Surface Area Measurement of Powders by Adsorption in Liquid Phase. (II)*

Effect of Adsorbates and Solvents

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The influence of various adsorbates and solvents in the measurement of specific surface area of powder by the adsorption method in liquid phase was investigated. The adsorbates have no appreciable effect, but the solvents appears to have conciderable effect upon the adsorption amount of monomolecular layer. This may be due to the remain of solvent molecules in the adsorption layer, and the ratio of surface area occupied by the remaining solvent molecules was about 3 % in benzene, 20 % in toluene and 50 % in carbontetrachloride.

I. INTRODUCTION

In the previous paper[1], it was shown that the B E T equation can be applied to the adsorption of stearic acid on calcium carbonate from benzene solution and the specific surface area obtained from the amount of monolayer adsorption using the B E T equation agrees with that measured by other methods. In the present work, the influence of various adsorbates and solvents was investigated and, moreover, heat and energy of absorption were calculated.

II. EXPERIMENTAL

The powders used were three kinds of calcium carbonate having different particle sizes. The adsorbates used were stearic acid, palmitic acid, oleic acid, benzoic acid, methyl stearate and glycol stearate, and the solvents used were benzene, toluene, and carbontetrachloride. These materials were all purified and dried. The experimental method used in the present work was identical with that described in part I.

III. RESULTS

(1) The adsorption isotherms from various adsorbates

The adsorption isotherms for several adsorbates from benzene solution for

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$CaCO_3$-A were determined.

   i) Saturated fatty acids (stearic acid and palmitic acid).

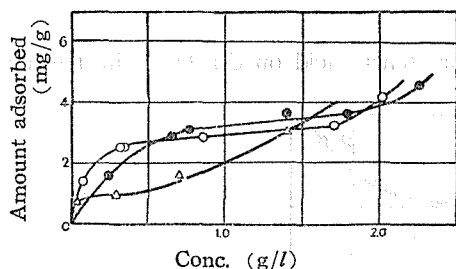Saturated fatty acids showed the S-type isotherms as in Fig. 1.

Fig. 1

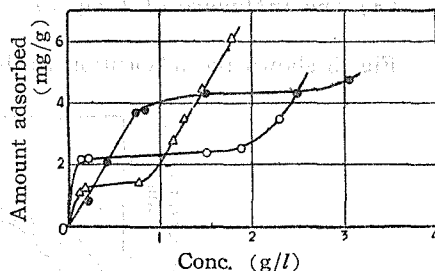—◯—: Stearic acid
—⬤—: Palmitic acid
—△—: Oleic acid

Fig. 2

—△—: Benzoic acid
—◯—: Methyl stearate
—⬤—: Glycol stearate

   ii) Unsaturated fatty acid (oleic acid).

Isotherm is shown also in Fig. 1 and is quite similar to the stearic acid curve. The horizontal part of the isotherm is, however, very short, and the adsorption amount at this part is about half that of the stearic acid.

   iii) Aromatic fatty acid (benzoic acid).

The result obtained with the benzoic acid is shwon in Fig. 2. In this case the horizontal part is shorter than the others.

   iv) Esters (methyl stearate and glycol stearate).

These isotherms are shown in Fig. 2 and are very similar to the stearic acid. The adsorption value of horizontal part for glycol stearate is about two times of methyl stearate.

(2) The influence of solvents.

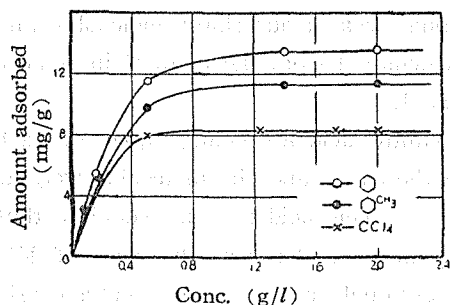Figs. 3 and 4 show the adsorption isotherms for stearic acid on $CaCO_3$-P and

Fig. 3.

—◯— ◯
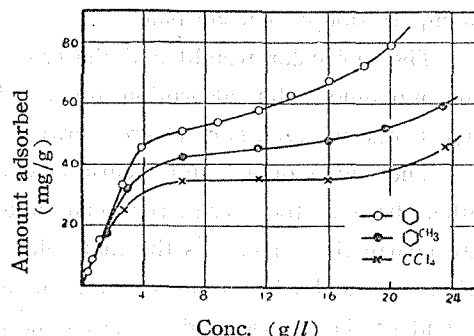—⬤— ◯^{CH_3}
—✕— CCl_4

Fig. 4.

