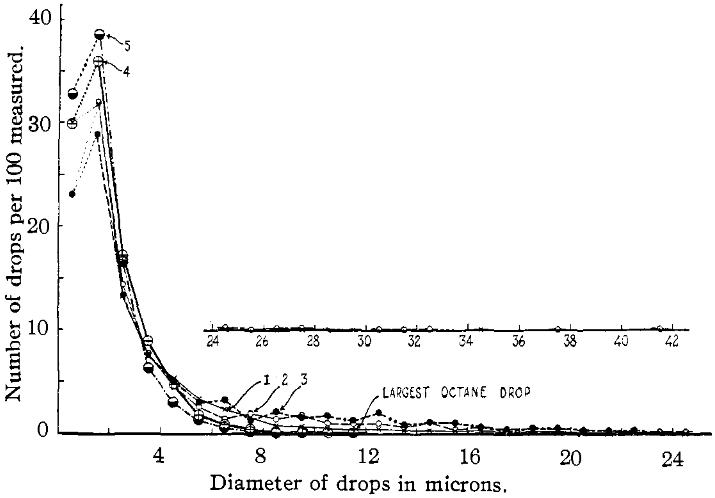

Fig. 4.—Distribution of diameters in emulsions of octane and Stanolax stabilized by sodium, potassium and cesium oleates. Stanolax emulsions: 1, sodium soaps, ×—×—×; 2, potassium soaps, ○--○--○; 3, cesium soaps, ●--●--●. Octane emulsions: 4, sodium soaps, ⊕—⊕—⊕; 5, cesium soaps, ⊖-·-⊖-·-⊖.

4. Influence of the Viscosity of the Oil

Although the viscous paraffin oil (Stanolax) had a viscosity more than 150 times that of the octane, it is remarkable that with either oil the greatest number of droplets occurs between 1 and 2μ, that is, the peak in the distribution according to diameters occurs at the same place for either oil. The marked difference illustrated by Fig 4 is that of the larger drops. Thus the *largest* of the 5668 octane droplets represented by this figure had a diameter of about 10.5μ, while the diameters of those of Stanolax were as great as 41.5μ, or nearly four times as great. The effect of the viscosity of the oil is exhibited by Tables IA and IB, and by Figs. 4 and 5. Fig. 5 illustrates a Stanolax emulsion produced by 0.1 *M* sodium oleate.

TABLE IA (SEE FIG. 6)

COMBINED OCTANE EMULSIONS MADE BY DRINK MIXER BUT DISREGARDING THE KIND OF SOAP (0.1 *M* AQUEOUS SOLUTIONS)

Mean diam.	Actual no. of drops	%	No. as taken from smoothed curve	1a % as taken from smoothed curve	2a Sq. cm. of area per cc. of oil $\times 10^{-3}$	3a Volume per cc. of oil, cc.
0.5	806	33.31	806	33.306	0.791	0.0099
1.5	918	37.93	918	37.934	3.605	.0901
2.5	408	16.86	408	16.859	4.452	.1855
3.5	171	7.07	171	7.066	3.656	.2133
4.5	73	3.02	73	3.016	2.580	.1935
5.5	29	1.20	29	1.198	1.531	.1404
6.5	10	0.41	10	0.413	0.737	.0799
7.5	2	.08	2.97	.123	.292	.0364
8.5	1	.04	1.08	.045	.136	.0193
9.5	0	.00	0.41	.017	.065	.0102
10.5	1	.04	.31	.013	.060	.0104
11.5	1	.04	.16	.007	.037	.0071
12.5	0	.00	.07	.003	.019	.0040
	2420	100.00	2420.00	100.000	17.961	1.0000

TABLE IB

COMBINED STANOLAX EMULSIONS MADE BY DRINK MIXER BUT DISREGARDING THE KIND OF SOAP (0.1 *M* AQUEOUS SOLUTIONS)

Mean diam.	Actual no. of drops	%	No. as taken from smoothed curve	1b % as taken from smoothed curve	2b Sq. cm. of area per cc. of oil $\times 10^{-3}$	3b Volume per cc. of oil, cc.
0.5	1283	31.923	1283	31.920	0.245	0.0031
1.5	1266	31.500	1266	31.500	0.969	.0242
2.5	538	13.386	538	13.380	1.144	.0476
3.5	314	7.813	337.6	8.400	1.407	.0821
4.5	242	6.021	227.5	5.660	1.567	.1175
5.5	165	4.105	154.7	3.850	1.592	.1459
6.5	98	2.438	97.6	2.430	1.403	.1520
7.5	68	1.692	56.3	1.400	1.077	.1347
8.5	18	0.448	31.7	0.790	0.779	.1104
9.5	16	.398	15.8	.395	.485	.0768
10.5	4	.100	4.9	.123	.184	.0322
11.5	1	.025	2.4	.062	.108	.0207
12.5	4	.100	1.4	.035	.074	.0165
13.5	0	.000	0.9	.023	.056	.0125
14.5	0	.000	.6	.014	.043	.0104
15.5	1	.025	.3	.009	.025	.0063
16.5	1	.025	.2	.005	.019	.0051
17.5	0	.000	.1	.003	.010	.0030
	4019	99.999	4019.0	99.999	11.187	1.0000

The most regular results are given by emulsions prepared by the drink mixer (Fig. 6).

