[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF RUTGERS UNIVERSITY]

MONOMOLECULAR SOAP FILMS IN EMULSIONS[1]

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In an earlier paper[2] the authors drew the conclusion that the average area of interface covered per molecule of soap is dependent upon the concentration of soap in the "concentrated" emulsion. As a matter of fact, the data can also be interpreted to mean that the area of interface per molecule depends upon the concentration of soap in the aqueous phase of the "dilute" emulsion. The present work was undertaken to decide between these alternatives.

An effort was also made to use purer materials. Since pure oleic acid is more easily obtained than pure ricinoleic acid, sodium oleate was used as the soap.

Experimental Part

Materials Used.—A sample of U. S. P. oleic acid was obtained and analyzed with the following results: water, 0.2%; sap. no. (dry basis), 198.67 (calcd., 198.70); iodine no. (dry basis), 89.63 (calcd., 89.90); d^{15}, 0.8963. This material was considered satisfactory and used in subsequent experiments.

The toluene distilled completely between 110.2° and 110.6°; d^{25}, 0.860.

The phenol melted at 40.7°. A solution of phenol in toluene was prepared, which was found to contain 19.44% of phenol by weight. This solution is referred to as "oil" in the subsequent discussion.

The water used in these experiments was saturated with toluene by shaking it with oil. Fifteen cc. of oil was used for each liter of water. The phenol concentration in this water was found to be 2.597 mg. per cc. In one case, however, the phenol concentration was 1.303 mg. per cc., as noted in Table I.

Sodium hydroxide, purified by alcohol, was used to prepare a solution which contained 28.64% of sodium hydroxide by weight.

Preparation of Emulsions.—The oil, oleic acid, sodium hydroxide solution and water were poured into a flask in the order given. The flask was then stoppered and shaken. The concentrated emulsion thus obtained was allowed to stand for three days or longer. Part of it was then diluted with water saturated with toluene, for analysis or for microscopic examination. The composition of the emulsions is given in Table I.

Investigation of Emulsions.—The percentage of soap in the interface of the dilute emulsions and the size of the globules were determined exactly as described in the previous article.[2] The average area of interface covered per molecule of soap was calculated as in the previous article with one minor correction. The assumption was made previously that the internal phase of the dilute emulsion consists of the oil, practically unchanged in composition. Subsequent investigation has revealed, how-

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[1] The material in this article is taken from a thesis submitted by Wm. Rieman 3rd in partial fulfilment of the requirements for the degree of Doctor of Philosophy at Rutgers University.

[2] van der Meulen and Rieman, THIS JOURNAL, **46**, 876 (1924).

TABLE I

COMPOSITION OF EMULSIONS

Emuls. No.	Concd. emulsion Oil G.	99.8% oleic acid G.	28.6% NaOH G.	H_2O	Dil. emulsion Dilution	Subs. added
1	45.29	11.18	5.57	0	10–500	....
2	45.33	9.42	4.68	2.62 g.	10–500	....
3	45.96	8.66	4.26	4.08	10–500	....
4	45.30	6.59	3.27	6.84	10–500	....
5	45.31	5.65	2.82	8.24	10–500	....
6	47.37	4.91	2.45	10.23	10–500	....
7	45.30	3.78	1.85	11.05	10–500	....
8	45.89	2.37	1.18	13.34	10–500	....
4A	55.20	3.96	1.96	4.14	10–500	....
4B	45.28	9.93	4.90	10.27	10–500	....
1C	Same as number 1				5–500	....
2C	Same as number 2				5–500	....
4C	Same as number 4				5–500	....
5C	Same as number 5				5–500	....
8E	Same as number 8				5–500	Sodium oleate
4D	Same as number 4				5–500	Phenol
5D	Same as number 5				5–500	Phenol
C3	35.42	6.68	3.36	3.14	10–500[a]	....

