[CONTRIBUTION FROM THE INSECTICIDE AND FUNGICIDE LABORATORY, MISCELLANEOUS DIVISION, BUREAU OF CHEMISTRY, UNITED STATES DEPARTMENT OF AGRICULTURE]

EMULSIONS OF MINERAL OIL WITH SOAP AND WATER: THE INTERFACIAL FILM

BY EDWARD L. GRIFFIN

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Emulsions in which mineral oil is dispersed in water by means of soap are largely used as insecticides. Both kerosene and higher fractions of petroleum are used. Certain difficulties in the manufacture and use of these emulsions make important an understanding of the actual state of the constituents in an emulsion.

Much work on emulsions of this type has already been done, but the exact manner in which the soap functions is still in dispute. Several theories have been advanced to explain its action, the most important being as follows.

1. Emulsification depends principally upon obtaining the proper surface tension and viscosity.[1,2,3]
2. Emulsions consist of droplets of oil surrounded by a film of discrete, insoluble particles which are more easily moistened by water than by oil.[4]
3. Emulsions are made by the dispersion of oil, not in a water solution of soap or other emulsifier, but rather in a hydrated colloid. Enough of the colloid must be present to bind all the water.[5]
4. Emulsions consist of droplets of oil which are surrounded by more or less plastic films.[6,7,8,9]
5. Emulsions consist of droplets of oil in water, with an interface composed of molecules of a third substance, the molecules being so orientated that the group which has an affinity for water is dissolved in the water, while that which has an affinity for the oil is dissolved in the oil.[10,11]

Very little work had been done to prove this last theory. In fact Harkins, Davies and Clark said that "what is presented in this paper on the problem of the formation of colloids and emulsions is only preliminary in nature but much may be expected from the application of the principles in regard to the setting of molecules in surfaces to this problem."

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[1] Quincke, *Ann.*, **35**, 571 (1888).

[2] Donnan, *Z. physik. Chem.*, **31**, 42 (1899).

[3] Donnan and Potts, *Kolloid-Z.*, **7**, 208 (1910).

[4] Pickering, *ibid.*, **7**, 11 (1910).

[5] Fischer and Hooker, "Fats and Fatty Degeneration," John Wiley and Sons, **1917**.

[6] Bancroft, "Applied Colloid Chemistry," McGraw-Hill Book Co., **1921**.

[7] Briggs, *J. Phys. Chem.*, **19**, 210 (1915).

[8] Holmes and Cameron, THIS JOURNAL, **44**, 66 (1922).

[9] Clark and Mann, *J. Biol. Chem.*, **52**, 157 (1922).

[10] Langmuir, THIS JOURNAL, **39**, 1848 (1917).

[11] Harkins, Davies and Clark, *ibid.*, **39**, 541 (1917).

Theoretical Consideration

If a kerosene emulsion consists of droplets of kerosene, each surrounded by a film of soap 1 molecule thick, the whole surrounded by a soap solution containing the unabsorbed soap, it might seem possible to determine the soap extracted from the water solution in the formation of the emulsion.[12] The quantity of soap removed from aqueous solution would be directly proportional to the area of interface formed and entirely independent of the concentration of soap originally present, provided, of course, that sufficient soap is present to form the film.

It is also possible to measure the area of the droplets formed. From a comparison of the amount of soap removed by each cubic centimeter of kerosene with the area of interface formed by the same amount, the average area covered by each molecule of soap can be calculated.

In a molecule the size of that of stearic or oleic acid the replacement of a hydrogen atom by sodium would hardly be expected to greatly increase the average area occupied by a molecule and in this case the results would be expected to agree rather closely with those obtained by Langmuir for the average area occupied by each molecule of the various fatty acids when placed on water in a film 1 molecule thick ($46, 22$, and 21×10^{-16} sq. cm. for oleic, stearic, and palmitic acids, respectively). The possibility that the soap might be heavily hydrated is not precluded. In this case the area occupied by each molecule of soap might be much greater than that occupied by a molecule of the corresponding fatty acid.

