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# Surface Area Measurement of Powders by Adsorption in Liquid Phase. (I)\*

## Calculation of Specific Surface Area of Calcium Carbonate Powders from the Adsorption of Stearic Acid

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The measurement of specific surface area for various kinds of calcium carbonate powder by the adsorption of stearic acid in benzene solution has been investigated. The shape of the adsorption isotherms showed the S-type and was quite similar to the adsorption isotherms for gas phase at low temperature, and adsorption state on powder surface was unchanged irrespective of particle size and shape. For these isotherms, the B E T plot was linear and the  $V_m$ , the value of monolayer adsorption, was obtained from the intersect and the inclination of these straight lines. The value of  $V_m$  calculated by the B E T equation agreed with the end of horizontal part of adsorption isotherms and, moreover, agreed with the value of monolayer adsorption from the change in surface pressure of the powder-liquid interface caused by the adsorption of stearic acid calculated by using Gibbs equation.

### I. INTRODUCTION

Determination of the particle size of powder is very important for industrial as well as theoretical use, and various measuring methods are used. The authors investigated the determination of particle size distribution by the sedimentation method<sup>1)</sup> and the reaction rate method<sup>2)</sup>. In the present work the measuring of specific surface area by the adsorption method in liquid phase has been studied.

The B E T equation, which is an adsorption isotherm based on a multilayer theory developed by Brunauer, Emmett and Teller<sup>3)</sup> was in good agreement with the experimental data for the low temperature adsorption of gas as  $N_2$ ,  $NH_3$ , Ar, etc. on solids, and made possible the calculation of a reasonably accurate value for the surface area of the adsorbent. However, the apparatus and experiments of liquid phase adsorption are very simple as compared with the gas phase method and it is interesting in connection with the problem of surface coating for some industrial powders as fillers and reinforcers.

\* This is a translation of the same article which appeared in Japanese in *Journal of the Chemical Society of Japan*, 75, 596~599 (1954).

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It is well known that when a long chain polar compound is brought into contact with the various powders in benzene solution, it may be adsorbed on the powder surface. Successful studies have been made in adsorbed oleic acid on titanium dioxide from benzene solution by Harkins and Gans<sup>4)</sup>, in adsorbing methyl stearate and glycol dipalmitate on zinc oxide from benzene solution by Ewing<sup>5)</sup>, and in adsorbing long chain electrolytes on graphite from aqueous solution by Corrin, Lind, Roginsky and Harkins<sup>6)</sup>. Moreover, the experiments with several inorganic powders<sup>7) 8) 9)</sup> and metal powders have been made in connection with lubricating properties<sup>10~13)</sup>. But the theoretical explanation was not satisfactory. The authors measured and discussed the specific surface area of calcium carbonate powders by the adsorption of stearic acid in benzene solution.

## II. MATERIALS

The powders used in the present experiments were five kinds of calcium carbonate (A,B,C,P and ultra fine powder U) having different sizes and shapes. They were prepared by the reaction of  $\text{Ca(OH)}_2$  suspension and  $\text{CO}_2$  gas, and their shapes, sizes and size distribution of particles were observed by electron microscope<sup>14)</sup>. The samples A,B,C and P had spindle shapes and sample U had rhombic shape, but all of them showed the calcite type by X-ray analysis. Their particle sizes were in the order  $C > B > A > P > U$ .

The stearic acid used as adsorbate was of the commercial grade, and the benzene used as solvent was sufficiently clarified by removing the water contained.

## III. EXPERIMENTAL

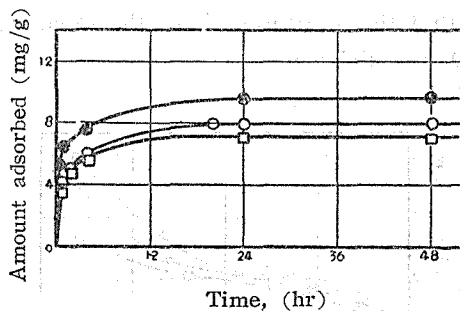
About 2 g of powder, dried at 300°C for 8 hrs. in high vacuum, was gathered in glass tube of about 50cc, then 20cc of benzene solution of stearic acid was added and they were sealed and kept standing for some time after enough shaking at 20°C. Supernatant solution (10cc) was withdrawn in a weighing bottle by pipette and the concentration of stearic acid in the solution was measured after the evaporation of solvent. The adsorption amount of the stearic acid on the surface of powders was calculated by the decrease of the concentration of the stearic acid in clear liquid after the adsorption.