[a] The water for dilution contained 1.303 mg. of phenol per cc. See discussion.

ever, that most of the phenol leaves the toluene and dissolves in the water, leaving only about 1% by weight of phenol in the internal phase. The error introduced into the preliminary publication by this erroneous as-

TABLE II

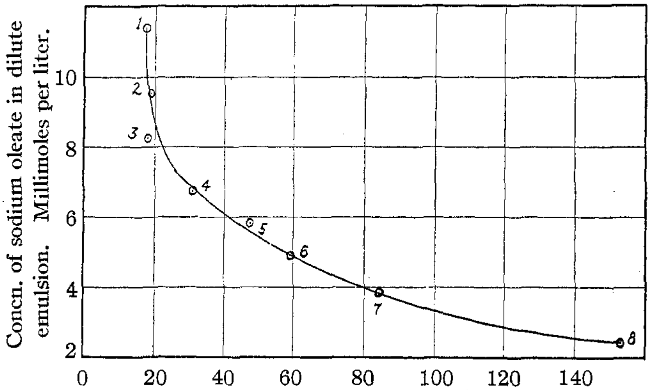
RESULTS

Emuls. No.	Diam. of globules, μ	Soap in film, %	Phenol, concn. in aq. Ph Mg. per cc. Calcd.	Found	Molarity of soap × 1000	Area Sq. Å.
1	1.230	4.97	5.14		11.39	17.36
2	1.170	5.72	5.14	5.08	9.53	18.79
3	1.338	5.72	5.14		8.26	18.19
4	1.337	4.37	5.14		6.76	30.8
5	1.180	3.77	5.14		5.83	47.3
6	1.287	3.33	5.14		4.89	59.2
7	1.165	3.21	5.14		3.88	84.1
8	1.206	2.75	5.14		2.44	153.0
4A	1.213	2.83	5.49		3.89	106.8
4B	1.146	4.78	4.85	4.76	8.92	21.9
1C	1.230	2.91	3.87		5.78	29.7
2C	1.170	2.67	3.87	3.83	4.82	40.2
4C	1.337	2.01	3.87	3.87	3.45	67.2
5C	1.180	2.47	3.87		2.94	72.2
8E	1.206	4.11	5.14		6.31	38.1
4D	1.337	1.249	5.14	5.12	3.45	95.5
5D	1.180	1.702	5.14		2.94	104.8
C3	1.232	5.76	3.87	3.83	8.61	20.5

sumption is well within the 10% which was estimated to be the error of the determination.

The results are given in Table II.

Discussion of Results.—Emulsions 1 to 8 were prepared so that the volume ratio of oil to water plus soap in the concentrated emulsion is approximately 3. They were all diluted 10 to 500 cc. They exhibit a regular increase in average area of interface covered per molecule of soap, as the quantity of soap present is decreased. Just as in the case of the emulsions with sodium ricinoleate, described in the first article, two methods of interpretation are possible. Either the concentration of soap in the aqueous phase of the dilute emulsion or the concentration of soap in the concentrated emulsion may be considered as the governing factor. The results are plotted in Fig. 1 according to the former assumption. The curve indicates that the area per molecule cannot decrease below 17 sq. Å.; that is, it approaches an asymptote. The curve is extended as far in both directions as possible. Concentrated emulsions with more soap than No. 1 or less soap than No. 8 are not clear.



Area per molecule in square Å.

Fig. 1.

Concentrated emulsions 4A and 4B contain the same relative quantities of soap and water as Emulsion 4, but the ratio of oil to soap plus water is 6 and 2, respectively. The results are plotted in Fig. 2. Curve A of this figure is the curve of Fig. 1, reproduced for comparison. The points corresponding to Emulsions 1 to 8 are not located in Fig. 2, but the areas for all other emulsions are plotted in this figure. Point 4B is on the curve within the experimental error. Point 4A lies off the curve. The cause of the discrepancy is discussed later.

