Studies on the Adsorption at the Solid—Liquid Interface. IV. Relations among the Adsorption, the Oiliness and the Flocculation of the Powder.

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Introduction. When the surface of a solid contacts with a liquid or some powder is immersed in a liquid, the property of the surface of solid is changed by the solvation or the adsorption of a certain substance from the solution. There are many phenomena which depend on such property of the surface of solid. The action of the lubricant or the flotation process is the example of the application of such phenomena. To explain those phenomena we always assume the adsorption layer on the surface of the solid material. In practice, however, it is troublesome to find the method of investigating the adsorption layer, for the amount of the substance adsorbed is very small and the effect is very sensitive. We get the informations, in many cases, by the indirect method or by the analogy to some other cases, for instance, by the behaviour of the monomolecular film on the surface of water.

In our laboratory, the effects of the liquids on the friction coefficient of the glass surface have been studied,(1) and moreover, some results were

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(1) J. Sameshima and coworkers, this Bulletin, **11** (1936), 659, 791; **12** (1937), 96, 127; **13** (1938), 127, 134; **14** (1939), 270, 297; **15** (1940), 288, 467. J. Sameshima, H. Akamatu and T. Isemura, *Rev. Phys. Chem. Japan*, **14** (1940), 55.

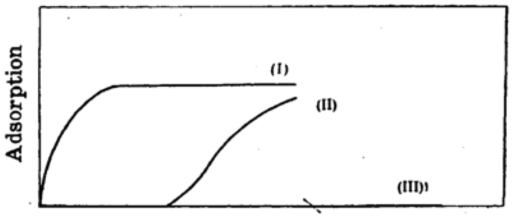
obtained regarding the adsorption by glass.(2) The relations between those phenomena will be considered in the present report.

Summary of the Results on the Adsorption by Glass. The adsorptions by the glass powder of such substances as carboxylic acids, esters, nitrobenzene, aniline and chlorobenzene from their solutions dissolved in a non-polar solvent such as benzene or toluene were studied in the preceding papers.(2) The adsorbing behaviours can be classified into the following three groups.

(I) The compounds having carboxyl radicals were adsorbed selectively from their benzene or toluene solution by glass, and the adsorption took place readily in the region of the low concentration of the solution (e.g. in the order of 10^{-3} mol/l.). In these cases, the adsorption layer seemed to approach to the monomolecular layer and then saturate, except the compound having small molecular weight such as acetic acid, which was much adsorbed.

(II) Alcohols did not show such strong selective adsorption as carboxylic acids, and no remarkable adsorption has been observed in the region of the low concentration. When the concentration of the solution, however, was beyond a certain range (e.g. 10^{-2} mol/l.), the selective adsorption took place, and things were like to the case of carboxylic acids.

(III) In the case of nitrobenzene, aniline and chlorobenzene, notwithstanding their large dipole moments, any considerable selective adsorption was not observed even in the range of the pretty high concentration of the solution. Those results are shown schematically in Fig. 1.



Concentration of Solution.

Fig. 1.

The relations between those results of the adsorption and the oiliness of liquids, and the flocculation or the apparent sedimentation volume of the powder in liquids will be discussed in the following sections.

Adsorption and Oiliness. The mechanism of the oiliness of the lubricant has not yet been understand thoroughly. However, two things, at least, are considered to be necessary. The first is the protecting action by the molecules of the lubricant combining with the surface of the solid. When the lubricant is pure liquid, this is caused by the solvation, and if the lubricant is a solution, it is necessary that the selective adsorption of a certain molecules take place. The adsorption is a necessary condition to reduce the friction, though it is not a sufficient one for good oiliness. For the second condition, the adsorption layer at the friction surface must have a special property to reduce the friction. As for this property, however, there is no definite theory. With regard to a certain homologous series of the lubricant, the larger the molecule, especially having the long

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(2) H. Akamatu, this Bulletin, **17** (1942), 141, 161, 260.

hydrocarbone chain, the better the oiliness is. This is the most remarkable and suggestive fact. Things which are considered from this fact are as follows. (1) The shape of the molecule is associated with the good oiliness. Especially the flexibility of a molecule attracts the attention of the investigators. (2) The good orientation of molecules in the adsorption layer is necessary for good oiliness. As the lateral force between molecules oriented is greater, the adsorption layer will be more stable, by which the friction surface will be covered homogeneously. (3) The large molecules have the effect to separate the friction surfaces from each other. All of those things have the parallelism with the size or the length of the molecules. In the practical lubricating action, all of those things may be involved at the same time.

