VOL. XLI. APRIL, 1919. NO. 4.

THE JOURNAL

OF THE

American Chemical Society

with which has been incorporated the

American Chemical Journal
(Founded by Ira Remsen)

MEASUREMENT OF THE THICKNESS OF FILM FORMED ON GLASS AND SAND.

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Received July 11, 1918.

Introduction.

A large amount of work has been done up to the present time on the formation of a film on the surface of glass or silica, in which water has been used as the liquid to produce the film. Thus, Ihmori,[1] Parks,[2] Briggs,[3] Katz,[4] and Langmuir,[5] give values for the thickness of the film formed on glass, silicate or quartz surfaces.

There is a considerable difference in the values obtained as might be expected, since the materials used differed considerably in chemical composition and nature of surface. A part of the material was in the form of small grains (sand and quartz), some being relatively coarse and some extremely fine powder. The glass used was in the form of thin sheets, in some cases curved (spherical), and in others plane. Each of these factors would have an influence on the thickness of film obtained, as would also the temperature and vapor pressure at which the film was formed.

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[1] *Wied. Ann.*, 31, 1006 (1887).

[2] *Phil. Mag.*, [6] 5, 517 (1903).

[3] *J. Phys. Chem.*, 9, 617 (1905).

[4] *Proc. Acad. Wetenschappen*, 1915, p. 445.

[5] THIS JOURNAL, 38, 2221 (1916).

Some typical results obtained for the film thickness are given in the following table:

TABLE I.—FILM THICKNESS VALUES.

No.	Nature of material.	Film thickness.	Investigator.
1.	Glass globes	0.0000033	Ihmori
2.	Cotton silicate (glass wool)	0.0000133	Parks
3.	Sand (microscopic powder)	0.00000045	Briggs
4.	Quartz (very fine powder)	0.0000013	Katz
	Anorthite (as above)	0.0000062	Katz
5.	Glass (incandescent lamp globes)	0.00000166	Langmuir

There are two theories regarding the formation of a film on a solid. According to the first the force acting is physical in its nature, and the intensity of its effect varies inversely as some power of the distance between the two molecules concerned. The force is similar to the force of gravitation but acts through the distance between molecules. According to this theory successive layers of molecules may be built up on the surface of a solid to a thickness such that the attractive force of the solid just equals the tendency of the outer layer of the film to evaporate.

The second theory assumes that a chemical reaction takes place and that the water taken up becomes a part of a more or less stable chemical compound. According to this theory a variable amount of water could be taken up by solids depending only on the capacity of the solid to form a loose compound with it.

The second theory has usually been assumed to hold for the film of water forming on glass surfaces, free or loosely combined alkali present in the glass, being the substance with which the water reacts. Ihmori,[1] found that keeping the glass in boiling water for some time decreased the amount of water which it would take up. He believed that alkali was removed during this boiling, and that the decrease in the amount of moisture taken up was due to this fact.

It seemed worth while to check the values obtained using glass and sand, having known surfaces, if possible. Since no work had been done to determine the thickest film which can form without free liquid appearing, a method of doing this was worked out. This film was compared with the film formed with other liquids to see whether there was any basis for the theory that a chemical compound formed with water.

Materials.

Solids: Sand.—Ordinary river sand was used. It was treated with conc. hydrochloric acid until no test for iron was shown. The acid was then washed out with distilled water and the sample dried in the air. Four samples were obtained by sifting. The first sample contained all of the sand which passed the 10-mesh screen but was retained by the 20-mesh screen. The second, third and fourth samples consisted of the

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[1] *Loc. cit.*

fractions from the original lot retained by the 40-, 60- and 80-mesh screens, respectively. These are called 10-, 20-, 40- and 60-mesh sands in this paper.

The grains in this lot of sand were far from spherical, no two diameters being the same. An approximation of the surface was obtained by weighing a counted number of grains (4000 to 5000), to get the average weight per grain, and determining the specific gravity. On the assumption that the grains were spherical the diameter and surface of a single grain could be calculated. It was realized when these values were obtained that they were at best only approximations.

Ottawa Sand.—A single sample of sand called in this paper "Ottawa Sand," consisted of well-rounded grains. This sample gave values by the above mentioned method which were very close to the true value for the diameter and surface. It was considered to be of known surface.