Concentrated Emulsions 1, 2, 4 and 5 were diluted 5 to 500 cc. instead of 10 to 500 to give the dilute emulsions called, respectively, 1C, 2C, 4C and 5C. If the concentration of soap in the concentrated emulsion be the governing factor, these emulsions ought to have the same area per molecule as Emulsions 1, 2, 4 and 5, respectively. Since this is not the case, we may reject this hypothesis. When plotted according to the assumption that the concentration of soap in the aqueous phase of the dilute emulsion is the governing factor, the results are more satisfactory. The points do not, however, lie exactly on Curve A. Instead, they form a similar curve, B, to the left of the curve A. Again we are confronted by a secondary disturbing factor.

Additional support of the hypothesis that the soap concentration of the dilute emulsion is the governing factor is found in Emulsion 8E. This was prepared by diluting concentrated Emulsion 8 with water saturated with toluene, to which a little sodium oleate had also been added. The point is located on Curve A of Fig. 2.

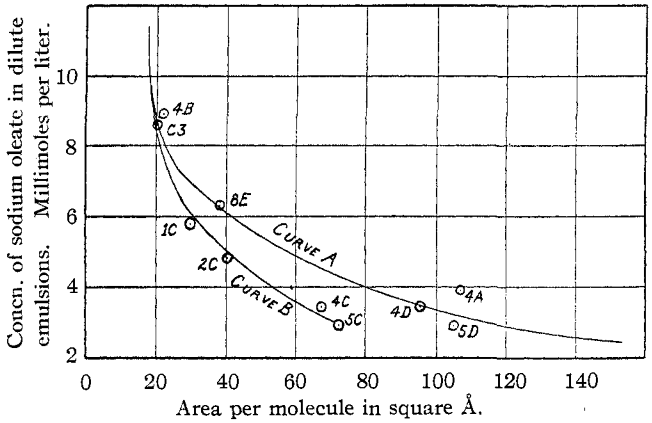


Fig. 2.

We may conclude from the results discussed above that the average area of interface covered per molecule of soap is variable, and depends primarily upon the concentration of soap in the external phase of the dilute emulsion. But a secondary influence must also be at work, for Emulsions 4A, 1C, 2C, 4C and 5C lie off the curve.

A study of the concentration of phenol in the aqueous phase of the dilute emulsions throws light upon these discrepancies. Herz and Fischer[3] have determined the distribution coefficient of phenol between toluene and water. Extrapolation of their results indicates that the coefficient is practically constant (1.718) within the range of concentrations used in the present work. By use of this coefficient and the composition of the emulsions, we can calculate the concentration of phenol in the aqueous phase of the dilute emulsions.

These calculations were verified in a few cases by an actual determina-

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[3] Herz and Fischer, *Ber.*, **38**, 1143 (1905).

tion of the phenol. The dilute emulsion was centrifuged; the upper layer, containing the toluene, was removed. A sample of the lower layer (that is, aqueous phase) was treated with sodium hydroxide solution to prevent volatilization of phenol during heating. Barium chloride solution was then added to the warm solution, and barium oleate removed by filtration. The phenol in the filtrate was determined by the usual volumetric bromine method.

The analytical results do not agree exactly with the calculated results. Apparently some phenol is carried down by the precipitate of barium oleate. Nevertheless, the results are in sufficiently close agreement to substantiate the correctness of the calculations.

A study of Fig. 2 in connection with the phenol concentration, as given in Table II, reveals (1) that all emulsions whose phenol concentration is 5.14 mg. per cc. lie on Curve A; (2) emulsions of higher phenol concentration (No. 4A) lie to the right; (3) emulsions whose phenol concentration is 3.87 mg. per cc. lie on a separate curve to the left of the curve A.

Therefore the working hypothesis is adopted that phenol plays a role in the interface and can partially displace the soap. To test this hypothesis dilute Emulsions 4D and 5D were prepared by adding to Emulsions 4C and 5C sufficient phenol to raise the total concentration of phenol in the aqueous phase to 5.14 mg. per cc., which is the phenol concentration corresponding to dilute emulsions of Curve A. The points lie on Curve A and support the hypothesis.

Phenol consists of a polar hydroxyl group joined to a non-polar hydrocarbon ring. When it goes into the interface it is probably oriented with the hydroxyl group in the water and the hydrocarbon ring in the toluene.

