

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF RUTGERS COLLEGE AND THE STATE UNIVERSITY OF NEW JERSEY]

## MONOMOLECULAR FILMS OF SODIUM RICINOLEATE IN EMULSIONS

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Langmuir<sup>1</sup> and Harkins<sup>2</sup> have expressed the opinion that in emulsions in which soap is the emulsifying agent the droplets of oil are surrounded by a film of soap one molecule thick. It is supposed that the molecules in this film are oriented with their active groups, carboxyl, hydroxyl, and double bond toward the water and the hydrocarbon chain toward the oil. Griffin,<sup>3</sup> working with emulsions of kerosene oil in water and palmitic, stearic and oleic soaps, determined the average area of interface covered by each molecule of soap. His figures are somewhat larger than those which Langmuir obtained, working with the free acids on a surface film of water. When the difficulty of the determination is taken into account, however, the agreement is good.

The purpose of the present work is to determine the average area of interface covered by a sodium ricinoleate molecule in emulsions consisting of a solution of phenol in toluene, dispersed in water. The work was undertaken before the appearance of Griffin's article and without any knowledge that such work was in progress. No repetition or conflict has resulted, however, since the emulsions and the methods are quite different.

Since the lower fatty acids in aqueous solution decrease the surface tension of water, it follows that they are adsorbed at the surface. Langmuir has pointed out that when the solution is dilute the hydrocarbon chain of an adsorbed molecule lies flat on the surface. But in more concentrated solutions the adsorbed molecules are oriented with their chains perpendicular to the surface.

It is reasonable to expect that sodium ricinoleate will show a similar phenomenon when it is adsorbed at the interface in oil in water emulsions. In dilute soap solutions we may expect to find the molecule lying flat at the interface, and in more concentrated solutions the COONa group is perhaps the only group at the interface, the remainder of the molecule being drawn into the oil. The cross section area of the carboxyl group has been measured by Langmuir<sup>1</sup> and Adam<sup>4</sup> and found to be 22 square Ångström units. The COONa group may occupy a slightly larger area. If it be assumed that the cross section is square in shape we can calculate

<sup>1</sup> Langmuir, *Met. Chem. Eng.*, **15**, 468 (1916); *THIS JOURNAL*, **39**, 1848 (1917).

<sup>2</sup> Harkins, Davies and Clark, *ibid.*, **39**, 541 (1917).

<sup>3</sup> Griffin, *ibid.*, **45**, 1648 (1923).

<sup>4</sup> Adam, *Proc. Roy. Soc. London*, **99A**, 336 (1921).

that the area occupied when the molecule of ricinoleic acid lies flat is 110.8 square Å. Thus we should expect the average area of interface per molecule to vary between the limits 22 square Å. and 111 square Å.

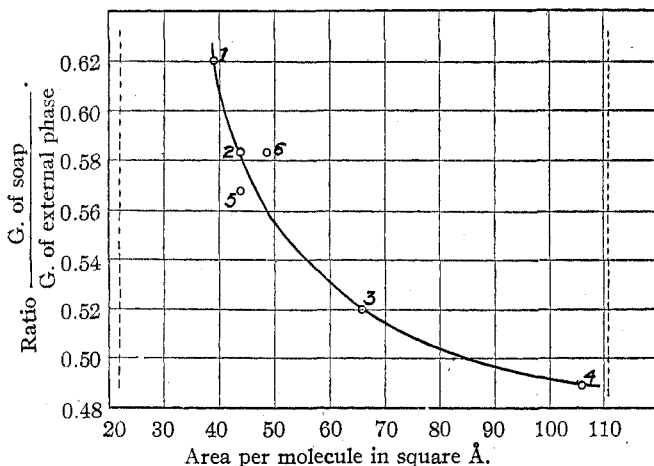


Fig. 1.

### Experimental Part

**Materials Used.**—The oil used as the internal phase was a solution of u. s. p. phenol in toluene, containing 20% of phenol by weight. The toluene was a good quality, having a specific gravity of 0.866 at 20°. Sodium hydroxide purified by alcohol was used.