Glass Pearls.—The glass pearls used were solid, round and of various sizes, as indicated in the table below. A few, which were poorly formed, were removed from the lot by rolling them down an inclined board. Those which were not round could be easily picked out in this way. The pearls were from two different sources, and apparently of different kinds of glass. They differed considerably in specific gravity.

The first lot was purchased at retail. The material was sold under the name of "Glistening Dew" and was used to decorate fancy cards. Two samples were obtained from this lot by "elutriation." A quantity of the pearls were placed in a tube and delivered from it at a slow rate into a rising column of water. Under these conditions by properly regulating the current, the lighter ones were carried up and the heavier ones sank to the bottom. These samples are No. 9 and No. 10, in the tables.

The second lot consisted of 5 samples, Nos. 1, 3, 5, 7, and 8. The individual pearls in each sample were of the same diameter except for No. 7 which contained pearls of two sizes. These samples were obtained from Germany and when received were coated with dye.

All of the samples were cleaned by boiling in conc. nitric acid, washing free from acid and air drying. The diameter, surface and volume of the pearls in each lot were determined by the method used for the sand.

Liquids.—Distilled water and a series of organic liquids were used to form the films.

Specific Gravity of Solids.—The specific gravity of the sand and the pearl samples was determined by displacement of water. A specific gravity bottle was weighed, empty, full of water, and then with a known weight of sample substituted for a part of the water. To avoid air bubbles, the weighed sample was run into water in a fine stream. The bottle was then placed in a partial vacuum and let stand for several hours before the final filling and weighing was done.

Method of Determining Film Thickness.—In most of the previous work done on determining film thickness, the film has been formed by subjecting the sample to the vapors of water and establishing an equilibrium at the contact surface. Usually the water vapor was at or near its saturation point. As a check on the results obtained in this way, the method used in this paper was evolved, which consists in getting an equilibrium of the film, by the use of liquid water rather than vapor, and getting it with the air saturated. This would give the maximum film which could form, and at the same time, would, by the magnitude of the results obtained, indicate whether there was an essential difference between a film formed from the vapor and one formed from the liquid.

Considering the sand and pearl samples already described, the method involves the addition of small amounts of liquid to them, thus gradually building up on them a film of water. As successive layers of molecules are added to this film a thickness is finally reached at which the surface molecules act as normal molecules. That is they evaporate, flow, exert surface tension, etc. Any liquid beyond this amount would remain in the liquid condition. It was only necessary to get a definite test for the point at which these new properties exhibit themselves.

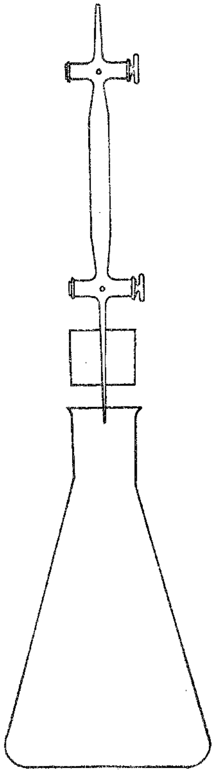

Fig. 1.

Apparatus.—The first and simplest arrangement used for this purpose consisted of a buret and an Erlenmeyer flask. The weighed sample of sand was placed in the flask and liquid added from the buret a drop at a time, with thorough shaking between, until a final drop caused the grains to stick to the flask. When this occurred water was present as free liquid. This "sticking point" was taken as the end-point of the titration.

An ordinary buret soon proved unsatisfactory for delivering the liquid, especially so in cases where the liquid was volatile. Delivering the liquid into an open flask also introduced errors with these liquids. To avoid these losses due to volatility of the liquids, and to limit definitely the volume of air saturated during a titration, a weight buret, Fig. 1, was substituted for the ordinary buret and the liquid was delivered into a closed flask.

Procedure.—In carrying out a single determination the following procedure was used: 200 g. of the air-dry sample was weighed and transferred to the clean, dry, Erlenmeyer flask. The flask was then closed by means of the stopper carrying the weight buret. The liquid was run in a drop at a time, the sand being thoroughly shaken after the addition of each drop. Toward the end of the titration only fractions of a drop were added, these being removed by tipping the flask to bring the pearls in contact with the tip of the buret.

A final addition of liquid caused a large number of the pearls to stick to the walls of the flask. The weight of the liquid used gave the amount of liquid taken up when a film of maximum thickness formed. Corrections were made in the case of volatile liquids for the amount of liquid necessary to saturate the air in the flask under the working conditions.