5. Influence of the Concentration of the Soap

No appreciable influence of change in soap concentration upon the distribution of diameters in *freshly made* emulsions was discovered. Isolated cases here and there might suggest such a relation but on the whole no positive conclusions could be drawn. With emulsions permanent enough to measure, the difference in soap concentration produced little or no detectable effect. On the other hand, as the emulsions aged, a decided effect was observed in the cases of dilute emulsions. This effect is discussed in the next paragraph.

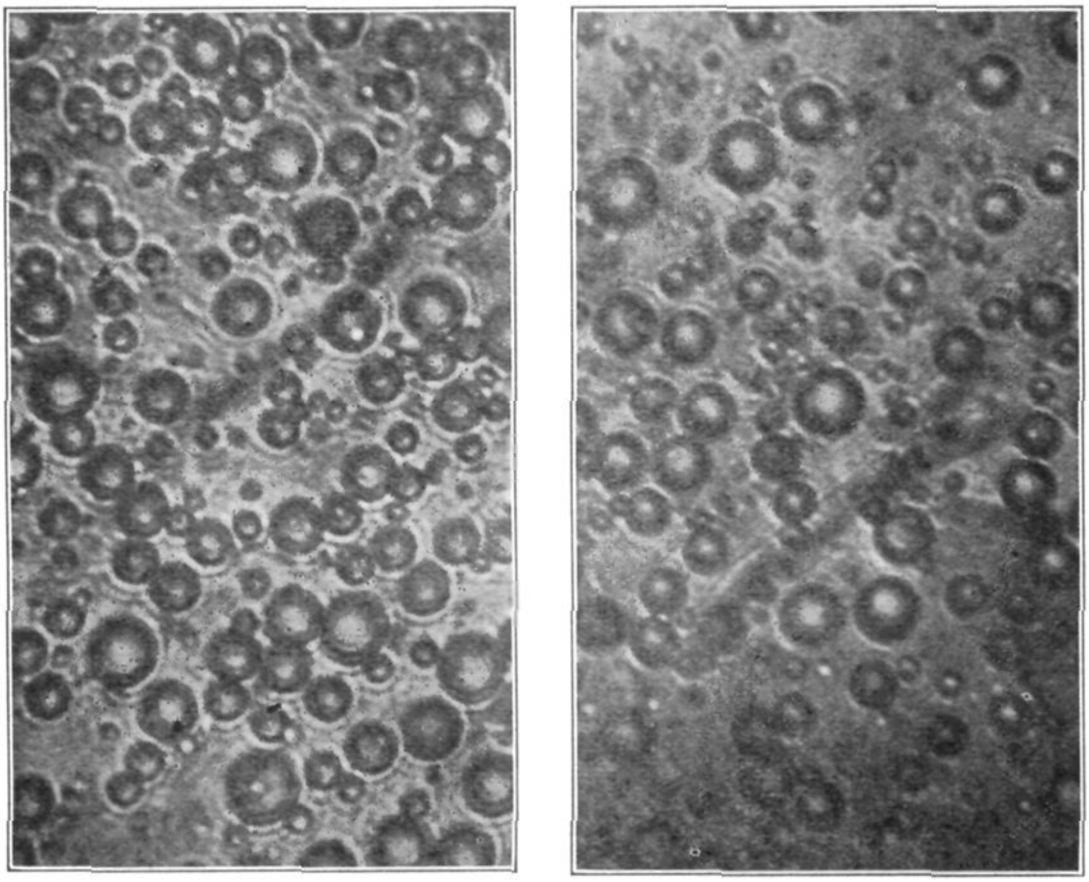

Fig. 5.—Stanolax emulsion (× 1000). Diluted 100 times. The emulsifying agent was 0.1 *M* sodium oleate. (Taken by R. S. Dean.)

6. Stability: Effect of Aging

The stability of certain emulsions has been ascertained by a determination of the variation of the distribution of sizes (diameters, areas and volumes) with the time. It is evident that this gives much information concerning the stability not indicated at all by the older method of merely observing the gross features of the emulsion such as the separation of oil in bulk (Tables II and III).