To prepare the ricinoleic acid a good quality of castor oil was saponified with sodium hydroxide and treated with hydrochloric acid. Stearic acid was removed by filtration. The product was transparent but had a slight color somewhat like that of dil. dichromic acid. A comparison between its properties and those of the pure acid with the theoretically correct numbers is given in Table I.

TABLE I  
PROPERTIES OF RICINOLEIC ACID.

Ricinoleic acid	Saponification no.	Iodine no.	d <sub>4</sub> <sup>15</sup>
Calcd.....	188.1	85.2	0.945
Found.....	189.4	93.4	.9467

The difference in saponification number is insignificant. The high iodine value indicated that the product contained some doubly unsaturated compound. Assuming that the only impurity is ricinostearolic acid, or an acid containing two double bonds, calculation shows that the prepared material was 90.5% pure. Since most unsaturated liquids are more dense than the corresponding saturated compounds, the slightly high density confirms the view that ricinostearolic acid is the chief impurity. Hence, it may be assumed that the acid was of a purity of at least 90%.

**Preparation of Emulsions.**—The materials listed in Table II were placed in an Erlenmeyer flask. The flask was stoppered and shaken until a transparent reddish-brown liquid, apparently homogeneous, was formed. The shaking required about two minutes.

TABLE II  
COMPOSITION OF "CONCENTRATED" EMULSION  
60.0 G. of oil and 5.0 g. of water were used in each mixture

Ricinoleic acid, g.....	21.7	14.5	10.9	7.2	14.5	14.5
NaOH soln. (d., 1.8) g.....	10.8	7.2	5.4	3.6	6.2	7.9

The "concentrated" emulsion was allowed to stand for three days or more before it was used. This appears to increase the uniformity of the globules with respect to size. When water is added in small quantities, the emulsion changes to a cloudy jelly. But when some "concentrated" emulsion is added to a relatively large volume of water a "dilute" emulsion results which resembles milk in appearance. The globules of such an emulsion are very uniform in size. The "concentrated" emulsions showed no signs of separating when kept for longer than a year. The dilute emulsions cream on standing and a very slow partial separation of oil also takes place.

**Analysis of the Emulsions.**—Ten cc. of a "concentrated" emulsion was diluted to 500 cc. with water. Part of the dilute emulsion was centrifuged immediately at a speed of 3000 r.p.m. in closed tubes, to prevent evaporation. The emulsion thus formed was separated into two equal parts. The lower part consisted of soap solution practically free from oil globules, while the upper portion contained twice as many oil globules as the original dilute emulsion. Both upper and lower portions and also a sample of the original dilute emulsion were analyzed as follows.

Fifty cc. of the liquid to be analyzed was transferred to a separatory funnel and 40 to 50 cc. of 0.01 *N* to 0.02 *N* hydrochloric acid was added from a buret, so that the solution was slightly acid. The toluene and fatty acid were removed by extraction with 50 cc. of ether which had been freshly distilled from potassium hydroxide. The ether was washed twice with water and the washings were added to the main portion. Cochineal was then added as an indicator and the excess of acid was titrated with 0.01 *N* alkali.

If *a* is the acid used to neutralize 50 cc. of the lower fraction, *b* that used to neutralize 50 cc. of the whole dilute emulsion and *c* the fraction of the external phase in the whole dilute emulsion as computed from the composition of emulsion, then the percentage of soap in the film is  $\frac{b - ac}{b} \times 100$ .