After a determination in which sand was used the sand was air-dried and then heated to strong redness in a large platinum dish. After partial cooling it was transferred to a desiccator over phosphorus pentoxide, and kept for future determinations. The pearl samples were not ignited. They were boiled with strong nitric acid, to which some hydrochloric was added and were air-dried after being washed free from acid.

This procedure was followed for the purpose of determining whether a chemical reaction was involved in the holding of the liquid. If the pearls were air-dried, there would be much less tendency for an unstable chemical compound to be broken down, than if they were dried *in vacuo*. The intention was to have the chemical compound, if it formed at all, present at the time of titration, and not formed during it. It seemed improbable that any chemical compound formed by the method used, would decompose on exposure to ordinary conditions of temperature and pressure.

Experimental.—In order to obtain the relationship between surface and amount of liquid to produce sticking, a series of determinations was conducted using the glass pearls, water being used as the titrating liquid. Under these conditions the only variables were those of the solid, including the nature of the surface, the size and the specific gravity of the pearls. For samples from the same source no difference in the nature of the surface was to be expected.

During the whole of this work an attempt was made to find other material suitable for titration and of known surface. Results with this material would permit conclusions to be drawn regarding the capacity of different surfaces to hold liquid films and would thus show the effect of the other variants. No other material was found that could be used in this way.

Reproducibility of Results.—The apparatus as used was subject to some error due to the fact that the quantity of liquid added could only be controlled by opening the lower stopcock of the weight buret. To give an idea of the accuracy obtainable with this apparatus, a series of results obtained with each of two liquids is included. The remaining liquids gave results correspondingly accurate.

Liquid.	Water.	Nitrobenzene.
Sample	200 g. pearls No. 8	200 g. pearls No. 3
Weight of liquid, grams	0.119	0.040
	0.119	0.041
	0.117	0.039
	0.116	0.042
	0.120	0.042
	0.121	0.038
	0.116	
	0.118	
Average	0.118	0.040
Greatest variation from average	0.003 = 2.5%	= 5%
Variation between highest and lowest values	4.2%	10%

The percent error introduced depended principally on the amount of surface titrated or on the amount of liquid added, the greatest variation amounting to from 0.004 to 0.006 g. of liquid.

The results obtained and the calculations of film thickness are given in the accompanying table:

TABLE II.—TITRATION VALUES USING WATER.

Sample. Pearls.	Diameter in cm.	Surface sq. cm./g.	Sp. gr.	Weight.	Titration liquid per g.	Film thickness.
No. 1	0.1367	14.67	3.101	0.003988	0.000190	0.0000129
No. 3	0.1180	17.09	3.090	0.002626	0.000218	0.0000128
No. 5	0.0808	24.03	3.079	0.000853	0.000303	0.0000126
No. 7	0.0542	35.46	3.125	0.000261	0.000402	0.0000113
No. 8	0.0410	46.40	3.069	0.000121	0.000595	0.0000128
No. 9	0.0540	44.93	2.505	0.000206	0.000297	0.0000066
No. 10	0.0460	53.14	2.496	0.000122	0.000375	0.0000070
SANDS.						
Ottawa	0.0790	28.58	2.656	0.000686	0.000374	0.0000130
10-mesh	0.0494	46.00	2.643	0.000168	0.001310	0.0000285
20-mesh	0.0430	52.28	2.646	0.000110	0.001120	0.0000214
40-mesh	0.0280	81.90	2.650	0.000030	0.001100	0.0000135
60-mesh	0.0170	129.57	2.666	0.000007	0.001480	0.0000114

Discussion of Results.—The liquid required for a titration may be used to form a uniform film of liquid over the surface of the pearls up to the thickness at which flow would occur. If this is the case a negligible amount of liquid would be required actually to support the grains, this amount being added after the uniform film had been added, and "sticking" would result from a concentration of this added amount at the contact surface of flask and pearl through the action of capillary forces.

On the other hand, the whole amount of liquid required may be necessary to support the pearls through the action of surface tension. In this case no film would form but all of the liquid added would concentrate at the contact surface, and "sticking" would occur as soon as the surface tension was sufficient to support the pearl.

In order to determine which of these two hypotheses held or whether the amount used in titrating was the resultant of both effects, some calculations were made of the amount of liquid necessary to support a single grain. Fig. 2 will explain the letters used and the method of calculation followed.

