Studies on the Adsorption at the Solid—Liquid Interface. II. On the Thickness of the Adsorption Layer.

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Among many problems regarding the constitution of the adsorption layer, the problem on the thickness of the layer is still attractive. Since the theory of monomolecular adsorption was proposed by Langmuir, this is believed in general, notwithstanding the fact that the direct experimental proof is rather poor especially in the case of the solid—liquid interface. There are several investigations(1) which prove the monomolecular adsorption. However, most of them contain many assumptions in themselves. This problem may be solved if we know directly the surface area of the adsorbent and the adsorbed amount on that surface. Fortunately, the author has been able to measure relatively small amount of adsorption as well as the surface area of glass by making the glass powder of spherical particles.

Preparation of Adsorbent (Spherical Glass Powder). Spherical glass powder has been made by the method which was devised by Bloomquist and Clark,(2) with some modifications.

The apparatus which is shown in Fig. 1, consists of two parts, i.e., the part in which the powder is heated with gas flame to melt the particles into spherical shapes, and the other part in which the powder is collected by a suction apparatus combined with an electric precipitator.

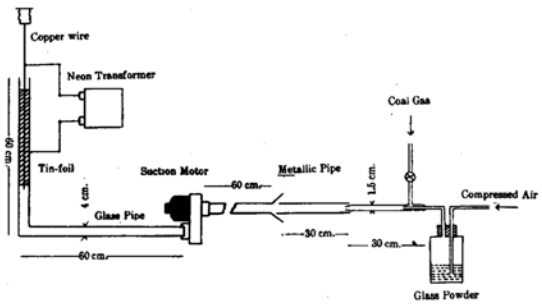


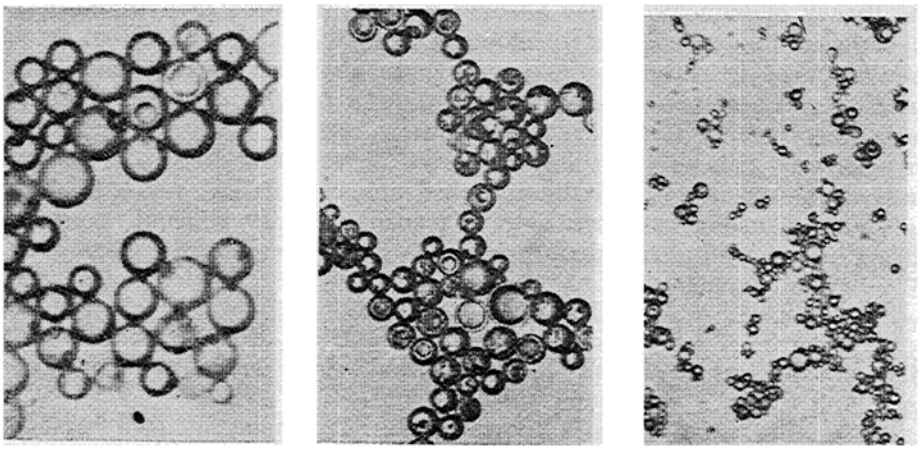
Fig. 1.

The glass powder has been made by crushing glass tubing commonly used in the laboratory. After the large particles have been roughly removed by levigation, the powder is thoroughly dried. A part of them is taken in a vessel, driven into gas flame with compressed air (Fig. 1.), and particles are melted into spherical shapes. Those particles are collected by a suction motor which is connected to an electric precipitator. The precipitator is made of L shaped glass pipe and its diameter is about 4 cm. By using a neon-transformer, electric potential is applied between a copper wire which is hanging in the pipe and a tin-foil which covers

(1) Freundlich, "Kapillarchemie," 1930, P. 320; Harkins and Gans, *J. Phys. Chem.*, **36** (1932), 86; W. Ewing, *J. Am. Chem. Soc.*, **61** (1939), 1317; Fowkes and Harkins, *J. Am. Chem. Soc.*, **62** (1940), 3377.