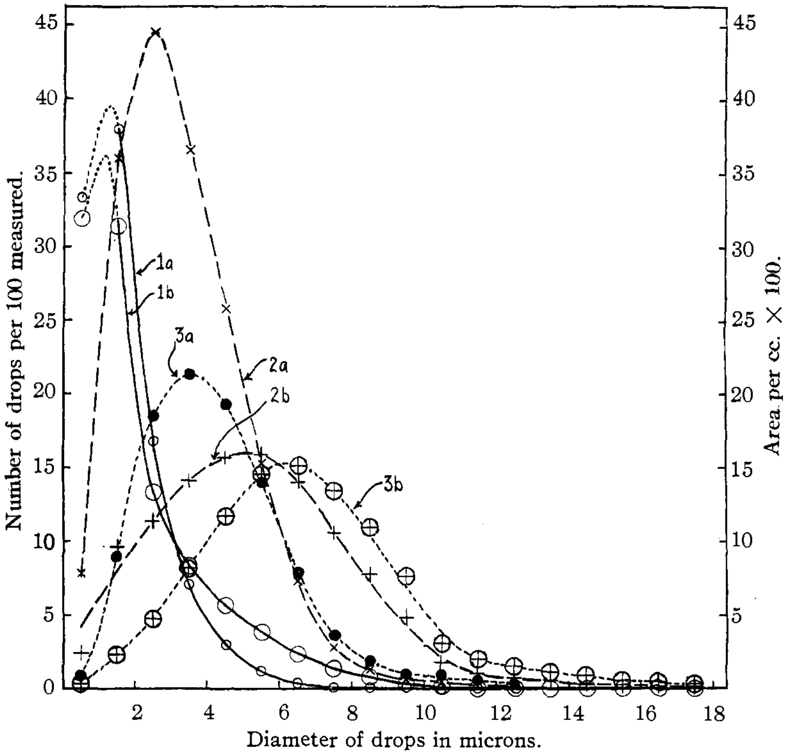

Fig. 6.—This figure represents measurements on about 2500 droplets of octane and 4000 of Stanolax, numbers so large as to give smooth curves. Comparison of octane and Stanolax emulsions made by drink mixer. Diameter distribution: 1a, octane, o—o—o; 1b, Stanolax, ○—○—○. Area distribution (area/cc. × 10): 2a, octane, ×—×—×; 2b, Stanolax, +—+—+. Volume distribution (vol. × 100): 3a, octane, ●--●--●; 3b, Stanolax, ⊕--⊕--⊕.

Table II (See Fig. 8)

Changes in Distribution of Diameters with Aging

$M/200$ NaOl and octane stirred by the drink mixer

Mean diam.	1a First day No. of drops	%	1b Third day No. of drops	%	1c Seventh day No. of drops	%
0.5	100	30.9	15	4.7	8	4.3
1.5	139	42.9	71	22.4	19	10.1
2.5	68	21.0	103	32.5	23	12.2
3.5	15	4.6	72	22.7	36	19.2
4.5	2	0.6	36	11.4	40	21.3
5.5			12	3.8	29	15.4
6.5			5	1.6	23	12.2
7.5			2	0.6	7	3.7
8.5			1	0.3	2	1.1
9.5					1	0.5
	324	100.0	317	100.0	188	100.0

TABLE II (*Concluded*)

$M/200$ CsOl and octane stirred by the drink mixer

Mean diam.	2a First day No. of drops	%	2b Third day No. of drops	%	2c Seventh day No. of drops	%
0.5	142	34.9	20	6.4	7	3.6
1.5	183	45.0	87	27.8	16	8.2
2.5	59	14.5	80	25.5	23	11.8
3.5	19	4.7	62	19.8	38	19.5
4.5	3	.7	40	12.8	40	20.5
5.5	1	.2	14	4.5	29	14.9
6.5			6	1.9	16	8.2
7.5			3	1.0	14	7.2
8.5			0	0.0	8	4.1
9.5			1	0.3	1	0.5
10.5					1	.5
11.5					0	.0
12.5					1	.5
13.5					1	.5
	407	100.0	313	100.0	195	100.0

TABLE III (SEE FIG. 9)

CHANGES IN AREA AND VOLUME WITH AGING

$M/200$ NaOl and octane (same emulsion as given in Table II)

Mean diam. in microns	Changes in area, sq. cm. of area per cc. of oil × 10^{-3} 1a First day	 1b Third day	Changes in volume, cc. of volume per cc. of oil 2a First day	 2b Third day
0.5	1.407	0.039	0.0176	0.0005
1.5	7.822	0.735	.1955	.0184
2.5	10.629	2.960	.4429	.1233
3.5	4.595	4.055	.2681	.2365
4.5	1.013	3.352	.0759	.2514
5.5		1.669		.1530
6.5		0.971		.1052
7.5		.517		.0646
8.5		.332		.0471
	25.466	14.630	1.0000	1.0000

$M/200$ CsOl and octane (same emulsion as given in Table II)

