Studies on the Adsorption at the Solid—Liquid Interface. I. On the Adsorption of Some Fatty Acids by Glass.

By Hideo AKAMATU.

(Received November 25, 1941.)

Introduction. Numerous investigations have been carried out with regard to the adsorption of the solute molecules from solution on the solid surface, nevertheless, the information of the adsorption layer are rather scarce. The usual way of determining adsorption is to measure the amount of a dissolved substance which disappears from a known quantity of solution when it is brought into contact with the adsorbing powder. By such a method the adsorbed amount is estimated as the difference between two comparatively large quantities, and is, therefore, liable to be inaccurate unless the amount adsorbed is comparatively large. Investigators, consequently, have turned their attention principally to the adsorbents which have exceptionally great adsorbing power in order to simplify the experimental technique. Charcoal, or other porous substance such as silica gel has been used as the adsorbent in general. It is impossible, however, to interpret the results obtained on these substances, for practically nothing is known with the definitenes about surfaces of those substances. Moreover. the results obtained are considered to be composed of the overlapping of complex phenomena, that is the reason why called "sorption" instead of "adsorption."

The author has carried out some experiments with the hope that the phenomena may be treated as relatively simple matter, if a substance which has definite surface is used as adsorbent. As adsorbent which serves for such a purpose, powdered glass was used.(1)

On the other hand, the problems of flotation, lubrication or the behavior of pigments suspended in oil, the informations of the adsorbed layer of a specific substance on the surface of solid materials are demanded for the practical purpose. On the surface of the general material, however, it is difficult to carry out the experiment on adsorption, since the amount adsorbed is too small.

The method hitherto used for this purpose consists of, e.g.(2) the determination of the amount of solute by titration or weighing it directly after the complete evaporation of the solvent. As for such a method, the selection both for the solvent and the solute is limited.

The present author has determined the change of concentration of a solution before and after the adsorbing procedure, by measuring its

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(1) The surface of the glass powder is not so simple as it has been expected at the beginning, and matters relating to this will be discussed in the next chance.

(2) Harkins and Gans, *J. Phys. Chem.*, **36** (1932), 86; Holmes and Thor, "Colloid Symposium Monograph. *VII.*" 1930, p. 213; W. Ewing, *J. Am. Chem. Soc.*, **61** (1939), 1317.

density, using the float method. The float method(3) of measuring density was used at the beginning, for the determination of the concentration of a binary solution. In recent years, however, it is used exclusively for measuring the amount of heavy water in common water, and the experimental technique has been improved by many investigators in connection with the studies of heavy water.

Experimental Procedure. A float, made of a boro-silicate glass, is put into the solution to be tested. By controlling the temperature of the solution, the float is made brought to suspention amid the solution. In this state, the density of the float and the solution is identical.

The apparatus is shown in Fig. 1. In this figure, S and S′ are the thermostats, the temperature of the inner thermostat can be kept constant within the range of ±0.002°C by the regulator R. The temperature is controlled by increasing or decreasing the amount of mercury in the regulator which is connected to the mercury reservoir. C is the cell in which the solution to be tested and the float is contained. This cell and the float are made of boro-silicate glass (Terex glass). B is a Backmann thermometer. The motion of the float is observed through the telescope of a cathetometer. It is difficult to control just the temperature so as to keep the float in suspension amid the solution, and such temperature is found in the following way. Using a stop-watch the velocity of the float which moves up or down in the solution at a certain temperature is measured. From the temperature and the velocity curve, the temperature at which velocity is zero will be found. This is the usual way of measuring the density of a solution by the float method.

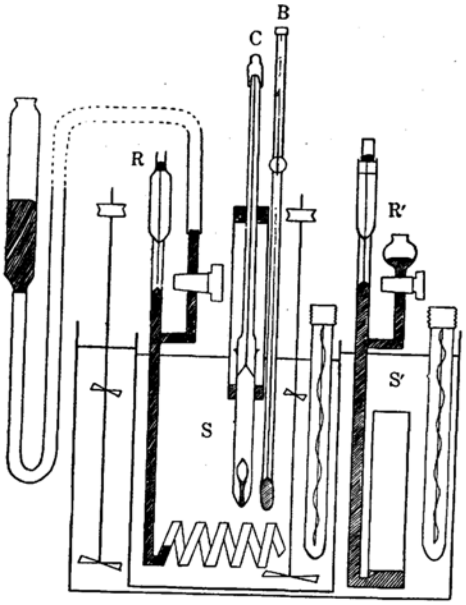

Fig. 1.