(2) Bloomquist and Çkark, *Ind, Eng. Chem.*, **12** (1940), 61.

a part of the pipe. After the particles have been captured, the precipitator is taken down, and the particles are poured out with water. In order to remove dust-like substances, the powder has been treated with dilute hydrochloric acid, then with chromic acid mixture and washed with water. As the powder consists of various size of particles, they have been collected in the following three parts by fractional levigation and used as adsorbents. No. 1 is the portion of which particles have settled in the water column, about 30 cm. in height, in 5–20 minutes, No. 2, in 20–40 minutes, and No. 3, in 40 minutes to 24 hours. Fig. 2 is the microscopic photographs of these three portions.



No. 1. No. 2. No. 3.

Microscopic photographs of glass powder. (×300)

Fig. 2.

The specific surface area (S) of the spherical powder is calculated by

$$S = 6 \sum D^2 / \rho \sum D^3 ,$$

where D is the diameter of each particle, and ρ, the density (2.50 for the glass used). The particle size was measured on the microscopic photograph, where the readings of the diameters of 550 particles for No. 1, 700 particles for No. 2, and 2000 particles for No. 3 were taken, and the average specific surface areas for 1 g. of powder were calculated as follows; No. 1: 1070 cm.^{2}, No. 2: 1810 cm.^{2}, No. 3: 4690 cm.^{2}.

For each experiment, the adsorbent is subjected to the following treatment. After washed with freshly distilled alcohol and benzene respectively, using a Soxhlet apparatus, the powder is heated at 250°–270°C for about 6 hours under the reduced pressure of a rotary pump.

Adsorption of Benzoic Acid. One of the methods of measuring the small amount of adsorption consists in determining the change of concentration of a solution before and after the adsorbing procedure by measuring its density, the float method being used. The description of

this method was given in the preceding paper.[3] The accuracy of this method will be greater when the difference of the densities of components of solution used becomes larger. Expecting the so-called "polar and non-polar adsorption" to take place, benzoic acid is used as the solute while benzene as the solvent.

Benzoic acid used was the product designated "Kahlbaum to analysis" and benzene was purified in ordinary way. The experimental procedure was just like as described in the preceding paper. The experiments were also carried out at room temperature.

At first, the powder No. 1 was used as adsorbent, however, the density difference of solution before and after the adsorbing procedure was so small as in the order of the error of this method, and it might also be expected if the adsorption layer, in this case, be so thin as one molecular in thickness. To investigate the amount adsorbed by this method, larger surface area will be necessary. So, the powder No. 3 was next used as adsorbent, and the results obtained are shown in Table 1.

Table 1.

Adsorbent: Spherical glass powder No. 3.
Solution : Benzoic acid/Benzene.

Volume of Solution (c.c.)	Weight of adsorbent (g.)	Initial conc. (mol/l.)	Final conc. (mol/l.)	Amount adsorbed per 1 g. adsorbent (mol)	Area occupied by one molecule
10	5.244	3.56×10^{-2}	3.39×10^{-2}	3.1×10^{-6}	25 sq. Å
10	5.167	1.78 "	1.66 "	2.1 "	38 "
10	5.370	0.89 "	0.74 "	2.8 "	27 "

Adsorption of Palmitic Acid. Palmitic acid, as a typical surface active substance, has been chosen as the second adsorbate. But in this case, a good result in accuracy cannot be expected by the float method, for the difference of density between palmitic acid and benzene is not so large. The surface balance method has been devised instead of the float method to investigate smaller amount of change in concentration of solution before and after the adsorbing procedure.

The principle of the surface balance method is as follows. A definite volume of benzene solution of palmitic acid of known concentration is put on the surface of water. The solution spreads over the surface and, soon after, benzene will evaporate up leaving the monomolecular film of palmitic acid. The surface area of this film can be determined by the surface balance, under a certain surface pressure. Next, exactly the same volume of the solution of unknown concentration (e.g. the solution after the adsorbing procedure), is put on the surface of water and measure the area of the monomolecular film of palmitic acid under the same surface pressure as before. Then the concentration of the latter solution will be known from the ratio of these two values of surface area.

(3) H. Akamatu, this Bulletin, **17** (1942), 141.

In practice, it is preferable to measure the compression curve of the surface film under various surface pressures. In Fig. 3, A is the compression curve of a solution of which concentration is known (C), and B is the one of which concentration is not known (x), a and b are the lengths of the abscissa axis by which the extrapolations of the curves cut the axis. The concentration of the solution B will be found from $x=C\times b/a$.