Mean diam. in microns	Changes in area, sq. cm. of area per cc. of oil × 10^{-3} 1a First day	 1b Third day	Changes in volume, cc. of volume per cc. of oil 2a First day	 2b Third day
0.5	1.679	0.048	0.0210	0.0006
1.5	8.657	0.842	.2164	.0210
2.5	7.753	2.150	.3230	.0896
3.5	4.894	3.265	.2855	.1905
4.5	1.277	3.483	.0958	.2612
5.5	0.0636	1.821	.0583	.1669
6.5		1.090		.1181
7.5		0.726		.0907
8.5		.000		.0000
9.5		.388		.0614
	24.896	13.813	1.0000	1.0000

The more concentrated soap solutions seem to form emulsions which are very stable even over long periods of time. Emulsions made with 0.1 *M* soap solutions and with greater concentrations, where the soap is soluble enough to remain in solution, were not observed to change appreciably in the course of a year. One possible exception was 0.1 *M* potassium chaulmoograte and Stanolax (see under "Influence of Different Hydrocarbon Chains"). Curves 2 and 3, Fig. 2, are fairly representative of the effect of aging emulsions produced by 0.1 *M* soaps. Curve 2 is for a 0.1 *M* cesium oleate and octane emulsion; Curve 3 is for the same emulsion more than a month later.

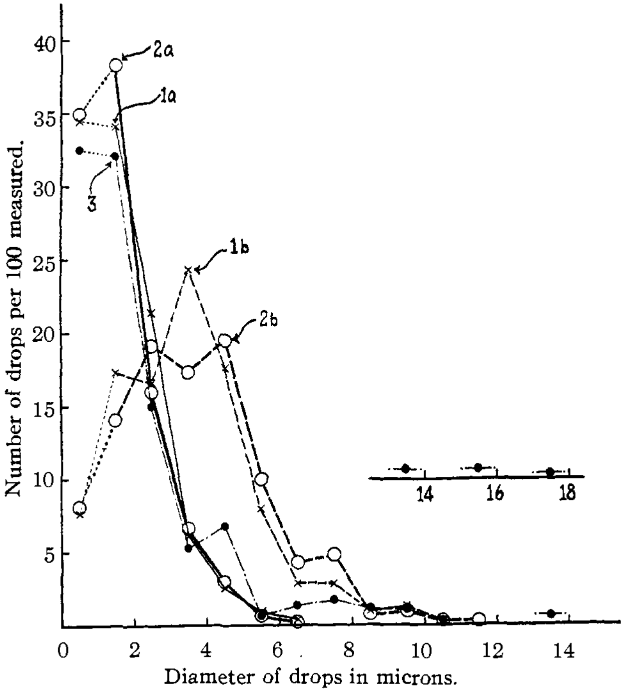

Fig. 7.—Changes in diameter distribution with aging. *M*/100 sodium oleate and octane (drink mixer): 1a, measured on first day; 1b, measured on tenth day. *M*/100 cesium oleate and octane (drink mixer): 2a, measured on first day; 2b, measured on tenth day. *M*/100 sodium oleate and octane (egg beater and different soap): 3, measured fifteen and one-half months later.

At the other extreme, emulsions produced by very dilute soaps were found to change rapidly. Thus 0.0005 *M*, 0.0008 *M* and 0.008 *M* soaps gave unstable emulsions which showed signs of breaking within a few hours after making. The most dilute soap which produced an emulsion (Table IV) stable long enough to measure had a concentration of 0.0008 *M*.

(A measurement required from one to two hours.) Soaps of a concentration of 0.005 *M* gave emulsions which broke markedly within a few days in some cases, while in others they were stable to all appearances except to microscopic observation. In every case, whether they broke ultimately or not, the microscope showed unmistakable changes in all of the 0.005 *M* emulsions studied. Figs. 7 and 8 exhibit the changes produced by aging in the diameter distribution and Figs. 9 and 10 in the area and volume distributions for emulsions of octane made with 0.01 *M* and 0.005 *M* solutions of cesium and sodium oleates. An actual shift in maxima and a relative increase in the number of large drops accompany aging of all the emulsions made with 0.005 *M* sodium and cesium oleates.