## IV. RESULTS

### (1) Rate of adsorption

The adsorption amount by the powder was measured at several intervals of time at a definite concentration of solution. Typical examples are plotted in Fig. 1. The rate of adsorption was initially very rapid, but became extremely slow as the adsorption neared completion. As the adsorption equilibrium may be complete-

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Time, (hr)

Fig. 1.

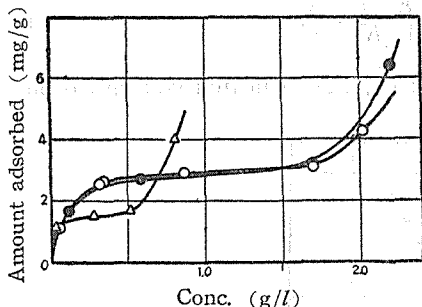
- : CaCO<sub>3</sub>-A 0.004 mole
- : CaCO<sub>3</sub>-P 0.003 mole
- : CaCO<sub>3</sub>-B 0.01 mole

ly attained in 24 hrs., the experiments for adsorption isotherm were done after the standing for 24 hrs.

The adsorption amount at equilibrium state was about 60 % of the total amount of adsorbate for all kinds of CaCO<sub>3</sub>.

(2) Adsorption isotherm

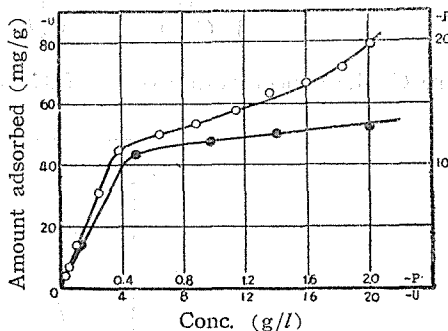
The adsorption amount after 24hrs. was measured at various concentration of stearic acid. The relation between the adsorption amount and the concentration of stearic acid, i.e. the adsorption isotherm is shown in Fig. 2 for the CaCO<sub>3</sub>-A,B, C, and in Fig. 3 for the CaCO<sub>3</sub>-P and -U. At first, the adsorption amount increases



Conc. (g/l)

Fig. 2.

- : CaCO<sub>3</sub>-A
- : CaCO<sub>3</sub>-B
- △—: CaCO<sub>3</sub>-C



Conc. (g/l)

Fig. 3.

- : CaCO<sub>3</sub>-U
- : CaCO<sub>3</sub>-P

ed with the concentration then it remained practically constant up to some concentration (*horizontal part*) and again increased to the highest concentration, i.e., showed the S-type isotherm. Although the shape of the adsorption isotherms is the same for all samples, but the larger the surface area of the powder, the higher and longer is the horizontal part. All of the adsorption isotherms for the five kinds of CaCO<sub>3</sub>, of which the adsorption amounts per unit area are plotted against the concentration per unit area, fall very nearly on the same curve as shown in

Fig. 4. This suggests that the adsorption is of the same type even if the particle size and shape of  $\text{CaCO}_3$  are different.

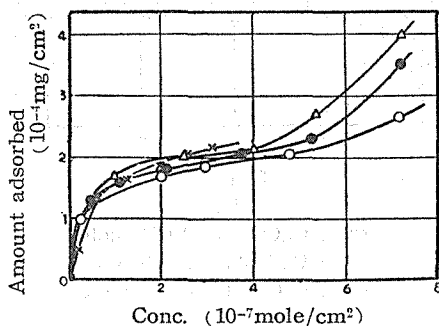


Fig. 4.