When kerosene is emulsified in fairly dilute sodium oleate solution by shaking and then allowed to stand, the oil droplets cream out at the top, leaving a clear or nearly clear aqueous soap solution at the bottom. If this soap solution is analyzed before and after emulsification of the kerosene, the difference in the quantity of soap carried will be that taken up by the kerosene.

The area of interface may be calculated as follows. An oil emulsion contains droplets of various sizes. Let us assume that these droplets are assigned to various classes whose radii, expressed in centimeters, are r_1, r_2, r_3, r_4 ...., respectively. Let us measure a large number of drops, denoting those with radius r_1 by x_1, those with radius r_2 by x_2, those with radius r_3 by x_3, and so on. The area of interface associated with each cubic centimeter of kerosene is the sum of the areas of these droplets divided by the sum of their volumes or

$$\frac{3(x_1r_1^2 + x_2r_2^2 + x_3r_3^2 + \dots\dots\dots\dots)}{x_1r_1^3 + x_2r_2^3 + x_3r_3^3 + \dots\dots\dots\dots}$$

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[12] Briggs, Ref. 7, made titrations which showed that soap was removed but says that absolute measurements were not obtained. His results are to be considered only as comparative.

The area of interface associated with 1 cc. of kerosene, divided by the number of molecules of soap removed, gives the area of interface formed for each molecule of soap removed. Millikan's value,[13] for the number of molecules in a mole (6.06×10^{23}) was used.

Experimental Part

Materials Used

U. S. P. stearic and oleic acids were used. The stearic acid had been purified by alcohol. While both of these acids usually contain small amounts of impurities, the errors in the other measurements are such that it was believed that the results would not be affected.

A sample of impure commercial palmitic acid, having a yellow color, and somewhat soft, was first employed. Later, a sample of pure palmitic acid with a melting point of 62° and an iodine number zero, was obtained from Dr. George E. Jamieson of the Bureau of Chemistry.

Emulsions

Soap solutions were made as follows. The calculated amount of fatty acids was weighed into a flask. About 500 cc. of water was added, and heat was applied when necessary to melt the acid; the mixture was then shaken while the calculated amount of normal alkali necessary to form a neutral soap was added, the mixture heated and shaken until all dissolved. This was then cooled to room temperature, made up to 1 liter, and mixed by shaking. An approximately 0.2 or 0.1 *M* solution was usually prepared as a stock solution, weaker solutions being made from it by dilution as needed.

Except where otherwise stated, emulsions were made by the following procedure. The required volume (usually 100 cc.) of soap solution was measured into a flask and an equal volume of kerosene was added. Then the whole mixture was drawn up into a large pipet by vacuum and rapidly expelled by compressed air, repeating the process about 10 times. The emulsified product was next poured into a cylinder and the cylinder was stoppered and allowed to stand. One or two days later when the emulsion had come to equilibrium, the contents of the cylinder were run from end to end several times to guard against local differences of concentration, then allowed to stand, usually for about 2 weeks, until the oil drops had arisen to the top as a cream, leaving a clear or nearly clear aqueous lower layer sufficient for analysis.

Another portion of the same soap solution was preserved under the same conditions for comparative analysis.

Fatty Acid Determination.—Twenty-five or 50 cc. of the solution to be analyzed was pipetted into a 120cc. Squibb funnel. Enough *N* sulfuric

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[13] Millikan, *Phil. Mag.*, [6] **34,** 1 (1917).

acid was then added to break down the soap and leave a slight excess of acidity, followed by 40 cc. of U. S. P. ether. The contents of the funnel were well shaken and allowed to separate into layers, and the lower layer was drawn into Funnel 2. About 40 cc. of ether was added to this and the material was well shaken and allowed to separate. The lower layer was drawn into Funnel 3, where it was again washed with ether and then discarded. The ether layers in the 3 funnels were next washed with water, until the last washing contained no more than traces of acid, after which they were combined in a beaker. Nearly all of the ether was evaporated on the steam-bath. About 50 cc. of neutral alcohol was poured into the beaker containing the fatty acids and the acids were titrated with 0.1 *N* sodium or potassium hydroxide solution, using phenolphthalein as an indicator.

