

9. Surface Area Measurement of Powders by Molecular Adsorption at Solid-Liquid Interface

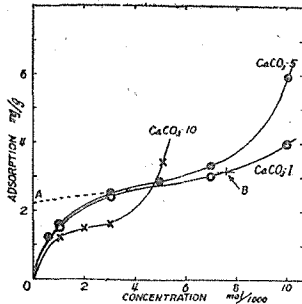
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Various powders of calcium carbonate and zinc oxide were added in the benzene solution of stearic acid and they were kept standing for 24hrs. The adsorption amount of the fatty acid on the surface of powders was measured by the decrease of the concentration of the fatty acid in clear liquid after the adsorption.

Results. Rate of adsorption: The rate of adsorption is initially very rapid, but as adsorption approaches completion the rate become extremely slow and equilibrium may be completely attained after 20hrs.

Fig. 1.



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The adsorption isotherms: The adsorption amount by the powders after 24hrs. was measured about various initial concentration of fatty acid. The relation between the adsorption amount and the initial concentration of fatty acid *i.e.* the adsorption isotherm is shown in Fig. 1. In liquid phase, the B.E.T. equation will be as follow, 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,

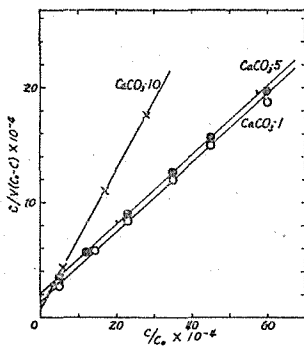
C_0 : the saturated concentration,

V : the adsorption amount,

V_m : the necessary value to form the adsorption monolayer,

K : the constant.

Fig. 2.



About those isotherms, the plot of C/C_0 against $C/V(C_0 - C)$ become linear with some deviation at low and high concentrations as shown in Fig. 2. Therefore, it is sure, the B.E.T. equation can be applied to the molecular adsorption in liquid phase. The V_m was obtained from intersect and inclination of straight line in Fig. 2. The specific surface area S_w can be calculated, when the cross-section area of stearic acid was 21\AA . The value of S_w and the mean diameter d_m of various powders are shown in Table 1,

along with the area calculated by other methods.

Table 1.

Sample	Measurement						
	Adsorption		Sedimentation		Permeability		Electron Microscopy
	S_w (cm ² ./g.)	d_m (μ)	S_w (cm ² ./g.)	d_m (μ)	S_w (cm ² ./g.)	d_m (μ)	c_m (μ)
CaCO ₃ -1	15,160	1.5	15,147	1.5	14,495	1.6	1.5
" -5	13,390	1.6	12,438	1.8	16,281	1.4	1.8
" -10	7,480	3.0	5,171	4.3	8,395	2.8	4
" -S	323,937	0.067	-	-	23,446	0.78	0.04
ZnO-1	230,916	0.047	-	-	-	-	0.1
" -2	313,500	0.035	-	-	-	-	0.02

This value agrees well with that measured by other methods. In this case, the value of V_m calculated by the B. E. T. equation agrees with the point B in Fig. 1, but V_m is at the point A in gas phase and this difference is thought to be due to the weak adsorption of solvent molecules.

Calculation of free energy of adsorption: The change in surface free energy of a solid due to adsorption was calculated from isotherm using Gibbs equation which is usually written:

$$\Gamma = -C/RT \cdot d\gamma/dC, \quad (2)$$

where C : the concentration,

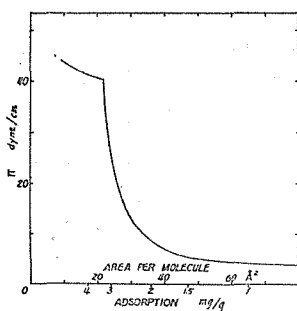
γ : the decrease in surface free energy,

Γ : the surface excess.

Rewriting and integrating

$$\pi = \int d\gamma = -RT \int \Gamma \, d \ln C. \quad (3)$$

Fig. 3.



For the adsorption from solution, π represents the change in surface free energy, i. e. surface pressure of the solvent solid interface caused by adsorption of the solute. Thus using eq. (3), it is possible to calculate π from the adsorption data. The curve obtained for stearic acid on CaCO₃-1 using eq. (3) is shown in Fig. 3. The adsorption value of typical inflection in this curve agrees with V_m by the B. E. T. equation.

Conclusion. The value of V_m using the B. E. T. equation, can be considered as the completed value of the monolayer adsorption. Thus it is confirmed to be possible to calculate the specific surface area of powders using the adsorp-

tion in the liquid phase and it agrees well with that measured by other methods.

10. Studies on Microcrystals by Electron Microscope and Electron Diffraction. (III)

On the Colloidal Particles formed by Ultrasonic Stripping Method

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When a clean metal surface is dipped in the solution of an electrolyte, the reduced positive ions in the solution are deposited on the metal surface as the pure metal crystal, if the ionization potential of the former is lower than the latter. By the strong shearing action of the ultrasonic wave, these deposited metal crystal are stripped to fine particles and dispersed into the solution as colloidal suspension. Investigations were made in relation to these dispersed systems, especially in the morphological aspect of the particles with electron microscope and in their crystalline characters with electron diffraction patterns, as it was a problem of much interests whether such dispersed systems suffered oxidation by the subsidiary action of the ultrasonic wave. The reduced positive ions used in this studies were Cu, Zn and Pb, and were deposited from 0.05% CuSO_4 , 0.05% ZnCl_2 , and 0.1% PbNO_3 solution respectively. The inserted reducing metals were Fe for Cu and Pb ions, and Mg for Zn ions. When ultrasonic wave, generated by a quartz plate forced to oscillate in a frequency of 800kc per second by driving circuit with SN-204, whose in-put power supply was about 300W, were applied to these systems, dispersion took place at once in the case of Pb solution whereas after an induction period of about 10 minutes in the case of Cu solution. For Zn solution, because of the acidity of the solution, hydrogen gas was evolved and the dispersing aspects were ambiguous.

Saturation points were reached after continuing such ultrasonic dispersion for about 20-30 minutes, and the solution became turbid in black for Cu, and in white for Pb and Zn. These suspensions were separated from the inserted reducing metals, and purified by centrifugal sedimentation method. These three suspensions were named Sample A, B and C for Pb, Cu and Zn respectively.

Electron micrographs were taken for these samples and their morphologic characters, i.e. shapes, particle sizes and size distributions, were obtained. Except for Cu, Sample B, dispersed particles were all very thin crystals. This may show that these metals oriented on the inserted metal sur-