○:  $\text{CaCO}_3$ -A    △:  $\text{CaCO}_3$ -C  
 ●:  $\text{CaCO}_3$ -B    ×:  $\text{CaCO}_3$ -U

### V. APPLICATION OF BET EQUATION

Rather successful attempts have been made recently by Bartell and co-workers<sup>6)</sup> in modifying the B E T equation to apply to the adsorption from solutions. In liquid phase, the B E T equation will be as follows, substituting the concentration for the pressure,

$$\frac{C}{V(C_0 - C)} = \frac{1}{V_m K} - \frac{K-1}{V_m K} \cdot \frac{C}{C_0} \quad (1)$$

where  $C$ , the concentration of the fatty acid;  $C_0$ , the saturated concentration;

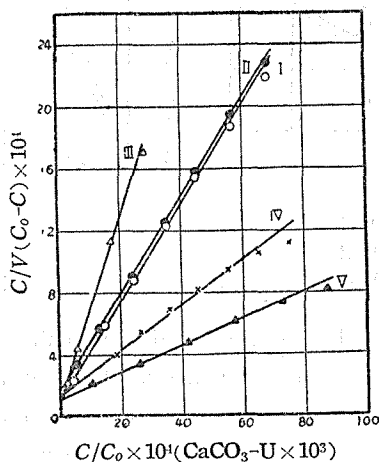


Fig. 5.

I:  $\text{CaCO}_3$ -A    IV:  $\text{CaCO}_3$ -U  
 II:  $\text{CaCO}_3$ -B    V:  $\text{CaCO}_3$ -P  
 III:  $\text{CaCO}_3$ -C

$V$ , the adsorption amount;  $V_m$ , the necessary amount to form the adsorption monolayer;  $K$ , the constant about the adsorption heat. Applying these isotherms to our data, the plot of  $C/C_0$  against  $C/V(C_0 - C)$  becomes linear with a slight deviation at low and high concentrations, as shown in Fig. 5. The  $V_m$  and  $K$  can be obtained from intersect and inclination of straight line in Fig. 5. The values of  $V_m$  of various samples are shown in Table 1 (5th column).

## VI. CALCULATION OF SPECIFIC SURFACE AREA OF POWDERS

In the calculation of specific surface area and particle size, it is assumed that stearic acids were adsorbed as a monomolecular film with the carboxyl group attached to the calcium carbonate surface and the particles had round spheres with no pore or crevices. The cross-sectional area of the stearic acid molecules was considered to be the same as that formed in a compressed film of fatty acid on water/air interface<sup>(6) (15)</sup>.

Basing on this, specific surface area was calculated from the equation

$$S_w = 10^{-20} na/g, \quad n = V_m \cdot A/M \quad (2)$$

where  $S_w$ , the surface area in  $m^2/g$ ;  $n$ , the number of molecules adsorbed;  $a$ ,  $21\text{\AA}^2$ ;  $g$ , the gram of sample used;  $A$ , Avogadro number;  $M$ , the molecular weight of adsorbate; and  $10^{-20}$  is the conversion factor between  $\text{\AA}^2$  unit and  $m^2$ . The particle diameter is calculated from the equation

$$d_m = 6/\rho S_w \quad (3)$$

where  $\rho$  is the density of the sample powders and  $d_m$  the particle size in  $\mu$ . The value of  $S_w$  and the mean diameter  $d_m$  of various powders from  $V_m$  are shown in 6th and 7th columns of Table 1.

Table 1. Specific surface area calculated by various methods ( $m^2/g$ ).