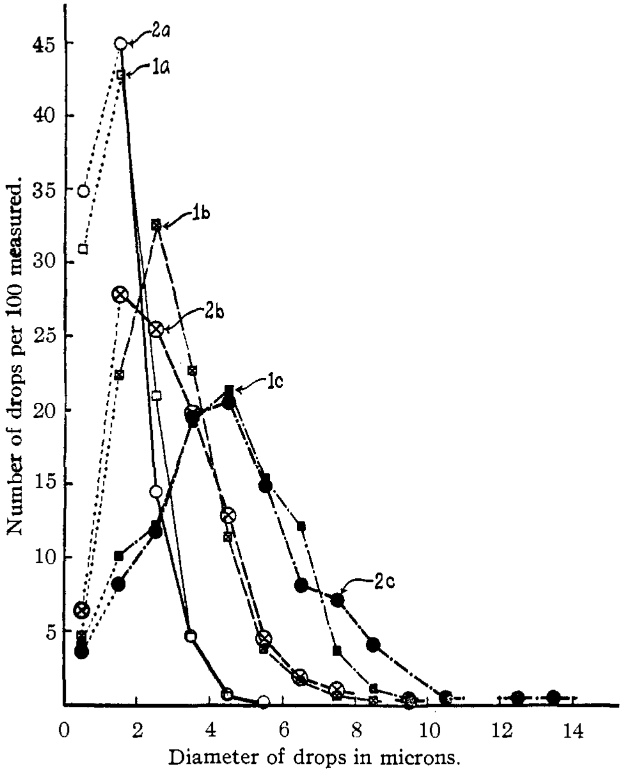

Fig. 8.—Changes in diameter distribution with aging. *M*/200 sodium oleate and octane (drink mixer): 1a, measured on first day; 1b, measured on third day; 1c, measured on seventh day. *M*/200 cesium oleate and octane (drink mixer): 2a, measured on first day; 2b, measured on third day; 2c, measured on seventh day.

Thus an emulsion produced from equal quantities of octane and a 0.005 *M* aqueous solution of *sodium oleate* gave an area of 25,466 sq. cm. per cc. of oil immediately after it was prepared, and 14,630 sq. cm. on the third day later. It is remarkable how closely these values were duplicated by an emulsion prepared with the same concentration of cesium oleate: 25,000 sq. cm. at first, and 13,813 sq. cm. on the third day.

Emulsions produced by 0.01 *M* soaps were much more stable (Fig. 7), and changed less in ten days than those with 0.005 *M* soap in seven days.

7. Influence of Different Methods of Preparation

It was found that twenty minutes' stirring with a motor-driven egg beater, or ten with a high-speed drink mixer gave the same distribution of sizes as double these periods. The drink mixer gave fewer large drops, but the remarkable feature was that either the beater or the mixer, or shaking by hand, gave the same position for the peak in the curve.

TABLE IV

RELATION OF AREA AT INTERFACE TO VOLUME OF A VERY DILUTE EMULSION

M/1200 NaOl and Stanolax stirred by drink mixer

Mean diam.	Actual no. of drops	%	Sq. cm. of area $\times 10^5$	Sq. cm. of area per cc. of oil $\times 10^{-5}$	Cc. of volume $\times 10^{10}$	Cc. of volume per cc. of oil
0.5	338	41.4	0.597	0.469	0.747	0.006
1.5	331	40.5	2.340	1.836	5.849	.046
2.5	83	10.2	1.630	1.279	6.790	.053
3.5	28	3.4	1.077	0.845	6.286	.049
4.5	9	1.1	0.573	.449	4.294	.034
5.5	10	1.2	0.950	.746	8.711	.068
6.5	8	1.0	1.062	.833	11.504	.090
7.5	2	0.2	.353	.277	4.417	.035
8.5	0	.0	.000	.000	0.000	.000
9.5	3	.4	.851	.667	13.468	.106
10.5	2	.2	.693	.544	12.122	.095
11.5	0	.0	.000	.000	0.000	.000
12.5	1	.1	.491	.385	10.227	.080
13.5	0	.0	.000	.000	0.000	.000
14.5	0	.0	.000	.000	0.000	.000
15.5	1	.1	.755	.592	19.498	.153
16.5	1	.1	.855	.671	23.521	.185
	817	99.9	12.227	9.593	127.434	1.000

8. Influence of the Addition of a Second Substance to the Soap

Surface tension work in this Laboratory has shown the marked effects of the addition of a substance like sodium hydroxide or oleic acid to a solution of sodium oleate. In contrast, the results obtained in this investigation when sodium hydroxide or oleic acid was added to the sodium oleate used as an emulsifying agent showed only slight effects upon the distribution curve. Various concentrations of sodium hydroxide were added to a 0.1 *M* sodium oleate solution and emulsions made by the use of each of these for the aqueous phase. Measurements were made on each emulsion but no markedly great effect was noticed until the concentration of the base had reached 1 *M*. At this concentration the diameter distribution was altered by a decrease in the number of large drops and an increase in the number of small drops. A similar change was obtained with the addition of 0.1 *M* oleic acid. The emulsion seemed to be more sensitive to the addition of oleic acid than of sodium hydroxide, though not sensitive to low concentrations of either.

9. Influence of Different Hydrocarbon Chains

Sodium stearate, elaidate and cerotate were used as stabilizing agents with the result that the same general distribution of sizes was obtained. Some other means of measuring particles smaller than one micron in diameter might indicate differences in the distribution of diameters of the smaller drops. In the case of the cerotate the emulsion which formed was very stiff and jelly-like and measurement was so difficult it could only be carried out roughly.