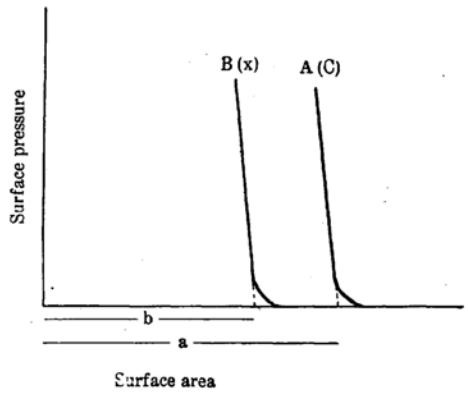


Fig. 3.

In this method, it is necessary to take exactly the definite volume of the solution to put on the surface of water, and this is easily attainable by using an automatic micropipette.

In practice, however, the favourable concentration and the volume of solution, which are put on the surface of water, are limited within a certain range by the ordinal operation of the surface balance. For example, the most favourable concentration of benzene solution dissolving palmitic acid is in the order of 10^{-3} mol/l. In consequence, in the procedure of the adsorption, the concentration of the solution used is also demanded to be not far from this range. By this method, it is possible to investigate the amount adsorbed in the order of 10^{-7} mol or less adsorbate per 1 g. of adsorbent.

The experimental procedure is as follows. About 5 g. of adsorbent is taken in a test tube, and only 5 c.c. of solution is introduced into the tube. The test tube is then hermetically sealed and is shaken at intervals. After about a week, the upper liquid is taken out by using the automatic micropipette, after having been separated thoroughly from adsorbent by centrifuging.

The sample of palmitic acid from T. Schuchardt is recrystallized twice from alcohol. The experiments were carried out at room temperature. Results are shown in Table 2.

Table 2.

Adsorbent: Spherical glass powder No. 2.
Solution : Palmitic acid/Benzene.

Volume of Solution (c.c.)	Weight of adsorbent (g.)	Initial conc. (mol/l.)	Final conc. (mol/l.)	Amount adsorbed per 1 g. adsorbent (mol)	Area occupied by one molecule
5	4.124	3.2×10^{-3}	2.7×10^{-3}	5.9×10^{-7}	51 sq. Å
5	4.770	1.6 "	0.8 "	7.6 "	39 "
5	4.885	0.8 "	0.3 "	4.9 "	61 "
5	4.369	0.4 "	0.0 "	4.1 "	72 "

Discussion. In the 6th column of the table, the areas which one molecule of the adsorbate would occupy in the adsorption layer are shown,

assuming that the adsorption layer is one molecule in thickness. It is well known, from the information of the insoluble films on water, that in a tightly packed monomolecular film of normal long chain paraffin derivative, the smallest area which one molecule occupy is 20 sq. Å, and of benzene derivative, is 24 sq. Å. The observed values of the present investigation are 25–38 sq. Å for benzoic acid, and 40–70 sq. Å for palmitic acid. These values seem to indicate not only that the adsorption layer is monomolecular, but also in the case of benzoic acid, the complete monolayer has almost been saturated, while in the case of palmitic acid, the concentration of the solution has not been sufficient to form a complete monolayer, at the solid—liquid interface. However, considering that the apparent specific surface area which has been determined geometrically, cannot be larger than the true surface area of the adsorbent, it can be said with certainty that the adsorption layer is a type of monolayer, and in most case, the layer is not so closedly packed in orientation as anticipated for the insoluble films on water.

Summary.

(1) The glass powder, each particle of which is spherical, was prepared, and their specific surface areas have been determined.

(2) Using this glass powder as adsorbent, the amounts of palmitic acid and benzoic acid, adsorbed from their benzene solutions, have been measured respectively.

(3) Two methods of determining adsorption, have been used. In the first method, the density determination by the float method is applied to determine the change of concentration of solution before and after the adsorbing procedure, and in the second method, the surface area of insoluble film on water has been measured by surface balance.

(4) It has been concluded that the thickness of the adsorption layer is monomolecular.

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