The adsorption is not a sufficient condition for good oiliness, while it is a necessary condition at least. For instance, fatty acids are readily adsorbed by glass in general. Among them, acetic acid seems to be most readily adsorbed, and consequently, it reduces more or less the friction coefficient of the glass surface, though it shows no remarkable oiliness. The friction coefficient of glass without any lubricant is almost unity. In the case of using acetic acid as lubricant, the friction coefficient is reduced to about 0.6; on the other hand, with more favourable fatty acids having long hydrocarbon chains, the values are far more small, with oleic acid, for instance, this value is 0.24.

Molecules, consisted of the hydrophilic radical and the hydrophobic radical at the same time, orient themselves at the surface of water in such a manner as their hydrophilic radical sets in water. This idea has been expanded to the surface of hydrophilic solid instead of water, and it is assumed that such molecules also orient themselves anchoring their polar groups on the solid surface and the adsorption takes place as the results. However, such an assumption cannot be applied imprudently to the case of the glass surface, at least, as mentioned above.

Among the polar radicals, the carboxyl radical is most readily adsorbed by the glass surface. This fact is consistent with the carboxylic acid, especially fatty acids, have much or less good oiliness. The fact(3) that the oiliness of toluene or xylene solution dissolving small quantity of fatty acid, was identical with the oiliness of the fatty acid itself independing on the solvent, has been understood by the assumption that the fatty acid is selectively adsorbed by the friction surface and that the friction depends on it only. This assumption is consistent with the experimental results that the fatty acids are always preferentially adsorbed by glass. Hydroxyl radicals, on the other hand, are not selectively adsorbed by glass so strongly as carboxyl radicals. The alcohols are adsorbed from their benzene solutions only at the high concentration of the solution. This relation has also been investigated from the oiliness of the solution containing alcohol. For instance, in the case of the xylene solution dissolving palmitic acid, the oiliness is pretty good in the range of the low concentration of the solution and as the concentration increases the oiliness approaches to a saturated value. On the other hand, the oiliness is not good in the case of the toluene solution containing tetradecyl alcohol, not-

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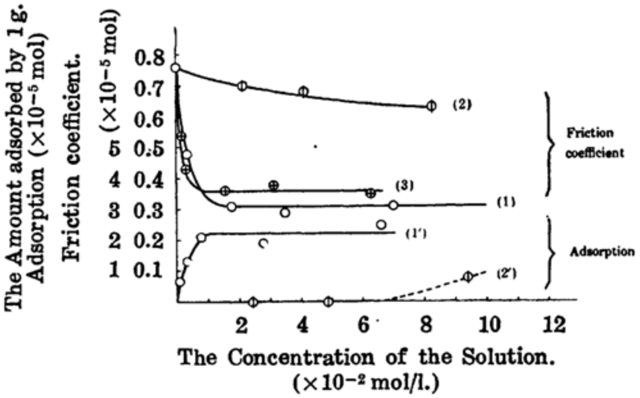
(3) H. Akamatu, this Bulletin, **13** (1938), 127.

withstanding the good oiliness being anticipated from the molecular structure of tetradecyl alcohol. The reason is that tetradecyl alcohol does not adsorbed preferentially at the glass surface as palmitic acid. This relation is shown in Fig. 2. The considerable adsorption of tetradecyl alcohol does not take place until the concentration of the solution approaches to the saturation.



(1): Palmitic acid/Xylene (1'): Palmitic acid/Toluene
(2): Tetradecyl alcohol/Toluene (2'): Tetradecyl alcohol/Benzene
(3): Oleic acid/Toluene

Fig. 2.

Notwithstanding that the fatty acids and the alcohols have much or less good oiliness, their esters⁽⁴⁾ have rather poor oiliness. This is also understood from their small adsorbability.

With regard to nitrobenzene, aniline and chlorobenzene, no notable selectivity against benzene has been observed, from the adsorption experiment. The reducing action of the friction of the glass surface by those substances⁽⁵⁾ are also poor just as the action by benzene or toluene. For the bad oiliness of those substances, the deficiency in the flexibility of those molecules has been assumed by many investigators, however, this may be also caused by their bad adsorbability to the surface. Since benzoic acid is selectively adsorbed by glass and the xylene solution dissolving benzoic acid has also much or less good oiliness as compared with xylene itself. Friction coefficients of those substances are shown in Table 1.

Table 1.