Additional evidence in support of the theory that phenol may enter the interface in partial replacement of the soap is seen in the following considerations. Griffin,[4] working with emulsions which contained no phenol, found that the average area of interface per molecule of soap is independent of the concentration of soap. Furthermore, if we assume that the molecule of oleic acid is a square prism we can calculate that the maximum area it can cover by lying flat on its side is only 111.2 sq. Å. But in Emulsion 8 there was one soap molecule for every 153.0 sq. Å. of interface. Apparently phenol was also a constituent of the protective film. Phenol is a necessary constituent of emulsions that can be prepared in the concentrated condition and diluted to give a milky emulsion with uniform globules. Attempts to prepare such emulsions with a simple internal phase, such as *iso*-amyl ether or geraniol, were unsuccessful. Determinations of the interfacial tension between solutions of phenol in toluene and solutions of phenol in water, made in this Laboratory by Mr. George W. Josten, indicate that phenol is very strongly adsorbed at the interface.

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[4] Griffin, This Journal, **45**, 1648 (1923).

Finally, in order to see whether both curves approach the same asymptote (area = 17), Emulsion C3 was prepared and investigated. The concentrated emulsion resembles Emulsions 1 to 8; but it was diluted with water containing only 1.303 mg. of phenol per cc. so that the phenol concentration in the dilute emulsion is 3.87. Consequently, it should lie on Curve B. The point as plotted in Fig. 1 indicates that both curves approach the same asymptote.

Evidently the minimum area of interface per molecule of soap is 17 sq. Å. Langmuir,[5] Adam[6] and others have found that the area of the carboxyl group is 22 sq. Å. A possible explanation of the disagreement is that in the closely-packed films of Emulsions 1, 2, 3 and C3, the heads of the molecules are drawn into the water to various depths and the hydrocarbon chains are packed as closely as possible. If this view is correct, then 17 sq. Å. may represent approximately the cross-sectional area of the hydrocarbon chain of oleic acid. In emulsions containing lower concentrations of soap in the aqueous phase, the molecules of soap in the film are less closely packed and phenol is also present in the film.

Equilibrium between Soap in Film and Soap in Solution.—In the centrifuging of the dilute emulsions no time was lost between the moment the emulsion was diluted and the moment the centrifuge reached full speed. (This was considered to be the moment of separating the cream from the external phase.) The operations of weighing equal samples into the centrifuge tubes and of bringing the centrifuge up to speed required 25 minutes.

The question may well be asked, whether at the moment of separating the emulsion there was an equilibrium between the soap in the interfacial film and the soap in solution in the aqueous phase, or whether there is a tendency for the soap to leave the film and go into solution. To throw light on this question we diluted Emulsion 8 in the usual manner but let it stand for various lengths of time before centrifuging it. The different parts were then analyzed as usual, and it was found that for times between diluting and centrifuging of 25, 78 and 211 minutes, the percentages of soap in the film were 3.33, 3.21 and 2.98, respectively.

The results indicate a small loss of soap from the film, slightly too large to be attributed to experimental error. If, then, we admit that soap does slowly leave the film, we can account for the fact by two different explanations. (1) It may be that there is not an equilibrium between the soap in the film and the soap in solution, and that the soap in the film gradually dissolves, thus increasing the average area of interface covered per molecule of soap; or (2) it may be that the area per molecule of soap is constant and the loss of soap from the film is due entirely to decreasing the total area of film by slow separation of the toluene. This latter assump-

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

[6] Adam, *Proc. Roy. Soc.*, **99A**, 336 (1921).

tion is not opposed to the existence of an equilibrium between the soap in the film and the soap in solution.

The question concerning the existence of the equilibrium was answered by the following experiment. Emulsion 8 was diluted as usual. After it had stood for a few minutes a small quantity of very concentrated sodium oleate solution was added so that the total soap concentration of the external phase was the same as that of Emulsion 8E. This emulsion, called 8F, was then centrifuged and analyzed as usual.