With 0.1 *M* potassium chaulmoograte and Stanolax, beaten by the egg beater, a surprisingly large number of the smaller drops was found. Thus the number of those of a mean diameter of 0.5 micron was almost twice the number of those of a diameter of 1.5 microns. Potassium chaulmoograte was found to be a very soluble soap but the emulsions made with it were not as stable as the emulsions made with potassium oleate. Very shortly after beating, whether the emulsion was run through the homogenizer or not, a thin layer of Stanolax separated out.

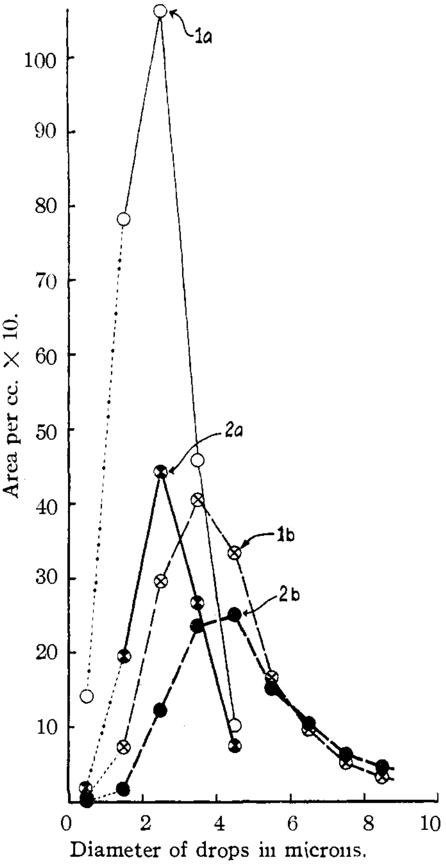

Fig. 9.—Changes with aging. *M*/200 sodium oleate and octane (same as in Fig. 8). Changes in area: 1a, measured on first day; 1b, measured on third day. Changes in volume: 2a, measured on first day; 2b, measured on third day.

10. Water in Oil Emulsions: Influence of Metals Other Than Univalent

Magnesium and aluminum oleates were dissolved in Stanolax and equal volumes of this oil and water were emulsified. They gave water in oil emulsions which when measured were found to give diameter distributions of the same type as those found for oil in water emulsions.

A Stanolax emulsion with 0.1 *M* sodium oleate made in the usual manner was inverted by the addition of the required quantity of aluminum nitrate. The inversion was carried out while beating. When this emulsion was measured it was found to be of the same general type (Curve 3, Fig. 3 and Table V). The same procedure was carried out with magnesium nitrate and again an inverted emulsion was the result, but in this case the drops were not spherical but irregular and gave the appearance of being inclosed in solid films. A careful set of measurements was impossible but a rough one was made and the usual distribution of sizes was indicated. These water-in-oil emulsions were not very stable and were almost entirely broken after a week or so.

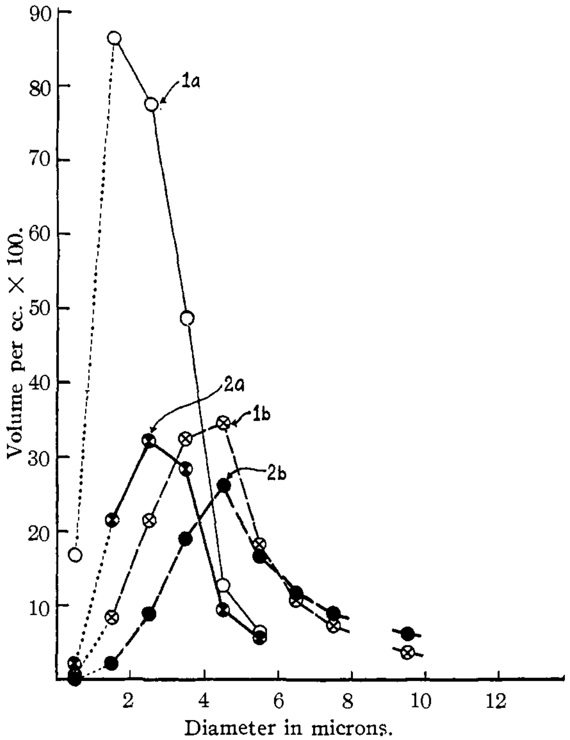

Fig. 10.—Changes with aging. *M*/200 cesium oleate and octane (same as in Fig. 8). Changes in area: 1a, measured on first day; 1b, measured on third day. Changes in volume: 2a, measured on first day; 2b, measured on third day.