Analyses were made of the clear layer from the emulsion and of the soap solution from which the emulsion was made. The quantity of fatty acid found was calculated to moles per liter. The difference between the moles of acid found per liter in the original solution and that found in the lower layer from the emulsion represents the number of moles removed by each liter of the kerosene inasmuch as the kerosene and the soap solution were used in equal volumes. The value thus obtained, divided by 1,000, gives the number of moles removed by 1 cc. of kerosene.

Measuring the Droplets.—The contents of the cylinder containing the emulsion were carefully run from end to end several times in order to mix it without changing the size of the droplets. A small quantity of the emulsion was then poured into distilled water in an Erlenmeyer flask and the flask was rotated until an even mixture was obtained. A small quantity of this diluted emulsion was placed on a microscope cover glass by means of a platinum loop, and mounted on a ground-glass slide just as a hanging drop of bacterial culture is mounted to study the motility of an organism. The droplets were immediately examined under the microscope, using a 4 mm. objective and a No. 10 eyepiece containing a micrometer disc. The slide was set at random and the sizes of all the droplets whose centers appeared on the scale were recorded to the nearest half scale-division up to 3, above that to the nearest division. Each scale division was equal to 0.00038 cm. The tube was moved up and down so as to find all the droplets in the area. The slide was moved from place to place until about 200 droplets had been measured and the number in each class obtained.

Sodium and Oleic Acid Removed by Emulsification

Emulsions were made from sodium oleate solutions of various concentrations and kerosene. When a soap solution containing 0.002 mole or less of sodium oleate per liter was used, the emulsion formed was not permanent. Permanent emulsions were formed with soap concentrations ranging from 0.003 to 0.124 mole per liter. Oleic acid was removed from the aqueous layer in the process of emulsification, the loss varying from 0.0022 to 0.0086 mole per liter. The area of interface formed was from 3,700 to 11,400 sq. cm. for each cubic centimeter of kerosene. The area of interface formed for each molecule of oleic acid lost was from 21×10^{-16} to 39×10^{-16} sq. cm.

These values, although somewhat lower, are of the same order of magnitude as those obtained by Langmuir for the average area of 1 molecule of oleic acid in a surface film (46×10^{-16} sq. cm.). If they differed from those for surface films it was expected that they would be higher for the reason that the sodium atom is larger than the hydrogen atom and also because hydration of the soap may be expected. It was considered possible that part of the oleic acid removed had gone into solution in the kerosene and not into the interface. If this were the case, more oleic acid than sodium would be extracted from the soap solution in making an emulsion and an excess of sodium would remain in the aqueous layer. It was decided, therefore, to conduct experiments in which both the sodium and the oleic acid removed by emulsification were determined.

Sodium Determination.—Sodium was determined as follows. A 25- or 50cc. aliquot portion of the solution was evaporated to dryness in a platinum dish and ignited at a low temperature. An excess of *N* sulfuric acid was added and the whole was evaporated to dryness and ashed completely. The silica was dehydrated by evaporation with hydrochloric acid, and drying for 1 hour at 110°. It was then treated with hydrochloric acid, filtered, and washed, and the filtrate was evaporated to dryness in a weighed platinum dish. Water, 0.5 cc. of *N* sulfuric acid, and ammonia in excess were added, and this mixture was evaporated to dryness, ignited, and weighed as sodium sulfate. The results obtained are shown in Table I.

TABLE I

SODIUM AND OLEIC ACID REMOVED FROM SOLUTION ON EMULSIFICATION

Concn. of sodium oleate in soap soln. Moles per liter	Material removed from aq. soln. Moles per liter		Area of interface $\times 10^{-3}$ per cc. of kerosene Sq. cm.	Cross section area of molecules in the interface $\times 10^{16}$ Sq. cm.	
	Sodium	Oleic acid		Calc. from sodium	Calc. from oleic acid
0.05	0.0038	0.0046	11.0	48	39
.025	.0037	.0049	10.3	46	35
.0125	.0037	.0058	10.9	49	31

In every case the loss of oleic acid exceeded the loss of sodium. Assuming that all of the sodium that disappeared from solution went into the interface in the form of a unimolecular layer of sodium oleate and that the excess oleic acid that disappeared went into solution in the kerosene, the areas calculated for the average cross section of a molecule of sodium oleate in the film agree very well with those obtained by Langmuir for a molecule of oleic acid in a surface film.

