Studies on the Adsorption at the Solid—Liquid Interface. III. Note on the Polar and Non-polar Adsorption.

By Hideo AKAMATU.

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On the Dielectric Theory of the Adsorption. Some relations between the adsorption and the dielectric nature of substances have already been known. It is about twenty years since the electrostatic theory concerning the force of the adsorption of gases or vapours has been proposed, and, since then, the theory has also been applied to the adsorption from the solution by many investigators.

According to the electrostatic theory(1) of the adsorption of vapour, the vapour molecules polarize the lattice of the adsorbent, and the certain molecules, which are near the surface of the adsorbent, is bound by the image force of itself in the lattice. In this case, the field induced by the adsorbent is not considered in general. In the case of the interface between the liquid and the solid, however, the potential difference between those two phases will vary widely as it depends on the dielectric structures of them. By the adsorption from the solution, moreover, the solvent molecules will be adsorbed, with the solute molecules at the same time, and therefore the amount of the adsorption will be given from the difference of these two amounts. In the dilute solution, with regard to a certain solute, the adsorption will increase, as less the adsorption of the solvent molecules is. Considering the electrostatic theory, the adsorption of the solvent molecules will be associated with their dipole moments. The adsorption will decrease, as greater the dipole moment of the solvent is. The adsorption of a certain solute are affected by the polarity of the solvent, and such phenomena were investigated by Nekrassow,(2) Heymann and Boye,(3) and Sata.(4) On the other hand, the solute will be more adsorbed from a certain solvent, as greater the dipole moment of itself is. From such a view-point, studies were also carried out by Tamamushi,(5) and Sata.(4) However, the general relation has not yet been found.

In the case of the adsorption from the solution, the phenomena depend on the combination of the solute, the solvent and the adsorbent, and the electrical natures are also affected by their combinations. So things are complex and the definite results has not been found, notwithstanding, there are many qualitative relations between the adsorption and the dielectric natures. The present author thinks that to use charcoal as the adsorbent for the sake of convenience of the experimental technique is one of the reasons for such confusions. For charcoal is a typical

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(1) Debye, *Physica*, 1 (1921), 362; Lorenz and Lande, *Z. anorg. Chem.*, **125** (1922), 47; E. Hückel, "Adsorption und Kapillarkondensation," 1928, Leipzig, p. 83.

(2) Nekrassow, *Z. physik. Chem.*, **136** (1930), 18.

(3) Heymann and Boye, *Z. physik. Chem.*, A **150** (1930), 219.

(4) N. Sata, *Kolloid-Z.*, **49** (1929), 275; *J. Chem. Soc. Japan*, **53** (1932), 617.

(5) B. Tamamushi, this Bulletin, **6** (1931), 74.

non-polar substance. Considering the electrical field of the interface, more general substance must be used as the adsorbent. The famous Traube's rule, i.e. fatty acid which has longer chain will be adsorbed more from the aqueous solution by charcoal than the one which has shorter chain is reversed(6) when silica gel (polar) is used as the adsorbent and toluene (non-polar), as the solvent. Freundlich and Heller(7) have shown that trans-azobenzene is adsorbed more by charcoal from the solution in methyl alcohol than cis-azobenzene, while, cis-form is adsorbed more than trans-form by aluminium oxide from the solution in petroleum ether. It is recognised, in general, that the non-polar adsorbent, such as charcoal, adsorbs well from the polar solvent, while the polar (or hetero-polar) adsorbent adsorbs well from the non-polar solvent, and such cases are called the "polar and non-polar adsorption."

To investigate the adsorption at the solid-liquid interface, and to consider the polar and non-polar adsorption also the present author has carried out some experiments on the behaviours of the molecules at the interface between glass (hetero-polar) and benzene or toluene (non-polar). The amount adsorbed by glass, though made into the fine powder, is so small that the method of the measurement must be specially devised. For such a purpose, the float method and the surface balance analysis were applied. In the preceding paper, the behaviours of fatty acids were reported (Part I),(8) and it was also reported that the adsorption layer is one molecular in thickness in the case of palmitic acid and benzoic acid (Part II).(9)

Adsorption of Some Benzene-derivatives by the Glass Powder. Some of benzene-derivatives have large dipole moments and it is anticipated, from the electrostatic theory, that they would be readily adsorbed at the glass-benzene interface. Nevertheless, among benzoic acid, nitrobenzene, aniline and chlorobenzene which were studied by the present author, benzoic acid alone was adsorbed by the glass-benzene interface, and the other compounds were not adsorbed, or the amount adsorbed might be too small to be measured by the present method. Results are shown in Table 1 and Fig. 1.

