ON THE DERIVATION OF ADSORPTION ISOTHERMS. II.

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In the previous work⁽¹⁾ the author has remarked that an exponential adsorption isotherm $C=ku^i$ could be derived from the equation of Gibbs, if we assume at the same time, the following relation,

$$(\gamma_0-\gamma)\frac{1}{u}=iRT \quad \cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots (1)$$

in which $(\gamma_0-\gamma)$ is the difference between the surface tension of solvent and that of solution, u the excess of solute per unit area in the surface, R the gas constant, T the absolute temperature and i a certain constant, the physical meaning of which remains to be explained.

Now the diminution in the surface tension by the adsorption film can be put equal to the pressing force P_s, across unit length of the boundary, and u the reciprocal of the adsorption surface A where the adsorption of one mol of solute takes place. So that equation (1) will be written down as follows, the correction i being dropped,

$$P_sA=RT. \cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots (2)$$

This is known as the equation for the so-called "gaseous film," and it holds when the solution is sufficiently dilute and the average kinetic energy in each degree of freedom in the surface, $\frac{1}{2}RT$ for each molecule, acts wholly to produce the pressing force on the boundary. When the solution becomes more concentrated, due corrections are necessary. In this respect, the intermolecular forces are to be taken into account in the first place, so that we have the following relation instead of equation (2):

$$\{P_s-f(E)\}A=RT \cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots (3)$$

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(1) Tamamushi, this journal 1 (1926), 185.

where $f(E)$ is a certain function which represents cohesion or repulsion between molecules. Certainly it is difficult to give this function a complete elucidation. At any rate, we can probable consider that molecules are electric dipoles and that there takes part potential energy of electric nature in the surface besides the thermal kinetic energy. Here let us assume that the polarization of dipole molecules in the surface is proportional to $\sqrt{A}$ i.e. to the mean distance between the molecules. Now, one end of the dipole molecules being attracted by the main body of the solution, the charge of the same sign will be arranged in the surface, the effect of which weakens the surface attraction. Let us further assume that the probability of a molecule in taking proper orientations fully to display this effect of polarization is proportional to $\sqrt{T}$, in other words, to the mean velocity of the molecule. The repulsive effect of a molecule will then be proportional to $\sqrt{A}\cdot\sqrt{T}$, and consequently the repulsive force between adjacent molecules can be represented by $q\frac{(\sqrt{A}\cdot\sqrt{T})^2}{A^2}$ or by $q\frac{T}{A}$, where q is a proportional constant.

If this expression is put into equation (3) in place of $f(E)$, the following relation will be obtained,

$$\left(P_s-\frac{qT}{A}\right)\cdot A=RT$$

or

$$P_s\cdot A=RT+qT$$

And if we put here

$$1+\frac{q}{R}=i \quad\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots(4)$$

we have

$$P_s\cdot A=iRT.$$

This is no other than equation (1).

Taking now Volmer's surface correction β into account and using the notations already mentioned, we obtain.

$$(\gamma_0-\gamma)\left(\frac{1}{u}-\beta\right)=iRT \quad\cdots\cdots\cdots\cdots\cdots\cdots(5)$$

as a general form of the characteristic equation of the surface.

Eliminating γ from this equation and the equation of Gibbs introduced with the surface correction β i.e.

$$\frac{u}{1-u\beta}=-\frac{C}{RT}\frac{d\gamma}{dC}$$

we obtain a new adsorption isotherm as follows:

$$\frac{u}{1-u\beta}=KC^{\frac{1}{i}} \quad\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots(6)$$

in which K and i are constants.

This formula is identical with that of Freundlich when u is small and it also expresses the state of saturation.

An example of the application of this isotherm for experimental data is given in the following. The data here referred are taken from one of the series of experiments made by Schmidt⁽¹⁾ on the adsorption of acetic acid solution by animal charcoal. For the convenience sake of calculation, the formula (6) is transformed into

$$\log\left(\frac{1}{u}-\frac{1}{S}\right)=\frac{1}{i}\log\left(\frac{1}{C}\right)-\log K\cdots\cdots\cdots\cdots(7)$$

in which $\frac{1}{S}=\beta$, S representing the amount of solute in saturation. And u is assumed to be proportional to the adsorption per unit mass of solvent.

Fig. 1.