A large quantity of sodium oleate dissolved in Stanolax by warming set to a jelly-like consistency upon cooling. To this solution of sodium oleate in oil was added water, while beating, and a water-in-oil emulsion was formed which broke within a few hours. This method was used by Harkins and Keith.[7]

TABLE V

DISTRIBUTION OF DIAMETERS IN A WATER-IN-OIL EMULSION OBTAINED BY INVERTING AN EMULSION OF STANOLAX PRODUCED WITH 0.1 *M* SODIUM OLEATE BY THE ADDITION OF ALUMINUM NITRATE

Diameter	0.5	1.5	2.5	3.5	4.5	5.5	6.5	7.5	8.5	9.5	Total
No. of drops	66	80	46	30	16	16	8	6	5	2	275
Per cent.	24.0	29.0	16.8	10.9	5.8	5.8	2.9	2.2	1.8	0.8	100.0

11. Emulsions Made without a Stabilizing Agent

It was noticed in the emulsion made with magnesium and aluminum oleates, which were of the water-in-oil type, that the aqueous layers had a very cloudy appearance. When examined under the microscope they were found to contain oil drops, that is, these aqueous layers were dilute oil-in-water emulsions. This led to the examination of both layers of an emulsion formed by stirring together equal volumes of Stanolax and water without using a stabilizing agent. About two hours after stirring samples were taken from each layer. In the oil layer was found a water-in-oil emulsion, and in the water layer an oil-in-water emulsion, but in the latter the concentration of droplets was about ten times greater than in the former. Measurements taken on the drops in these two layers showed diameter–distribution curves of the usual type except that the curves extended distinctly upward from the 1.5 micron to the 0.5 micron points, there being about 5% more drops of 0.5μ than of the 1.5 micron mean diameter in each case.

12. Emulsions of Benzene in Aqueous Soap Solutions

Benzene in water emulsions were made with different soaps. The distribution of diameters was of the usual type, except that more drops were observed between 0 and 1μ in diameter than between 1 and 2μ. As compared with those of Stanolax and octane, emulsions of benzene contained many more small particles.

13. Area at the Interface

Area is of prime importance in a study of colloids because of its relation to the phenomenon of adsorption. For those octane emulsions which are very stable it is seen that the greatest area is furnished by drops of approximately 2.0 to 2.5 microns in diameter[8] (see Curve 2a, Fig. 6). This holds

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[8] The first point in the area and volume curves is calculated upon the assumption that 0.75 micron is the mean diameter rather than 0.5 micron, though it is made to appear in the graphs as 0.5 micron. That is, it is felt that 0.75 micron rather than 0.5 micron represents more nearly the mean diameter of the very smallest drops visible by means of our optical system.

fairly well for the less stable emulsions also, but only if they are fresh (see Curves 1a, Fig. 9, and 1a, Fig. 10). Stanolax emulsions exhibit a different relation since the diameter which gives the maximum area is about 5 microns, since relatively fewer small drops are formed from the more viscous oil.

As indicated in Figs. 7 and 8 the aging of emulsions stabilized by rather dilute soaps is an important factor in the change of number, area and volume distributions. With a 0.005 *M* soap the shift of the maximum of the diameter-distribution curve for octane is about 3 microns in six days, or 0.5 micron per day. With 0.01 *M* soap the shift for the same oil, in two cases out of three, was about 2 microns in nine days, or 0.2 micron per day. This may be taken as a measure of the relative stability of these two emulsions. No shift in emulsions made with 0.1 *M* soaps was discovered, these apparently having more than enough soap to stabilize the interfacial film and, at the same time, enough soap in the aqueous phase to maintain equilibrium.

Table IV, fifth column, shows the area per cubic centimeter of oil calculated from the number distribution of drops measured in a Stanolax emulsion stabilized by 0.00083 *M* sodium oleate. This emulsion was not very stable and began to break shortly after measuring. The area per cubic centimeter of Stanolax in such an emulsion when fresh amounts to 9.6×10^3 sq. cm. Equal volumes of all and soap solution were used so, since 1 cc. of 0.00083 *M* soap solution would contain 0.505×10^{18} molecules, the area associated with one molecule of soap (if all of the soap were in the interface) would be 9.6×10^3 divided by 0.505×10^{18} or 190×10^{-16} sq. cm. This would be the *minimum* area which could be associated with one molecule of soap in the interfacial area of this emulsion. Since all the soap does not go into the interface the actual area is considerably larger. In comparison it may be noted that the area occupied by one molecule of oleic acid in a closely packed monomolecular film is 20.5×10^{-16} sq. cm.

In general only about 2% of paraffin oil is emulsified by pure water, but with soap as an emulsifying agent a highly concentrated emulsion, with about 75% of oil, is easily obtained by the formation of a highly dilute monomolecular film. The film gives such an emulsion even when it contains only one-tenth to one-fifth as many molecules of the soap as there are molecules of oleic or palmitic acid in a tightly packed monomolecular film. Such an emulsion is not stable, and on standing the area of its interface decreases and the area per molecule of soap in the film decreases, until the area becomes about that for a tightly-packed monomolecular film. Whether the film becomes thicker than this on long standing has not been determined but work on this problem is in progress.