The adsorbent was the same glass powder ("crushed" glass powder) as reported in the preceding paper (Part I), also the experimental conditions were the same. To determine the amount of the adsorption, the float method was applied. By this method, the difference of the concentration of the solution, before and after the adsorbing procedure, is determined from the change of the density, which is measured by a float. In Table 1, the notation of "Reading of Beckmann" means the arbitrary reading of the scales of a Beckmann thermometer, that indicate the temperature at which the density of the solution is identical with that of the float. The identity of this values before and after the adsorbing procedure shows that no measurable adsorption has taken place. In the case of aniline and chlorobenzene, things were just like as the case of nitro-

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(6) Holmes and McKelvey, *J. Phys. Chem.*, **32** (1928), 1522.
(7) Freundlich and Heller, *J. Am. Chem. Soc.*, **61** (1939), 2228.
(8) H. Akamatu, this Bulletin, **17** (1942), 141.
(9) H. Akamatu, this Bulletin, **17** (1942), 161.

Table 1. Adsorption of Benzene-derivatives by the "Crushed" Glass Powder.

Volume of Solution (c.c.)	Weight of Adsorbent (g.)	Initial Concentration (mol/l.)	Initial Concentration Reading of Beckmann	Final Concentration (mol/l.)	Final Concentration Reading of Beckmann	Amount adsorbed by 1 g. of Adsorbent (mol)
			Benzoic acid / Benzene			
10	4.958	0.92×10^{-2}	3.200	0.28×10^{-2}	3.107	1.3×10^{-5}
10	5.003	1.84×10^{-2}	3.465	1.13×10^{-2}	3.259	1.4×10^{-5}
10	4.936	3.67×10^{-2}	4.000	2.99×10^{-2}	3.791	1.4×10^{-5}
10	4.759	7.35×10^{-2}	5.054	6.65×10^{-2}	4.854	1.5×10^{-5}
			Nitrobenzene / Benzene			
10	4.812	1.27×10^{-2}	0.933	1.28×10^{-2}	0.934	0
10	4.407	2.55×10^{-2}	1.282	2.52×10^{-2}	1.278	0
10	5.258	5.10×10^{-2}	1.978	5.11×10^{-2}	1.981	0
10	4.616	10.20×10^{-2}	3.375	10.23×10^{-2}	3.380	0

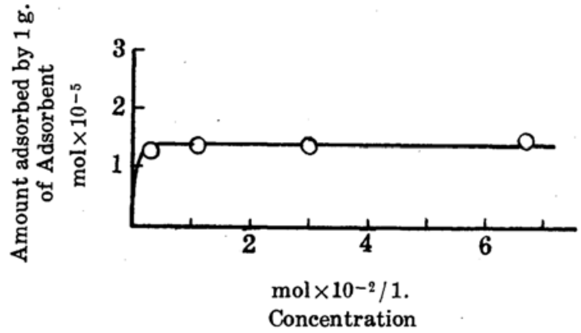

Fig. 1. Adsorption of Benzoic acid.

benzene, where the concentration of the solution which has been studied was in the region of 0.145 mol/l. and 0.089 mol/l. respectively for aniline and chlorobenzene.

Essentially, this method is not so acute when the difference of densities of the solute and the solvent is not large. However, when the densities of the compounds are much larger than benzene (solvent), it is expected that the change of the concentration would be observed acutely by measuring the density. Considering the result of the preceding paper (Part II), and the curve of Fig. 1, it is plausible to consider that the adsorption layer of benzoic acid is monomolecular in thickness. By this method, we can investigate the adsorption even when the adsorption layer is less than the monomolecular one. To make sure the above results, the adsorption measurement was carried out using the "spherical" glass powder⁽⁹⁾ of which specific surface area has been known in the case of nitrobenzene. However, no measurable adsorption also could be found.