—◯— ◯
—⬤— ◯^{CH_3}
—✕— CCl_4

-U in benzene, toluene and carbontetrachloride solution. The solvent had no

appreciable effect upon the rate of adsorption. The type of these isotherms showed also the S-type, whereas the adsorption amount at the horizontal part was very different from the solvents showing benzene>toluene>carbontetrachloride.

(3) The influence of temperature.

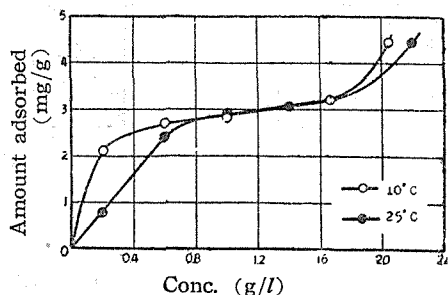Fig. 5 shows the adsorption isotherms for stearic acid on $CaCO_3$-A in benzene

Conc. (g/l)
Eig. 5.

at 10℃ and 25℃. The temperature had no effect upon the adsorption amount of the horizontal parts. It has, however, a considerable influence upon the concentration of solution necessary to reach horizontal parts, and the concentration at 10° C was about two times of that at 25℃.

IV. DISCUSSION

(1) Influence of adsorbates

The shape of the adsorption isotherms for a given adsorbate remains actually unchanged. Comparing the isotherms for stearic acid and palmitic acid it was found that, the latter requires a higher concentration for the completion of adsorption monolayer. The same results were also obtained by other workers[2] for the adsorption of fatty acids on metal powders, and agree with the fact that the longer the carbon chain of molecules, the higher is the adsorption heat at the adsorption of n-paraffine on carbon blacks[3].

The molecular weight and the cross-sectional area of adsorbate molecules and the monomolecular adsorption amount V'_m calculated from the point C in adsorption isotherms (see part I) are shown in Table 1.

The values of V'_m for stearic acid and palmitc acid are nearly equal to each other, because those cross-sectional areas are the same and the molecular weights are nearly the same. As the molecular weight of oleic acid is neary equal to that of stearic acid whereas its cross-sectional area is about 2 times, the value of V'_m is half of the stearic acid. And as the cross-sectional area of benzoic acid is nearly equal to the stearic acid whereas molecular weight is about half, of in the value of V'_m should be about half of stearic acid. For ester, V'_m is expected to be

Table 1.

	Stearic acid	Palmitic acid	Oleic acid	Benzoic acid	Methyl stearate	Glycol stearate
Molecular weight	284.29	256.26	282.27	122.05	298.30	594.60
Cross-sectional area ($Å^2$)	21	21	46	24	27	48
V'_m (mg/g)	3.2	3.4	1.6	1.4	2.3	3.8
Sp. surf. area of $CaCO_3$-A (m^2/g)	1.54	1.54	1.58	1.55	1.24	1.86

equal, since both the molecular weight and the cross-sectional area of glycol stearate are about twice of methyl stearate, whereas the value of V'_m was unequal (1.5 times).

The isotherms of these adsorbates are quite similar to that obtained for stearic acid in benzene solution in part I. The specific surface areas of $CaCO_3$-A obtained by using these adsorbates are shown in Table 1 and their values agree well each other.

(2) Influence of solvents

The solvent seems to have a considerable influence upon the adsorption amount of monomolecular layer, as is shown Fig. 4. The BET plot for these isotherms is linear with some deviation at low concentration, as is shown in Fig. 6. In
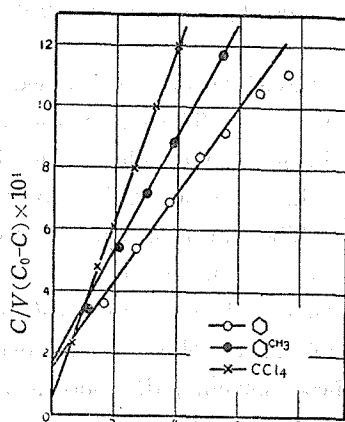

Fig. 6.