Sample	Adsorption						Sedimentation	Permeability	Microscopy	
	A	B	C	B E T equ.					Optic.	Elect.
				$V_m(\text{mg/g})$	$S_w(\text{m}^2/\text{g})$	$d_m(\mu)$				
CaCO <sub>3</sub> -A	1.08	1.22	1.54	3.2	1.52	1.5	1.51	1.45	1.47	1.51
// -B	0.91	1.17	1.49	3.1	1.33	1.8	1.24	1.63	1.22	1.26
// -C	0.58	0.61	0.75	1.6	0.75	3.0	0.52	0.84	0.55	
// -P	6.14	6.21	6.39	13.6	6.41	0.34	4.91			6.50
// -U	17.10	21.06	32.30	69.2	32.39	0.069		2.94		33.80

The value of  $S_w$  calculated from the adsorbed value at the points A, B, and C in adsorption isotherms (Fig. 6) is also shown in 2nd, 3rd and 4th columns of Table

1, along with that calculated by other method.

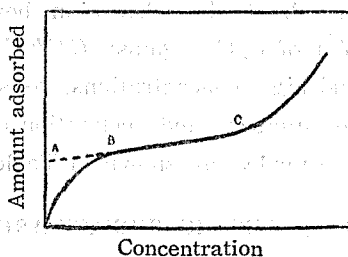


Fig. 6

The value of  $S_w$  calculated by the BET equation agrees with that calculated from the point C, and this value agrees with that measured by other methods, but does not agree with the value from the point A used in gas phase methods.

### VII. $\pi$ - $\Gamma$ CURVES USING THE GIBBS EQUATION

The Gibbs adsorption isotherms can be used to calculate the decrease in surface free energy due to the adsorption at gas-liquid interface. Since the Gibbs equation is derived from thermodynamic considerations, it can be applied to any other interface and so may be employed in the present case of adsorption on solid from solution. The Gibbs equation is usually written:

$$\Gamma = -\frac{C}{RT} \cdot \frac{d\gamma}{dc} \quad (4)$$

where  $C$ , the concentration;  $\gamma$ , the decrease in surface free energy;  $\Gamma$ , the surface excess; rewriting and integrating, we have

$$\pi = \int d\gamma = -RT \int \Gamma d \ln c \quad (5)$$

For the adsorption from solution,  $\pi$  represents the change in surface free energy, i.e. surface pressure of the solvent-solid interface caused by adsorption of the solute. Thus using equation (4), it is possible to be calculated from the adsorption data. The  $\pi$ - $\Gamma$  curve obtained for stearic acid on  $\text{CaCO}_3$ -A is shown in Fig. 7. The curve obtained for stearic acid on  $\text{CaCO}_3$  was quite similar to the  $\pi$ - $\Gamma$

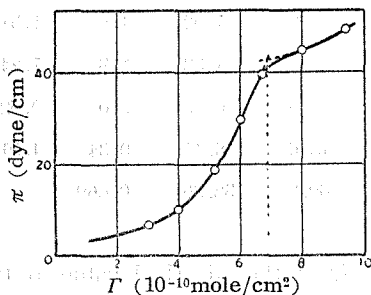


Fig. 7.

curve of a monolayer of substance at the air-liquid interface which gives a gaseous film at low surface pressure and passes from the state of a liquid-expanded film into a condensed film as the surface pressure is increased. The adsorption value of typical inflection point in this curve, that is the changing point from expanded film to condensed film, was  $6.8 \times 10^{-10}$  mole/cm<sup>2</sup> = 3.2 mg/g and it agrees with  $V_m$  by the B E T equation.

### VIII. SUMMARY

The adsorption of stearic acid from benzene solution on various kinds of calcium carbonate powder has been investigated.

- (1) The shape of the adsorption isotherms had the S-type and very similar to the gas adsorption at low temperature.
- (2) As the end point of horizontal part in the isotherm (point C in Fig. 6) corresponded to the completion of monolayer adsorption, the specific surface area and mean particle size could be calculated from this value.
- (3) The B E T equation could be applied to the adsorption in liquid phase. About these isotherms, the plot of  $C/C_0$  against  $C/V(C_0 - C)$  became linear. The value of  $V_m$  and specific surface could be calculated more accurately from the inclination and intersect of the straight line.
- (4) The change in surface pressure of the solvent-solid interface caused by adsorption of the stearic acid was calculated by using the Gibbs equation. The adsorption amount at a typical inflection point in this curve agrees with  $V_m$  by the B. E.T. equation.

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