It was thought that reduction of the hydrolysis of the soap by the addition of sodium hydroxide might make the concentration of the undissociated fatty acid in the soap solution so small that the quantity taken into solution by the kerosene would be negligible. An emulsion containing 0.1 mole of sodium oleate and 0.01 mole of sodium hydroxide per liter was therefore made. Equivalent quantities of sodium and oleic acid (0.0028 mole per liter) were removed from the solution. The interfacial area formed per cubic centimeter of kerosene was 7.45×10^3 sq. cm. and the area for each molecule of sodium oleate removed from the solution was 44×10^{-16} sq. cm.

The fact that the quantities of sodium and oleic acid absorbed were equivalent agrees with, but does not prove our theory. Since certain fatty acids form acid salts with the alkali metals, it was considered possible, in the case of the neutral sodium oleate emulsions with kerosene, that an acid salt might go into the interface, as suggested by Pickering.[14] This would account for the discrepancy in the quantities of sodium and of oleic acid absorbed. A direct method of extracting sodium oleate solution with kerosene was therefore sought.

No method presented itself of breaking an emulsion after it had been formed, without changing conditions in the mixture to such an extent that the results would be valueless. An extraction was, therefore, made in a rotating machine in the following manner, care being taken that no emulsion was formed. One hundred cc. of the soap solution was pipetted into a 300cc. round bottle; the formation of bubbles was carefully avoided. One hundred cc. of kerosene was carefully placed on top of the soap solution by means of a pipet, and in such a way that a smooth surface between the kerosene and the soap solution was maintained. The bottle was stoppered and carefully fastened on the rotating machine so that its long axis was parallel to the axis of rotation. The machine used had a diameter of rotation of about 15 inches and made 30 revolutions per minute; when it was properly run no emulsion resulted. After the required period of rotation the bottle was removed, and an aliquot portion of the clear kerosene was taken. An equal volume of neutral alcohol was added to the kerosene and the mixture was titrated with 0.1 N alkali, using phenolphthalein as an indicator. The mixture was shaken after each addition of alkali. A value of 0.10 cc. of 0.1 N alkali for 50 cc. of kerosene was subtracted in all cases as representing the value of a blank experiment.

To determine the time necessary to run the machine to insure complete extraction, 4 bottles, each containing sodium oleate solution of the same strength and kerosene, were placed on the machine which was set in motion. One bottle was removed at the end of each successive half-hour period up to 2 hours; the solutions then required 0.60, 0.65, 0.60 and 0.65 cc. of 0.1 N

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[14] Pickering, *J. Chem. Soc.*, 91, 2001 (1907).

sodium hydroxide, respectively; that is, at the end of a half hour the maximum amount of acid had been extracted by the kerosene. In the extractions noted in this paper 1 hour was the time ordinarily used, thus securing a sufficient margin of safety.

A portion of kerosene which had been used to extract sodium oleate solution by the method described and another portion obtained by breaking down an emulsion with heat were ignited. No weighable amount of ash remained, indicating that sodium oleate as such is not dissolved by kerosene.

Experiments were conducted to determine the quantity of sodium and oleic acid removed from the solution on emulsification and also that which was dissolved in the kerosene. The difference between the quantity of oleic acid dissolved in the kerosene and the total acid removed on emulsification was the part which went into the interface. The experimental results are shown in Table II.