Consider a pearl weighing 0.0001 g., held to the surface of the flask by surface tension. The liquid holding the pearl may be considered as occupying a volume represented in section by (OBCED), the lowest level of this volume being the circumference of a circle whose radius is *a*. Surface tension may be considered as acting along this circumference. If the surface tension and the weight supported by it are known, the length of the circumference required to support the pearl is given 0.0001/sur. ten. Substituting actual values and placing the quotient equal to the circumference of a circle enables one to calculate the value of *a* in the same units as are used for expressing the surface tension (cm.). Having the value of *a*, the value of *h* (thickness of liquid acting) may be calculated, since by geometry,

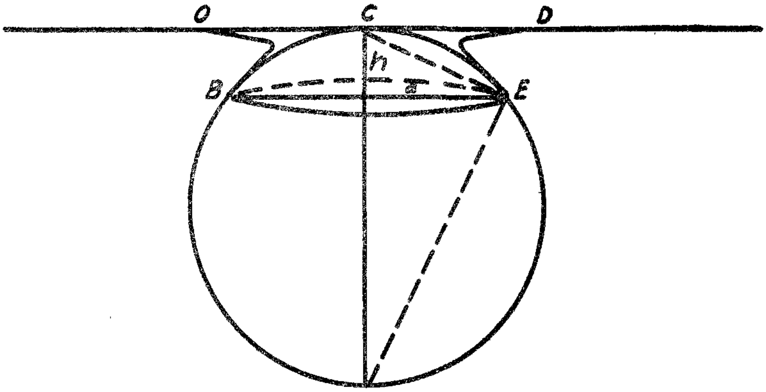

Fig. 2.

$$h : a :: a : (2R - h),$$

and all of the terms except *h* are known.

Knowing both *a* and *h*, the volume of liquid holding the pearl can be estimated. It was assumed that the volume of liquid necessary to support the pearl would be that required to half fill the volume represented on the figure by (OBED). This is believed to be in excess of the actual amount needed. Calculating this value for the smallest pearl used, one weighing 0.00012 g. gave 0.0_837 cc. per g. of pearls. Calculating the same value for pearls No. 1, the heaviest pearls used, gave 0.0_58 cc. per g. of pearls. These amounts are negligible when the amounts required for a titration are considered. This shows clearly that although the end-point is marked by the appearance of "sticking," which is a surface-tension effect, surface tension itself cannot account for the liquid required for a titration.

The amount of liquid required is directly proportional to the surface, and the film thickness is uniform for the same kind of glass.

As to the actual thickness of film found, it is of the same order as that found by earlier investigators who worked with the vapor phase of water in forming the film. The results are higher than those of all except Parks. It does not seem probable, in view of the results obtained, that there is any difference in the nature of the film itself, whether water in the vapor phase or water in the liquid phase is used to form the film. It also seems probable that what actually takes place on the surface of the grain is a condensation of water vapor. In the titrations in which water was used to form the film it was found that the titrated sample on air drying, would again take up the same amount of liquid. It is difficult to see how this could take place repeatedly if a chemical reaction was involved in holding the liquid.

The results obtained with samples No. 9 and No. 10, are only about half as large as those obtained with the rest of the samples. This can only be due to a different surface capacity for holding liquid. The results are close to those obtained by Katz with ornithite, and by Ihmori with glass globes.

Ottawa sand gives the same value for film thickness that the larger series of pearls does. It seems probable that this is a chance agreement, since the surface of the sand differed considerably from that of the pearls, both in hardness and in texture.

As a whole the results indicate that there are two factors which influence the amount of liquid necessary to form the maximum thickness of film. The first factor is the amount of surface, the actual area that the film must cover. The second is the nature of the surface itself, its capacity to hold a film.

Not a great deal is known regarding the variants which determine the capacity factor of a surface. It is probably related to the free energy present in the atoms of the surface layers.

The work up to this point indicated that the film thickness should be independent of the liquid used, providing the liquid is not too viscous to spread readily. It also indicated the desirability of applying the titration method to the determination of the surface of irregular particles like sand grains.

For the purpose of obtaining surface values for the meshed sands, complete titrations for each of these samples with water and with each of the organic liquids was carried out. An attempt was made also to titrate finer sands, 100-mesh, 150-mesh, 200-mesh. These however, would not permit of an even distribution of the liquid over the surface, and no satisfactory titrations were obtainable.