When the liquid is benzene or toluene, owing to their large coefficient of expansion, the velocity of the motion of the float is relatively large even in the small range of the temperature. It is preferable that the length of the cell is long, on the other hand, the capacity of the cell is desired to be small for the saving of the solution used. From these reasons, the shape of the cell is quite slender and consequently the float too.

What we need is not the absolute value of the density of solution for the purpose of measuring the adsorption but only the relation between

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(3) Richards and Shipley, *J. Am. Chem. Soc.*, **34** (1912), 599; Richards and Harris, *ibid.*, **38** (1916), 1000.

the concentration and the temperature at which the float stops in the solution. Practically this temperature is given by reading the Beckmann thermometer. By testing with a series of the solutions of known concentration, it has been found that there is a linear relation between the concentration and this temperature for a definite range of concentration. The experiment proceeds as follows, and its detailed description has been given in the preceding paper.(4)

A series of solutions of varying concentration is made. The density of each solution is measured and the relation between the density and the concentration is estimated. About 5 g. of adsorbent is taken in a test tube, and 10 c.c. of solution is introduced in the tube. The test tube is then hermetically sealed and is shaken at intervals. After about a week the upper liquid is taken out and separated thoroughly from adsorbent by the aid of centrifuge. The density of this upper liquid is measured and its concentration can be obtained from the known relation between the density and concentration. The amount adsorbed is given by the difference of the concentration of solution before and after the adsorbing procedure.

By the present method, as shown in the following section, it is possible to estimate the amount adsorbed in the order of 10^{-6} mol adsorbate per 1 g. of adsorbent. The accuracy will be better when the difference of the densities of components becomes larger.

In the present report, the experiments described are on the adsorption of some fatty acids from the toluene solution by the glass powder. The glass powder has been made by crushing the glass tubing, commonly used in the laboratory. The part between 100 and 140 mesh was selected and the small particles were removed by levigation. Then powder is washed with chromic acid mixture and consecutively with water. The powder thus obtained is designated as the "crushed" glass powder for the sake of convenience.

For each experiment, a part of this stock is taken and subjected to the following treatment. After washed in a Soxhlet apparatus with freshly distilled alcohol and then benzene, the powder is heated at 250–270°C. for about 6 hours under the reduced pressure by a rotary pump. The powder thus treated was used in the adsorption. The experiments were carried out at room temperature.

Results.

Results are shown in Table 1 and Fig. 2.

Table 1.

Solution	Weight of adsorbent (g.)	Initial concentration (g. in 100 c.c. solution)	Final concentration		Amount adsorbed by 1 g. adsorbent (Mol)
			(g. in 100 c.c. sol.)	Mol. in 1 l. sol.)	
Acetic acid/Toluen	5.724	0.1848	0.020	0.0033	4.8×10^{-5}
	6.873	0.3695	0.115	0.0192	6.2×10^{-5}
	6.989	0.739	0.360	0.0599	9.0×10^{-5}
	6.206	1.478	1.047	0.1744	11.6×10^{-5}

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(4) H. Akamatu, *J. Chem. Soc. Japan*, **61** (1940), 470.

Table 1.—(*Concluded*)