Table II

Experimental Data on Emulsions of Kerosene with Sodium Oleate Solution

Concn. in soap solution of		Material in the interface		Area of interface $\times 10^{-8}$ per cc. of kerosene	Av. cross section area of sodium oleate molecule $\times 10^{16}$	
Sodium oleate	Sodium hydroxide	Sodium	Oleic acid		Calc. from sodium	Calc. from oleic acid
Moles per liter		G. atoms or moles per liter		Sq. cm.	Sq. cm.	Sq. cm.
0.100	0.01	0.0028	0.0028	7.45	44	44
.100	...	.0031	.0028	8.47	45	50
.020	...	.0024	.0023	7.17	49	51
.005	...	.0024	.0023	6.87	47	49
.02	.002	.0026	.0026	7.9	50	50
.005	.0005	.0026	.0024	7.40	47	51
.0125	...	.0007	.0007	2.00	47	47
.01	...	.0009	.0009	2.40	44	44
.0033	.01	...	.0025	7.92	..	52
.01[a]	...	...	.0032	9.73	..	50

[a] This emulsion was made and kept at 55°.

Emulsions with Stearic Acid Soap

Sodium stearate is so insoluble in water that it is impossible to study emulsions made from it and kerosene by the method used for the sodium oleate emulsions. After a 0.05 *M* solution of potassium stearate made by the method described had stood at room temperature, soap separated. All of the experiments, therefore, were run at a higher temperature, 55° being chosen, but the final dilution for measuring the droplets was made at room temperature. If there is a unimolecular layer of soap around the oil droplets, the cross-sectional area, since it is measured at room temperature, will not be changed by the higher temperature of creaming out.

Under these conditions large quantities of glass were dissolved, as shown by the silica in the ash from the soap solution and by the etching of the cylinders. The potash determinations, therefore, were unreliable and were not used.

The stearic acid in the interface was determined by the methods used for oleic acid in the emulsions from sodium oleate. The kerosene was extracted at about 55°. The results thus obtained are shown in Table III.

TABLE III

EXPERIMENTAL DATA ON EMULSIONS OF KEROSENE WITH POTASSIUM STEARATE SOLUTION

Concn. in soap solution of potassium stearate	Potassium hydroxide	Stearic acid in the interface	Area of interface × 10^{-3} per cc. of kerosene	Cross section area of molecules in interface × 10^{16}
Mole per liter		Mole per liter	Sq. cm.	Sq. cm.
0.025	..	0.0050	7.48	25
.0062	..	.0045	6.91	25
.0031	..	...	Emulsion broke	..
.100	0.01	.0043	7.60	29
.020	.01	.0033	6.21	31
.005	..	.0038	5.64	24
				Av. 27

Emulsions with Palmitic Acid Soap

Emulsions made from a commercial sample of palmitic acid in the manner already described were held at a temperature of 40° while they settled. The cross-sectional area of the molecules in the interface determined in these experiments varied from 32×10^{-16} to 44×10^{-16} sq. cm. These results did not check well with the cross-sectional areas obtained for palmitic acid by Langmuir (21×10^{-16} sq. cm.). In fact, they agreed better with the values for unsaturated fatty acids. The iodine number of the palmitic acid was very high, indicating the presence of a large amount of unsaturated acids. These results, therefore, cannot be considered of any value in determining the cross-sectional area of molecules of palmitic acid in an interface.

Accordingly, a sample of C. P. palmitic acid having an iodine number of zero was obtained from the Oil, Fat and Wax Laboratory of the United States Bureau of Chemistry. The results obtained by using this acid at 55° are shown in Table IV.

TABLE IV

EXPERIMENTAL DATA ON EMULSIONS OF KEROSENE WITH POTASSIUM PALMITATE

Expts.	Concn. in soap solution of Potassium palmitate	Potassium hydroxide	Palmitic acid in the interface	Area of interface × 10^{-3} per cc. of kerosene	Cross section area of molecules in interface × 10^{16}
	Mole per liter		Mole per liter	Sq. cm.	Sq. cm.
37	0.01	..	0.0036	7.1	32
38	.01	..	.0047	7.6	27
39	.01	0.01	.0040	7.6	31
					Av. 30

Conclusions

The experiments here reported show that when kerosene is emulsified with a neutral soap solution the soap is partially hydrolyzed and some of the fatty acid is dissolved in the kerosene. This hydrolysis may be prevented, or at least reduced to a negligible amount, by the addition of free alkali. No sodium or potassium is dissolved in the kerosene.