It seems plausible to the present author to consider that nitrobenzene, aniline and chlorobenzene are not adsorbed at the glass-benzene interface, in the region of the concentration of the solution which has been studied. This fact is also deduced by the qualitative facts which are described in the following section.

On the Lateral Movement of the Float in the Solution. By the float method of density measurement, a float which was made of a boro-silicate glass was used. It is put in the solution to be tested, and the velocity of the motion of the float up and down at a certain temperature was observed. In this experiment a peculiar behaviour of the float has attracted notice of some investigators, namely, the float moves occasionally toward the wall of the cell and attaches to it. Sometimes this may be an accident caused, for instance, by the vibration of the stirrer, or the electrical charge of the float, etc. By the present author's experiences, however, it always occurs when the liquid is non-polar one such as benzene or toluene. Robinson and Smith(11) have reported that they had been troubled by this phenomenon in the case of silicon tetrachloride. On the other hand, the float never attach to the wall in the case of benzene or toluene dissolving fatty acid, or benzoic acid, while the float attach to the wall in the case of dissolving such as nitrobenzene or chlorobenzene as well as pure benzene. To prevent this behaviour of the float, it is necessary to take care not to be clean the float or the cell too much. Usually, the float is washed with benzene freshly distilled using a Soxhlet apparatus, and the cell is washed with chromic acid mixture, then with distilled water, and dried in an electrical drying oven, at each measurement. In those cases, however, the cell must be exposed in the open air for a long time (overnight, for instance) before the use, or the washing of the float must be neglected to prevent the adhering of the float to the wall.

The cause of such peculiar behaviour of the float may be the electrical charge (by the friction, for instance), or the heterogeneous contamination at the surface of the float. During the measurement of the density by the float method, the density of the float is almost identical to that of the solution. Consequently, the float can be moved by a very small force. The nature of this force is not known yet. The float does not attach to the wall of the cell when there exists any adsorption layer at the surface of the float or the wall,—it may be solvation, the contamination or the adsorption of a certain substance from the solution. The fact that the occurrence of this peculiar behaviour of the float in benzene solution dissolving nitrobenzene or chlorobenzene, corresponds to the non-adsorption of these compounds by the glass surface.

Adsorption of Alcohols and Esters. Alcohols are also adsorbed by glass from benzene solution. The results shown in Table 2 and Fig. 2 are also obtained by the float method.

Methyl alcohol and ethyl alcohol were much adsorbed, as the concentration of the solution was increased. The behaviours of alcohols seem to be alike to the fatty acids. In the case of fatty acids, however, the adsorption takes place still in the region of the low concentration of the solution, on the other hand, in the case of alcohols, no considerable adsorp-

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(10) Robinson and Smith, *J. Chem. Soc.*, **1926**, 2162.

Table 2. Adsorption of Alcohols and Esters by the "Crushed" Glass Powder.

Volume of Solution	Weight of Adsorbent	Initial Concentration	Final Concentration		Amount adsorbed by 1 g. of Adsorbent
(c.c.)	(g.)	(g./100 c.c.)	(g./100 c.c.)	(mol/l.)	(mol)
		Methyl alcohol / Benzene			
10	5.557	0.1065	0.0998	0.031	0.4×10^{-5}
10	5.615	0.213	0.190	0.059	1.3×10^{-5}
10	4.960	0.426	0.400	0.125	1.6×10^{-5}
10	5.222	0.852	0.808	0.252	2.6×10^{-5}
10	5.950	1.704	1.635	0.510	3.6×10^{-5}
		Ethyl alcohol / Benzene			
10	5.657	0.0912	0.0875	0.019	0
10	5.137	0.1823	0.170	0.037	0.5×10^{-5}
10	5.607	0.3645	0.3175	0.069	1.8×10^{-5}
10	5.240	0.729	0.646	0.140	3.4×10^{-5}
10	5.103	1.458	1.365	0.296	4.0×10^{-5}
		Propyl alcohol / Benzene			
10	4.811	0.266	0.265	0.044	0
10	4.693	0.532	0.530	0.088	0
10	5.307	0.761	0.752	0.109	0.3×10^{-5}
10	4.767	1.064	1.038	0.173	0.9×10^{-5}
10	5.186	1.308	1.287	0.214	0.7×10^{-5}
10	4.572	1.522	1.505	0.251	0.6×10^{-5}
10	5.080	2.128	2.125	0.354	0
		Tetradecyl alcohol / Benzene			
10	5.768	0.526	0.526	0.025	0
10	5.903	1.052	1.052	0.049	0
10	5.218	2.104	2.017	0.094	0.8×10^{-5}
		Butyl acetate / Toluene			
10	4.356	0.138	0.113	0.010	0.5×10^{-5}
10	4.333	0.275	0.240	0.021	0.7×10^{-5}
10	5.267	0.551	0.517	0.045	0.5×10^{-5}
10	4.942	1.101	1.080	0.093	0.4×10^{-5}
10	4.299	2.202	2.20	0.189	0
		Tripalmitine / Toluene			
10	7.158	0.461	0.461	0.006	0
10	5.995	0.923	0.923	0.012	0
10	6.489	1.845	1.845	0.023	0