Solution	Weight of adsorbent (g.)	Initial concentration (g. in 100 c.c. solution)	Final concentration		Amount adsorbed by 1 g. adsorbent (Mol)
			(g. in 100 c.c. sol.)	(Mol. in 1 l. sol.)	
Propionic acid/Toluene..	4.704	0.090	0.050	0.0068	1.1×10^{-5}
	4.690	0.180	0.133	0.0180	1.4×10^{-5}
	5.225	0.360	0.318	0.0429	1.1×10^{-5}
	4.356	0.478	0.466	0.0629	0.4×10^{-5}
	4.766	0.720	0.787	0.1063	-1.9×10^{-5}
	4.721	1.433	1.537	0.2076	-3.0×10^{-5}
Butyric acid/Toluene ...	4.773	0.1453	0.086	0.0098	1.4×10^{-5}
	5.473	0.2545	0.215	0.0244	0.8×10^{-5}
	5.438	0.2545	0.2025	0.0230	1.1×10^{-5}
	4.639	0.436	0.495	0.0562	-1.4×10^{-5}
	4.709	0.509	0.6125	0.0696	-2.5×10^{-5}
	4.314	1.018	1.1075	0.1258	-2.4×10^{-5}
	4.561	2.036	2.157	0.2449	-3.0×10^{-5}
Capric acid/Toluene ...	6.402	0.2218	0.035	0.0020	1.7×10^{-5}
	5.458	0.4435	0.292	0.0170	1.6×10^{-5}
	5.170	0.887	0.750	0.0436	1.5×10^{-5}
	5.296	1.774	1.708	0.0993	0.7×10^{-5}
Palmitic acid/Toluene ..	5.692	0.125	0.030	0.0012	0.7×10^{-5}
	4.915	0.250	0.085	0.0033	1.3×10^{-5}
	5.598	0.500	0.200	0.0078	2.1×10^{-5}
	5.671	1.000	0.720	0.0281	1.9×10^{-5}
	4.989	2.000	1.675	0.0655	2.5×10^{-5}
Stearic acid/Toluene ...	5.335	0.1085	0.077	0.0027	0.2×10^{-5}
	5.748	0.217	0.127	0.0045	0.6×10^{-5}
	5.439	0.434	0.220	0.0077	1.4×10^{-5}
	6.027	0.868	0.360	0.0126	3.0×10^{-5}
Stearic acid/Toluene ...	5.904	0.2663	0.197	0.0070	0.4×10^{-5}
	5.598	0.5325	0.487	0.0172	0.3×10^{-5}
	5.613	1.065	1.160	0.0411	-0.6×10^{-5}
	5.449	2.130	2.690	0.0953	-3.6×10^{-5}

Discussion. It is well known that, Traube's rule holds when fatty acids are adsorbed by charcoal (non-polar) from their aqueous solution (polar). However, on the other hand, the rule is reversed(5) when they are adsorbed by silica gel (hetero-polar) from their solution in non-polar solvent such as toluene. The results given in this paper seem to have nothing to do with this rule. There seems to be three types of adsorption:—The type I, where the amount adsorbed increases with the increase of the concentration of the solution as in the case of acetic acid. The type II, where the adsorption is positive in the region of the low concentration of solution, while it is negative in the region of high concentration as in the case of propionic acid or butyric acid. The type III, where the

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(5) Holmes and Mckelvey, *J. Phys. Chem.*, **32** (1928), 1522; Bartell and Fu, *ibid.*, **33** (1929), 676.

amount adsorbed seems to be nearly saturated at some concentration of solution, as in the case of palmitic acid.

The type I and the type III are observed usually. The type III may be considered as the case of the monomolecular adsorption. If it is admitable to assume that the type III is the monomolecular adsorption, then the type I is the multilayer ones. As to the type II, it can be expected that the propionic acid will be adsorbed positively from the solution of which solvent is non-polar liquid such as toluene. This is a case of "polar and non-polar adsorption." The type II is different also from the type of so-called "S" adsorption, for the transition happens in the region of very dilute concentration.

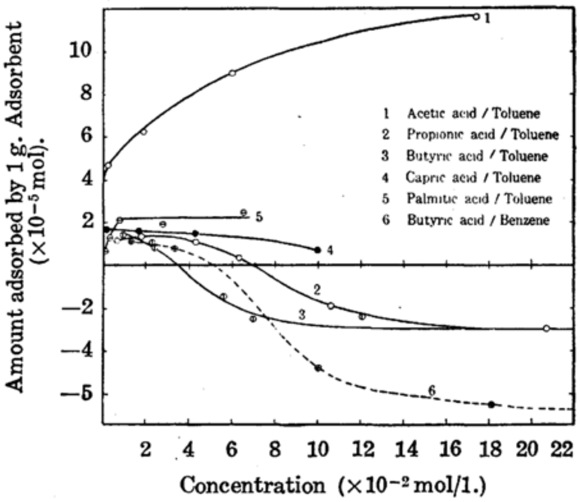

Fig. 2.