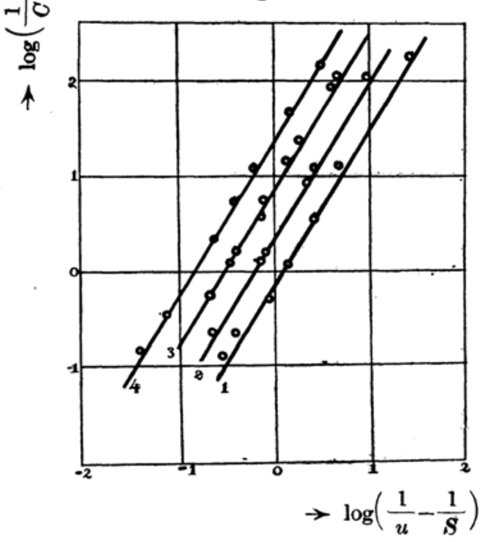

TABLE 1. 5 gr. Animal Charcoal.

$\log\frac{1}{C}$	$\log\left(\frac{1}{u}-\frac{1}{S}\right)$	$C_{\text{obs.}}$	$C_{\text{calc.}}$
$\bar{1}.12188$	$\bar{1}.54637$	7.553	11.07
$\bar{1}.37469$	$\bar{1}.57519$	4.220	6.898
$\bar{1}.69272$	$\bar{1}.95665$	2.029	1.510
0.07058	0.14259	0.850	0.720
0.53611	0.41380	0.291	0.244
1.12148	0.69346	0.0756	0.0751
2.20761	2.42586	0.0062	0.0043

$S=0.523$ $\underline{i=1.73}$ $\underline{K=0.86}$

TABLE 2. 10 gr. Animal Charcoal.

$\log\frac{1}{C}$	$\log\left(\frac{1}{u}-\frac{1}{S}\right)$	$C_{\text{obs.}}$	$C_{\text{calc.}}$
$\bar{1}.34008$	$\bar{1}.39445$	4.570	4.650
0.10237	$\bar{1}.90795$	0.790	0.774
0.17393	$\bar{1}.92788$	0.670	0.555
0.95078	0.34439	0.112	0.106
1.11238	0.41731	0.0772	0.0789
2.03152	1.00689	0.0093	0.0076

$S=1.058$ $\underline{i=1.73}$ $\underline{K=1.7}$

TABLE 3. 20 gr. Animal Charcoal.

$\log\frac{1}{C}$	$\log\left(\frac{1}{u}-\frac{1}{S}\right)$	$C_{\text{obs.}}$	$C_{\text{calc.}}$
$\bar{1}.76700$	$\bar{1}.38453$	1.710	1.466
0.11930	$\bar{1}.57634$	0.759	0.682
0.29826	$\bar{1}.64972$	0.5032	0.5087
0.56019	$\bar{1}.81558$	0.2753	0.2627
0.73731	$\bar{1}.90956$	0.1831	0.1807
1.18442	0.10789	0.0654	0.0819
1.40561	0.26670	0.0393	0.0435
1.97551	0.59051	0.01058	0.01198
2.04096	0.65591	0.00910	0.00923

$S=2.119$ $\underline{i=1.73}$ $\underline{K=3.4}$

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(1) Schmidt, *Z. physik. Chem.* **77** (1911), 645.

TABLE 4. 40 gr. Animal Charcoal.

$\log\frac{1}{C}$	$\log\left(\frac{1}{u}-\frac{1}{S}\right)$	$C_{\text{obs.}}$	$C_{\text{calc.}}$
$\bar{1}.21746$	$\bar{2}.61278$	6.06	8.50
$\bar{1}.56177$	$\bar{2}.89873$	2.74	2.72
$\bar{1}.69486$	$\bar{1}.02160$	2.02	1.67
0.36005	$\bar{1}.39410$	0.437	0.378
0.76447	$\bar{1}.62024$	0.172	0.158
1.12726	$\bar{1}.79078$	0.0746	0.0778
1.69680	0.17638	0.0201	0.0225
2.18046	0.51068	0.0066	0.0104

$S=4.434$ $\underline{i=1.73}$ $\underline{K=7.1}$

Fig. 1. shows that the linear relation between $\log\left(\frac{1}{u}-\frac{1}{S}\right)$ and $\log\left(\frac{1}{C}\right)$ is satisfactory. i Is found to be fairly constant for varying amounts of adsorvent and approximately equal to 1.73. The value of K found is almost proportional to the amount of charcoal taken. In the last two columns of each table the values of concentration C (gr. in 100 c.c.) are compared with that which are calculated by relation (7).

The present note, although still incomplete, is published, the author being obliged to put off further investigations for few months. In conclusion, the author wishes to express his sincere thanks to Prof. M. Katayama for his kind guidance.

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