In the formation of an emulsion a certain quantity of soap is removed from the soap solution and does not go into the kerosene. It must, therefore, go into the interface between the kerosene and the remaining soap solution. The quantity of soap absorbed is (within the experimental error) proportional to the area of interface formed and is not dependent upon the concentration of soap originally in the solution.

The droplets of oil in a good emulsion must be small. This work shows that when a quantity of soap insufficient to form the interface for these droplets is present, the resulting emulsion is not stable. All of the emulsions made with very small amounts of soap "broke" on standing.

On the theory that these considerations indicated that the interface consists of a monomolecular layer of soap, the area of interface formed by each molecule of soap present (or the average cross-section of the soap molecules) was calculated. The results bore out the theoretical belief that the areas thus measured should be the same as, or somewhat greater than, those measured by Langmuir for the corresponding fatty acids in surface films. The average values for the soaps as determined by this method are 48, 27 and 30 $\times$ 10^{-16} for sodium oleate, potassium stearate and potassium palmitate, respectively, and those for the corresponding fatty acids as determined by Langmuir are 46, 22 and 21 $\times$ 10^{-16}, respectively.

These results agree with the values expected and show that the film formed at the interface must be 1 molecule thick. The only other possible explanation would be the formation of a film of heavily hydrated soap of constant thickness at the interface. As these films came from solutions of widely varying concentration and as the hydration of soap in precipitates depends on the concentration of the solution from which it is precipitated, the second theory becomes untenable.

It may, therefore, be concluded that a unimolecular film must be formed at the interface when kerosene is emulsified with solutions of soap.

Summary

1. In an emulsion of mineral oil with soap and water, part of the soap is hydrolyzed, the fatty acids being dissolved by the oil droplets and the alkali remaining in aqueous solution.
2. Fatty acids may be kept from dissolving in the oil by the addition of excess alkali.
3. Part of the soap forms unimolecular films around the oil droplets.

The average areas occupied by each molecule of sodium oleate, potassium stearate and potassium palmitate, were found to be 48, 27 and 30 x 10^{-16} sq. cm., respectively. These areas agree rather closely with those found for the corresponding fatty acids in unimolecular films on the surface of water.

4. In case there is insufficient soap to form a unimolecular film the emulsion is not stable.
5. The excess soap remains in water solution.

WASHINGTON, D. C.

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ADSORBED MOISTURE AND WATER OF CRYSTALLIZATION IN CERTAIN COMMON DYES

BY H. WALES AND O. A. NELSON

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A discrepancy between the observed and calculated results for different samples of pure methylene blue when the molecular weight as given in the United States Pharmacopeia ($C_{16}H_{18}N_3SCl.3H_2O$) was used, always occurred during the work done on this dye in the Color Laboratory. As the authority for assuming the presence of 3 mols. of water of crystallization in this compound failed to give reliable experimental data, it was considered desirable to determine, if possible, whether or not the moisture in this dye, as well as in a few others, was present as adsorbed moisture or as water of crystallization.

From the literature, reference to which will be made as each dye is considered, it appears that no investigator has attempted to show by experiment how the moisture in his sample was held. The customary method was to heat the dye at a definite temperature for a definite period of time and calculate the amount of water present from the analytical determinations of elements. The water thus found was then considered in terms of mols. of water of crystallization when, from the data given, it might as readily be adsorbed water. Since adsorbed water is often held more tightly than the so-called water of hydration or crystallization, it seems obvious that the results obtained by such a method cannot be conclusive.

The primary object of this work was not so much to determine the quantity of water present in the dyes studied as to ascertain whether the water was present as adsorbed moisture or as water of crystallization.

Theoretically, if the vapor pressure of a hydrate be plotted against the weight of water present at constant temperature, the pressure remains constant until the last of the hydrate corresponding to this pressure has been removed. At this point the pressure drops to that of a lower hydrate,