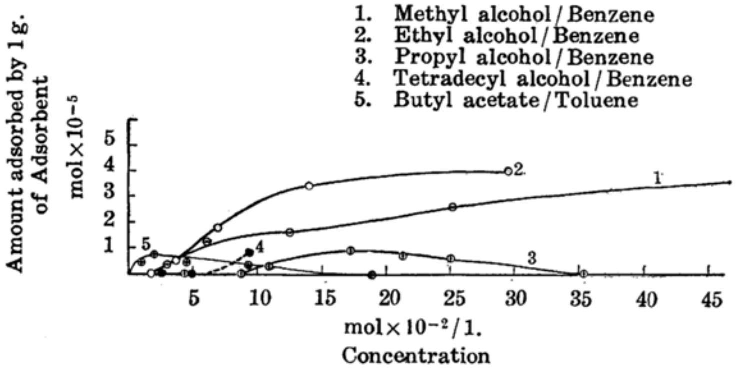

Fig. 2. Adsorption of Alcohols and Butyl acetate.

tion takes place until the concentration of the solution increases beyond a certain range. This is a remarkable fact that the range of the concentration of the solution, at which any considerable adsorption be observed, is narrow in the case of propyl alcohol, and it seems that some negative adsorption takes place at the higher concentration. For tetradecyl alcohol, this range of the concentration is also limited, because it has the limited solubility.

For butyl acetate and tripalmitine, the amount adsorbed were small. Especially, in the case of tripalmitine, the change of the concentration of the solution was not observed before and after the adsorbing procedure. However, there are many qualitative evidences to consider that tripalmitine is adsorbed. The density difference of tripalmitine and toluene is rather small, and moreover, the size of the molecule of tripalmitine is large, so the numbers of molecule necessary to cover the surface of the adsorbent will be small, and the amount of the adsorption may not be observed by this method. The surface balance analysis was used instead of the float method, since tripalmitine makes a good monomolecular film on the surface of water. Moreover, the "spherical" glass powder of which specific surface area has been known, was used as the adsorbent. The results are shown in Table 3.

Table 3.

Adsorbent: "Spherical" glass powder No. 2. (of which specific surface area is 1810 cm^2.)
Solution: Tripalmitine / Benzene.

Volume of Solution (c.c.)	Weight of Adsorbent (g.)	Initial conct. (mol/l.)	Final conct. (mol/l.)	Amount adsorbed by 1 g. Adsorbent (mol)	*Area occupied by one molecule.
5	5.328	0.44×10^{-3}	0.40×10^{-3}	0.4×10^{-7}	747 sq. Å
5	5.229	0.88×10^{-3}	0.80×10^{-3}	0.8×10^{-7}	353 "
5	4.709	1.77×10^{-3}	1.51×10^{-3}	2.8×10^{-7}	108 "

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* In the tightly packed monomolecular film on the surface of water, the smallest area which one molecule of tripalmitine occupies, is about 66 sq. Å.

From this result, it seems that tripalmitine is hardly adsorbed in the region of the low concentration of the solution. But at the higher concentration of the solution, the adsorption layer approaches to the monomolecular one.