**Measurement of Globules.**—The diameter of the globules was determined by two independent methods. One method was to count the globules in a given volume. Knowing the composition of the emulsion, the average volume of the globules could be calculated and hence the average diameter. As the globules were too small to count by the ordinary hemacytometer method, the following method was used. The hemacytometer was first treated with a very dilute solution of stearin in ether con-

taining not more than 0.8 mg. per 10 cc. so as to leave a very thin layer of the fat when the solvent evaporated. The globules on striking the glass were retained there by the fat film. In about two minutes practically all the globules had affixed themselves to the slide. The globules in any square of the hemacytometer could easily be counted. To this count were added the few globules remaining free in the liquid, and also the globules adhering to the cover glass immediately above that square. This number was equal to the number of globules originally contained in the volume whose dimensions are those of the square and the depth of the cell. A hemacytometer with 0.1mm. depth was used. For this determination the emulsion was diluted, one volume to 500, with water which had previously been shaken with an excess of oil of the same composition as the internal phase of the emulsion. Eight to ten squares were counted and the counts averaged.

The second method consisted in fixing the globules on the slide as described above and measuring them with a filar micrometer eyepiece. An average of at least 10 globules was taken. A 2mm. objective was used in both methods.

Chamot<sup>5</sup> states that the limit of accuracy of microscopic measurements is  $0.05\mu$  under favorable conditions but that ordinarily the limit is  $0.2\mu$ . The difference in results between the two methods was less than  $0.2\mu$  in every case and in most cases it was less than  $0.1\mu$ . The mean of the two was used in calculating the average area occupied by a molecule of soap in the interface.

### Discussion of Results

The results are tabulated in Table III and plotted in Fig. 1.

TABLE III  
RESULTS

Emulsion number	Ratio g. of soap to g. of external phase in "concentrated" emulsion	Diameter of globules $\mu$	Soap in interface %	Av. area per molecule of soap in sq. Å.
1	0.621	1.336	1.734	39.2
2	.583	1.336	2.32	44.2
3	.520	1.260	2.18	66.2
4	.489	1.386	1.88	105.6
5	.567	1.509	2.44	43.6
6	.583	1.242	2.25	48.8

It is evident that the average area covered per molecule does vary as the concentration of soap in the external phase of the concentrated emulsion is changed. Attempts were made to extend the curve further to the left by making an emulsion richer in soap, but the resulting "concentrated" emulsions were not clear and could not be used. No effort was made

<sup>5</sup> Chamot, "Elementary Chemical Microscopy," John Wiley and Sons, 1921, 2nd ed., p. 175.

to extend the curve downward and to the right. It is probable that an emulsion with less soap than No. 4 would be unstable. Emulsion 6 contained a 10% excess of alkali. Within the limit of experimental error, it is identical with No. 2 as regards the average area of interface per molecule. Emulsion 5 was prepared with a 16% excess of ricinoleic acid. This excess of acid is dissolved in the internal phase.<sup>3</sup> This point also lies on the curve within the limits of experimental error.

In interpreting the results indicated by the curve it is necessary to bear in mind that the ratio, internal phase to external phase in the "concentrated" emulsions, was not kept entirely constant. This was necessary in order to avoid the formation of jellies when the concentration of soap is increased beyond a certain limit. Impurities in the ricinoleic acid are also the cause of a slight error. The total experimental error is probably not more than 10%. This error is not sufficient to account for the observed variation of the average area of interface covered per molecule of soap. The inevitable conclusion is that the area per molecule does vary with the concentration of soap.

Hydrolysis of the soap is not an appreciable factor, for addition of a 10% excess of alkali which, according to Griffin,<sup>3</sup> prevents hydrolysis, did not cause an appreciable difference in the average area per molecule. Moreover, if hydrolysis were a factor, Point 6 would be to the left of Point 2 in the curve.

Emulsions of the type described in this paper are being further investigated in this Laboratory.

### Summary

1. Emulsions of the oil-in-water type, containing a solution of phenol in toluene as the oil phase and sodium ricinoleate as the emulsifying agent, have been studied.
2. A method is described for determining, with a probable error of less than 10%, the amount of soap in the interface.
3. The average size of the globules in these emulsions has been measured.
4. The average area of interface covered by a molecule of sodium ricinoleate is a function of the concentration of soap in the external phase of the concentrated emulsion. The area covered in the various cases, however, is not in disagreement with the theory that there is a monomolecular soap film at the interface.

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