Lubricant	Friction Coefficient
Benzene	0.78
Toluene	0.76
Xylene	0.76
Nitrobenzene	0.84
Aniline	0.73
Chlorobenzene	0.81
Xylene solution dissolving Benzoic acid (2%)	0.59

In the case when the lubricant is consisted of many components, the fact⁽³⁾ that the oiliness of such a system depends on only a certain material alone, may understood from the consideration of the selective adsorption.

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(4) T. Isemura, this Bulletin, **14** (1939), 270.
(5) T. Isemura, this Bulletin, **15** (1940), 288.

Adsorption and Flocculation of the Powder. It is well known that the stability or the swelling of the colloidal system depends on the nature of the dispersion medium. In the case when relatively large particles (microscopic) are suspended or sedimented in the liquid, the phenomena that the property of the system is affected by the nature of the liquid medium attract the attention of the investigators,⁽⁶⁾ not only because of its importance for the application, but also the fact that the system may be considered as a model of a colloidal system.

It is remarkable that the flocculation and the sedimentation volume of the powders in various kinds of liquids varied with the nature of the liquid.⁽⁷⁾ If the powder is hydrophilic, it is not liable to flocculate in the polar liquid, and the particles are dispersed, and consequently the sedimentation velocity is slow and the apparent sedimentation volume is small. On the other hand, in the non-polar liquid, the particles aggregate each other and become coarse particles, and consequently the sedimentation velocity is fast and the apparent sedimentation volume is large.

If the adhesion forces between the particles are strong, they aggregate each other by their contact points, and as the whole system they will take the loose packing, so the sedimentation volume will be large. On the other hand, if the adhesion forces are weak, the aggregation or the flocculation does not take place, and they will take the close packing as the whole system, and consequently the sedimentation volume will be small.

The aggregation of the particles may be prevented by the addition of some substances to the liquid even in the case of non-polar solvent, and as the results, the sedimentation volume of the system will be reduced. This phenomenon is remarkable and the addition of the substance to the solvent is analogous to the protecting action of the colloidal system. Taking the glass powder, for instance, this relation will be seen in Table 2.

Table 2.

Solvent	Solute		The ratio of the sedimentation volume of 1 g. powder.
Toluene	——		1.00
Benzene	——		1.00
Toluene	Oleic acid	(1%)	0.79
”	Palmitic acid	(2%)	0.82
”	Tripalmitine	(1%)	0.82
”	Benzoic acid	(1%)	0.88
”	Acetic acid	(5%)	0.94
Benzene	Palmitic acid	(0.02 mol/l.)	0.84
”	Nitrobenzene	(0.07 ”)	1.00
”	Chlorobenzene	(0.07 ”)	1.00

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(6) Wo. Ostwald and W. Haller, *Kolloidchem. Beihefte*, **29** (1929), 354; P. Rehbinder, *Z. physik. Chem.*, A **146** (1930), 63; Bloomquist and Schutt, *Ind. Eng. Chem.*, **32** (1940), 827; K. Suzuki, *J. Chem. Soc. Japan*, **62** (1941), 888; B. Tamamushi and S. Tomatsu, this Bulletin, **17** (1942), 23.

(7) H. Akamatu, this Bulletin, **13** (1938), 456.

In those cases, when the substance added to the solvent can be adsorbed selectively by glass, there are much or less reducing effect of the sedimentation volume. Nitrobenzene or chlorobenzene has no effect. This relation is quite like the case of the oiliness. The preventing action of the aggregation of the particles and the reducing action of the friction of the solid surface by the so-called surface active substances is quite parallel in each other. This fact shows that the adhesion force between the particles is the same sort with the friction force. A series of the studies by Búzagh⁽⁸⁾ on the "Abreisswinkel" also showed the analogous results.

The peculiar behaviour of the float, frequently experienced during the density measurement by the float method, seems to have some relation to the adhesion force between particles. As already described in the preceding paper,⁽⁹⁾ this phenomenon is as follows. In the non-polar liquid such as benzene or in the solution dissolving the non-adsorbable solute, the float occasionally moves laterally toward the wall of the cell and attaches to it. In the benzene solution dissolving the surface active substance, however, this behaviour does not occur in general. This phenomenon seems to be related to the aggregation of the particles of the powder. We may suppose, from this fact, that the aggregation takes place not only when the particles collide each other by the chance, but also when they approach each other by some attraction force in the liquid such as benzene or toluene.

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(8) A. von Búzagn, "Kolloidik", 1936, Dresden, p. 158; *Kolloid-Z.*, **85** (1938), 318.

(9) H. Akamatu, this Bulletin, **17** (1942), 260.