Primarily, the amount is given as only the difference of concentration of solutions before and after the adsorbing procedure, and consequently, in the case of the positive adsorption, the solvent molecules may be adsorbed with the solute molecules at the same time, and in the case of negative adsorption, the solute molecules may also be adsorbed with larger amount of the solvent molecules. The author, however, maintains the following opinion. It is plausible to thin that, in the case of propionic acid and toluene, the layer directly contacts to the solid surface consists of propionic acid exclusively. When the adsorption layer of propionic acid is completed, however, the solid surface is covered by the electric double layers due to the dipoles of propionic acid, and consequently some other forces may be present on the adsorption of the second layer. So it is convenient to think about the first layer and the second layer separately with regard to the adsorbing forces. In the first layer, the adsorption proceeds in the relation directly between the solid surface and the adsorbate molecules, while in the second layer, between the first layer and the adsorbate molecules. In the latter case, the effect of the field due to the dipoles of the first layer may be considered as one of the causes of the adsorbing force. At all events, propionic acid is preferably adsorbed in the first layer directly and contacts to the solid surface, however, as soon as this first layer is completed, it will be another problem whether the solute molecules or the solvent molecules are adsorbed in the second layer. It must be noticed, in the results of this paper, that the positive adsorption always takes place at first which follows by the negative adsorption. It is also remarkable that the adsorption in the first layer takes place very readily still in the region of the low concentration of solution, except relatively large molecules such as palmitic acid or stearic acid.

In the type I, acetic acid for example, the first, second and third layers etc. are all consisted of acetic acid. In the type II, propionic acid for example, after the first layer of the acid is completed, the solvent molecule, toluene, seems to be preferably adsorbed as the second layer. The results were similar, for the benzene solution instead of toluene. Table 2 shows the data obtained in the case of the solution of butyric acid in benzene, where the amount of the negative adsorption is somewhat greater than in the case of toluene solution.

Table 2. Butyric acid/Benzene.

Weight of adsorbent (g.)	Initial concentration (g. in 100 c.c. solution)	Final concentration (g. in 100 c.c. sol.)	Final concentration (Mol. in 1 l. sol.)	Amount adsorbed by 1 g. adsorbent (Mol.)
5.278	0.166	0.113	0.0128	1.1×10^{-5}
5.598	0.332	0.292	0.0332	0.8×10^{-5}
5.337	0.664	0.888	0.1008	-4.8×10^{-5}
5.174	1.328	1.625	0.1845	-6.5×10^{-5}
5.366	2.656	2.980	0.3384	-6.9×10^{-5}

If we assume that the negative adsorption is caused by the selective adsorption of the solvent molecules, then the adsorbed quantity of the solvent amounts enormously large to explain the results of Table 1 and 2. The amount, necessary to cover the surface of 1 g. of adsorbent is estimated roughly to be 2×10^{-5} mol. The calculation shows, from this figure, that the thickness of the adsorption layer of toluene, in the case of propionic or butyric acid solution, is about 100 molecular layers. For the solution of butyric acid in benzene, the corresponding figure attains 150 molecular layers. It is difficult to explain that such a large amount of solvent molecule is selectively adsorbed by a simple idea of the induction effect due to the field of dipoles in the first layer of propionic or butyric acid. No plausible explanation has yet been established.

In the type III, after the first layer is finished, neither the solute molecule nor the solvent molecule is adsorbed for the second layer. The type III may be constructed by the monomolecular adsorption. This assumption may not be far from the truth, since the author has carried out some investigations about the thickness of the adsorption layer and its description will be given in the next paper. In the case of palmitic acid, the effect of dipoles in the first layer will be too small to complete the second layer, for the length of hydrocarbon chain of the molecule is too long. Such an effect of the molecular length appears in the case of capric acid, where the negative adsorption proceeds in gradual manner. The satisfactory results have not been obtained by stearic acid, for its solubility in toluene is small. The solution of oleic acid in toluene belongs to the type II. In this case, oleic acid has a double bond in the middle part of the molecule, and seems to behave as a short molecule.

Summary.

(1) A method of determining relatively small amount of adsorption has been devised. To measure the change of concentration of solution

before and after the adsorbing procedure, the density determination using the float method is applied.

(2) The experiments are described on the adsorption of some fatty acids from the toluene solution by the glass powder.

In conclusion, the author wishes to express his sincere gratitude to Prof. Jitsusaburo Sameshima for his kind guidance and encouragement. The expense for the experiments has been defrayed by a grant given to Prof. Sameshima from Nippon Gakujutu Sinkokai (Japan Society for the Promotion of Scientific Research), to which the author's thanks are also due.

Chemical Institute, Faculty of Science,
Imperial University of Tokyo.