Griffin[9] carried out careful analytical work on emulsions of kerosene

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[9] Griffin, THIS JOURNAL, **45**, 1648 (1923); see also van der Meulen and Rieman, *ibid.*, **46**, 876 (1924).

and found that the soap film exhibited about half as many molecules (sodium oleate and oleic acid) as are present in a condensed film of oleic acid. His determinations would have been decisive if sufficient work had been done on the distribution of sizes of the droplets in the emulsions; but, since only about 200 droplets in each emulsion were measured, and these were observed in a drop of emulsion suspended from a cover glass, it is evident that the error in the interfacial area may have been very large. However, the areas per cubic centimeter of oil found by him are consistently lower than those obtained by us, so, unless the method of emulsification which he used was much less efficient, the areas which he obtained are probably too low. If this is true, the conclusion which he reaches, that the soap film is monomolecular and of a much lower concentration than a condensed film of the acid, would still be valid.

Table VI gives the area per molecule of soap (sodium oleate or oleic acid) for three emulsions, and minimum, not actual, areas for still others. The minimum areas given are those obtained on the basis of the (incorrect) assumption that all of the soap is in the interface.

Table VI

Molecular Areas for the Soap at the Interfacial Film in Oil-in-Water Emulsions (Actual and Minimum Areas $\times 10^{16}$)

Emulsion	First day, min.	Third day, min.	Third day actual	Seventh day, min.	Tenth day, min.	15.5 months, min.
0.00083 *M* NaOl and Stanolax	190	..	..	..	..	..
0.005 *M* sodium oleate and octane	84	46[a]	61[a]	35.6	..	..
0.005 *M* cesium oleate and octane	82	48	64	30	..	..
0.01 *M* sodium oleate and octane	32.4	24	50	..	18.3	12.7
0.01 *M* cesium oleate and octane	32.7	..	..	..	..	..

[a] Determined on the second instead of the third day.

The evidence thus far obtained does not indicate that any of the soap films are thicker than monomolecular.

14. Summary

The distribution of sizes for the droplets in emulsions, both of the oil-in-water and the water-in-oil types, has been determined by a statistical method by the use of a projection apparatus used in conjunction with a microscope.

The following conclusions summarize the results of the work.

1. Within the range of microscopic observation there is no progressive shift in the maxima of the curves which show the distribution of diameter for emulsions made with soaps, as the cation is changed from sodium to potassium and to cesium.

2. In general, the greater the viscosity of the oil the greater the diameter of the largest drops in oil-in-water emulsion, but the peak in the diameter-distribution curve is not shifted.

3. A study of the changes in diameter-distribution, area-distribution and volume-distribution of emulsoid particles with aging gives a more exact method for determining stability than the older method of merely observing the gross features of the emulsion such as the separation of oil in bulk.

4. The method used in preparing an emulsion is one of the factors determining the distribution, but the striking feature of the present work is that the shift of the diameter at the maximum is so slight with the different methods of shaking or stirring employed.

5. The distribution of diameters of the particles of emulsions stabilized by soaps is changed only slightly by the addition of moderate concentrations of oleic acid or of the corresponding base (as of sodium hydroxide to sodium oleate). However, 0.1 M base increased considerably the number of small drops. The stability is, however, usually lessened considerably by the addition, for example, of 0.1 M oleic acid to the organic phase, or either 0.1 M sodium hydroxide or 0.1 M sodium chloride to the aqueous phase before the emulsion is formed.

It may be noted that the addition of either sodium hydroxide or sodium chloride to an aqueous-sodium oleate solution of low or moderate concentration greatly lowers the interfacial tension against an oil.

6. Such variations in the hydrocarbon chains of the soaps as were tried had little or no effect upon the distribution, except in the case of *potassium chaulmoograte in which the number of the smallest drops was greatly increased* above that for the oleate or stearate.

7. Magnesium and aluminum soaps gave emulsions of water in oil in which the distribution of sizes is the same, in general, as that found for those of the oil in water types.

8. Exceedingly dilute emulsions made *without* stabilizing agents also exhibit the usual type of distribution, but the drops are much smaller.

9. The area per molecule of sodium oleate in the interfacial film was 61×10^{-16} sq. cm. (61 Å.^{2}) for an emulsion made with 0.005 molar soap. At the time this area was determined, two days after the emulsion was made, the concentration of the soap in the aqueous phase was 0.00105 molar. For emulsions produced by 0.0008 sodium oleate and of Stanolax the molecular interfacial area was *greater* than 190 Å.^{2} according to measurements made within four hours of the time of preparation. It is evident that concentrated emulsions may be produced by means of an interfacial soap film in which the number of molecules of soap is *considerably less* than corresponds to a closely packed monomolecular film. However, the total interfacial area decreases with the time in such cases until finally the film becomes more tightly packed, but the evidence obtained thus far does not indicate that the film becomes thicker than monomolecular.

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