If an equilibrium exists, some of the soap added after dilution will go into the interface and the average area of interface covered per molecule of soap would agree with Emulsion 8E (38.1 sq. Å.); but if there is not an equilibrium and if the soap in the interface gradually leaves the film, then the additional soap will not go into the film and the area per molecule of soap will agree with Emulsion 8 (153.0 sq. Å.). The percentage of soap in the film was found to be 3.67. From this we can calculate that the average area of interface covered per molecule of soap was 42.7 sq. Å. This is a fair agreement with the value for Emulsion 8E; the slight discrepancy is probably due partly to experimental error, and partly to the fact that separation of oil had caused a slight decrease in the total area of film.

We conclude, therefore, that there is a dynamic equilibrium between the soap oriented in the film and the soap dissolved in the water.

Sodium Stearate.—Attempts were made to use sodium stearate as the emulsifying agent, but it was found that soaps of stearic acid are not sufficiently soluble to give satisfactory emulsions.

Summary

1. Emulsions of the oil-in-water type, containing a solution of phenol in toluene as the internal phase and sodium oleate as the emulsifying agent, have been studied.

2. Variation of concentration of soap in the external phase of these dilute emulsions causes a variation in the average area of interface covered per molecule of soap.

3. The concentration of phenol in the dilute emulsion also affects the average area per molecule of soap. To a limited extent the phenol can enter the film in substitution for the soap.

4. Within the range studied, the area of interface covered per molecule of soap is in agreement with the hypothesis that the protective film is composed of a monomolecular layer of oriented molecules.

5. When the soap concentration in the external phase of the dilute emulsion exceeds 0.01 M, the protective film is composed of closely packed, oriented soap molecules, occupying an average area of 17 sq. Å. each.

6. In these emulsions neighboring carboxyl groups are probably drawn into the water to different depths. It is suggested that 17 sq. Å. may

represent the average cross-sectional area of the hydrocarbon chain of oleic acid.

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IONIUM. I. RECOVERY OF IONIUM FROM CARNOTITE. II. ADSORPTION OF IONIUM-THORIUM BY BARIUM SULFATE. III. IONIUM-THORIUM RATIO IN CARNOTITE[1]

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I. Recovery of Ionium from Carnotite Ore

Although a large quantity of carnotite ore has been worked for its uranium, vanadium and radium content during the last ten years, apparently no attempt has been made to recover the ionium. Constancy of the purely α-ray activity of ionium makes it useful in science, and it is probable that commercial uses might be found if sufficient quantities were available.

Ionium is an isotope of thorium, and thorium, in turn, is found in variable quantities in most mineral deposits. The ionium content of an ore is directly dependent on the uranium present, but is independent of the thorium.

Since ionium has little commercial value, it would have to be obtained as a by-product in the extraction of radium, and the extra expense incurred by its recovery would have to be small. This study began with an investigation of the precipitation of ionium and thorium from solution.

Procedure.—Direct precipitation of ionium with oxalic acid from solutions obtained by boiling carnotite with strong acids was unsuccessful. The presence of large amounts of other substances extracted from the ore seemed to prevent the precipitation of the oxalate. Precipitation of the fluoride with hydrofluoric acid gave good results, but the precipitate was bulky and hard to handle. The difficulty in handling hydrofluoric acid also makes this method unsatisfactory.

Ionium can be extracted with dilute acids, but results vary with different types of carnotite. From a relatively high-grade carnotite containing 18% of uranic oxide, boiling with twice its weight of hydrochloric acid (d., 1.09) brought practically all of the ionium into solution, while the same treatment of a carnotite concentrate, containing 3.5% of uranic oxide, seemed to leave about 75% of the ionium in the insoluble residue. As reported by Plum,[2] it was necessary to fume this residue with sulfuric acid to render the ionium soluble.

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[1] From a dissertation submitted to the faculty of the University of Pittsburgh in partial fulfilment of requirements for the degree of Doctor of Philosophy.

[2] Plum, This Journal, 37, 1797 (1915).