On the Surface of the Glass Powder. As reported in the preceding paper, the amount of benzoic acid adsorbed by 1 g. of the "spherical" glass powder, of which specific surface area is 4700 $cm.^2$, is determined to be about 3×10^{-6} mol. By the "crushed" glass powder, as reported in the present paper, this amount is about 1.4×10^{-5} mol. The shape of the particles of this powder are broken and irregular, and the surface area cannot be known. The particle size of this powder was estimated roughly by measuring the sedimentation velocity. As the result, it was found that the radius of the particles are distributed in the range of 3.5–7.5 micron, if the shape of the particle is assumed to be spherical. Taking the average radius to be 5.5 micron, the specific surface area is roughly assumed to be about 2180 $cm.^2$ It must be deduced, from the results, that the "crushed" glass powder adsorbs benzoic acid ten times as much as the "spherical" glass powder, with the same surface area. The surface of the "spherical" glass powder went once melted through the melting process, in the course of its preparation, while the surface of the "crushed" glass powder, was left as they have been made by the crushing. The surface area of the "crushed" powder, was estimated to be 2180 $cm.^2$, which was calculated under the assumption that the shape of the particle is spherical. The true surface area must be, of course, larger than this value owing to the irregularity or the brokenness. The estimation of the area, considering the geometrical shape of the particles, however, may not be larger than three or four times of the value estimated from the assumption that the shape of particles is spherical. Consequently, the two or three times out of the ten times larger adsorbability by the "crushed" powder, might be caused by the great adsorbability at the edges or the points, or otherwise, the existence of crevices and wrinkles has to be assumed. In the case of the adsorption of palmitic acid by the "crushed" powder and by the "spherical" powder, things are also alike to the case of the adsorption of benzoic acid.

It can be supposed, frequently, that the chemical as well as physical natures of the surface of glass might be varied by their treatment, for instance, natural or not (polished or melted). Nevertheless, the experimental informations are scarecely known. The adsorbability by the glass surface reported in the present paper is an example of such cases.

Note on the Results. Results investigated show that carboxylic acids are always and readily adsorbed at the glass-benzene interface, even in the low concentration of the solution. Alcohols are also adsorbed, but they are not so easily adsorbed like carboxylic acid, and the adsorption does not take place until the concentration of the solution increases beyond a certain range. Nitrobenzene, aniline and chlorobenzene are not adsorbed at the glass-benzene interface when the concentration of the solution is as large as about 0.1 mol/l. If the adsorption takes place as the result of the orientation of the adsorbate molecules at the interface, caused by the tendency of the molecules intending to moderate the potential gap, nitrobenzene, aniline and chlorobenzene will be the most adsorbable compounds, since they have large dipole moments(11) or the molecular polarisations.

Considering that alcohols and esters are also adsorbed, it cannot be assumed simply that, the adsorption by glass is a kind of the chemical reaction between the acid and the base in the usual sense. It seems a certain radical of a molecule, rather than the dipole moment as a whole, that associates with the adsorption. If the molecule be adsorbed by being approached closely to the atoms or molecules of the adsorbent, the cause of the attraction will not be the moment as a whole, but the local polarity in the molecule. Then, ultimately, the force of the adsorption is not far from the valency force. Among the forces which can be considered, the attraction(12) caused by the hydrogene bridge between oxygen of glass and $-OH$ radical, for instance, is also possible, but it is not beyond a speculation at present.

It must be noticed that, the substances which can be adsorbed by glass are rather limited and the amount of the adsorption is relatively small, while various substances are adsorbed in much quantity by charcoal, silica gel or alumina gel. It is probable that the mechanism of the adsorption is quite different for the case of the porous substance and the substance of compact surface, and it will not be caused simply by the surface area being large or small.

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

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(11) The dipole moments of benzene derivatives are as follows:—benzoic acid, 1.0; nitrobenzene, 3.90; aniline, 1.52; chlorobenzene, 1.52 ($\times 10^{-18}$ e.s.u.) (from the appendix of *Trans. Faraday Soc.*, **30** (1934)).

(12) The application of the hydrogene-bridge theory to the sorption by silica gel, was done recently by Elder and Springer. (*J. Phys. Chem.*, **44** (1940), 943.)