To determine whether the same thickness of film would be found with a different liquid, titrations were carried out first with the pearls and then with the sands making use of the organic liquids. The determinations with the pearls were not completed when they were found to check closely for the first liquids used but those on the sands were completed for all of the liquids.

The organic liquids used were chosen so that the specific gravity, volatility, surface tension, etc., varied.

The results obtained from these two series of titrations are given in Table III, and will be discussed together.

TABLE III.—TITRATION VALUES FOR SANDS AND PEARLS WITH ORGANIC LIQUIDS.

Sands.

Liquids.	10-mesh.	20-mesh.	40-mesh.	60-mesh.	Ottawa.
Nitrobenzene	0.00136	0.00117	0.00109	0.00148	0.00039
Water	0.00133	0.00108	0.00112	0.00151	0.00037
Aniline	0.00122	0.00107	0.00109	0.00148	0.00039
Dimethylaniline	0.00131	0.00108	0.00107	0.00155	0.00039
Phenyliodide	0.00126	0.00112	0.00112	0.00149	0.00039
Toluol	0.00134	0.00116	0.00110	0.00146	0.00038
Turpentine	0.00131	0.00116	0.00108	0.00142	0.00039
Pyridine	...	...	0.00109	...	...

Pearls.

Liquids.	No. 1.	No. 3.	No. 5.	No. 8.	No. 9.	No. 10.
Nitrobenzene	0.00018	0.00020	0.00030	0.00056	0.00027	0.00040
Water	0.00019	0.00022	0.00030	0.00059	0.00030	0.00037
Aniline	...	...	...	0.00055	0.00023	0.00039
Dimethylaniline	0.00017	0.00022	0.00032	0.00059	0.00029	0.00045
Phenyliodide	0.00018	...	...	0.00059	0.00030	0.00039
Toluol	...	0.00021	...	0.00053	0.00031	0.00038

Discussion of Results.—The results show that the thickness of the film is independent of the kind of liquid used for titrating, and that the sand titrations can be checked with as good an accuracy as titrations of pearls. Occasional results vary, but the uniformity for the whole series is pronounced. This proves definitely that the surface tension of the liquid has no effect on the amount of liquid required for a titration. The surface tension of water is much greater than that of the other liquids but the volume required per gram is the same. This could not be true if the surface tension influenced the amount of liquid required to produce "sticking."

It also proves that there is no chemical reaction in the ordinary sense of the term, when a film of water forms on glass. While it might be possible to imagine such an effect between water and glass, it is obviously impossible to do so with the rest of the liquids of the series. In addition to this the calculated film thickness for different sizes of pearls is found to be the same, showing that the volume for titration varies with the surface.

The definite conclusion can be drawn that these films are not due to the formation of a chemical compound, but that they are held by the free surface energy of the solid. It seems certain that the same force holds a thinner film.

While these films are formed by the addition of liquid to the solid, the inference is that the same conclusion may be drawn for a film formed from the vapor phase. This inference is supported by the fact that the values obtained for the film thickness when formed from the vapor phase are only very slightly lower than those formed by the addition of liquid. It seems probable that a liquid film forms in both cases, but that with the unsaturated vapor phase it never becomes thick enough to show as a normal liquid on the surface of the solid, while when liquid is used the formation of free liquid marks the end of the titration and indicates the thickest film that can form without free liquid being present.

In titrating sands a simple relationship such as was found for the pearl samples does not exist between titrated amount and calculated surface. This is partly due to error in calculating the surface, on the assumption that the grains are spherical, and partly to the fact that extra liquid is required to fill the etchings in the surface. However, if relative effective surfaces are sought they may be expected to be proportional to the titration values since there is no application of the surface which would not involve the etchings and so produce results which would be proportional to those obtained by the titration method.

Summary.

This paper describes a new method of obtaining the thickness of the maximum film which can form on a surface without free liquid being present. Evidence is presented to show that the liquid forming the film does not combine chemically with the solid. The method has been applied to sand and to glass, and films have been formed with water and with several organic liquids. The film thickness is found to be independent of the liquid used and of the size of the solid particle. The method gives accurate values for the effective surface of sand particles, providing that surfaces of the same kind are compared.

In conclusion I wish to express my indebtedness to Prof. I. H. Derby, for his advice and suggestions in the preparation of this paper.

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