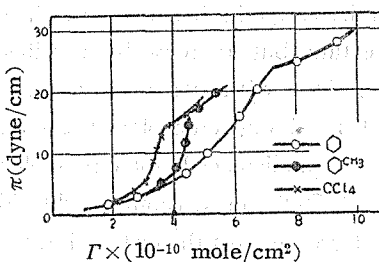$\Gamma \times (10^{-10} \text{ mole/cm}^2)$

Fig. 7.

this case, it is identical with those described in part I, that is, the value of V_m calculated from the BET equation agrees with that V'_m calculated from the point C in adsorption isotherm. The $\pi - \Gamma$ curves which were calculated from isotherms by using the Gibbs equation for $CaCO_3$-U, are shown in Fig. 7. For the same solvent, the adsorption amount of monomolecular layer obtained from the

(11)

break point in $\pi - \Gamma$ curves agrees with V'_m calculated by the isotherms and V_m by the B E T equation. Table 2 shows typical results. Accordingly, it is conside-red that monomolecular adsorption layer in toluene and carbontetrachloride is also cmpleted at C-point in isotherm as in the case of benzene. For different solvents, however, the adsorption amount of monomolecular layer differed from each other.

Since the shape and particle size distribution of CaCO₃-P and -U were pre-cisely obtained by electron microscope, it is possible to calculate the amount of

Table 2.

	Solvent	Adsorption value for mono-molecular layer (mg/g)				Sp. surface area m²/g		π (dyne/cm)	Solubility of stearic acid (g/100cc)
		V'_m	B E T	Gibbs	E.M.*	B.E.T.	E.M.*		
CaCO₃-U	Benzene	69	69.2	67	73.0	32.4	33.8	21.5	24
	Toluene	51	52.4	45	73.0	26.5	33.8	15.5	33
	CCl₄	37	36.6	36	73.0	18.0	33.8	14.0	53
CaCO₃-P	Benzene	13 6	13.6	13 5	13.8	6.4	6.5	21.5	24
	Toluene	11.5	12.0	11.0	13.8	5.7	6.5	15.5	33
	CCl₄	8.4	8.2	8.1	13.8	3.9	6.5	14.0	53

* Electron microscopy.

stearic acid necessary to form the monomolecular layer on these surfaces. These values and specific surface areas calculated from the value by electron microscope are shown in Table 2.

The values calculated by using the BET equation agreed with those obtained by electron microscope in benzene, but diffe red in other solvents. The reason for this is not certain but it may be ascribed to the remain of solvent molecules in the adsorption film with constant ratio, and it seems that the adsorption layer is completed involving undisplaced solvent molecules. The ratio of surface area occupied by undisplaced solvent molecules was about 3 % in benzene, 20 % in toluene and 50 % in carbontetrachloride. The π values calculated by the Gibbs equation decrease with the order above mentioned (Table 2, 9th column). Moreover, the higher the solubility of the stearic acid in these solvents, the more is the amount of undisplaced molecules (10th column). This suggests that the interaction of solvent and adsorbate must be taken consideration.

(3) **Calculation of free energy and heat of adsorption.**

It is possible to calculate the standard free energy of adsorption, ΔF, and the heat of adsorption, ΔH, from the initial part of isotherms and their variation with temperature respectively. The standard free energy, ΔF, for the adsorption process is given by

$$\Delta F = -RT \ln C_s/C_c, \tag{1}$$

where C_s is the concentration of adsorbate in the adsorbed layer and C_c the concentration of the adsorbate in the bulk solution. To be more exact, Eq. (1) should refer to activities but by restricting the calculation to a very low concentration, this difference becomes unimportant. The value of ΔF calculated from the isotherms of stearic acid on CaCO$_3$–A was –4.35 kcal/mole at 10° C –4.02 kcal/mole at 25° C respectively for benzene solution and 83.7 kcal/mole at 15° C for toluene and carbontetrachloride solution. The value of ΔH calculated from ΔF value at 10°C and 25°C was –10.8 kcal/mole for stearic acid in benzene. The values of ΔH were also calculated from the constant, K, in the B E T equation and they were about –20~–25 kcal/mole. The value of ΔH obtained by Daniel[2] for stearic acid on some metal powders was 12 kcal/mole.

V. SUMMARY

(1) Stearic acid, palmitic acid, oleic acid, benzoic acid, methyl stearate and glycol stearate were used as the adsorbate. The adsorption isotherms obtained all showed the S type and the specific surface area calculated from those agreed well with each other.

(2) However, the solvent appears to have a considerable influence upon the adsorption amount. Although the reason for this is not certain, it may probably ascribed to the remain of solvent molecules.

(3) The free energy of adsorption and the heat of adsorption were calculated from the adsorption isotherms and the B E T equation.

REFERENCES

(1) E.Suito, M.Arakawa and T.Arakawa : This Bulletin, 33, 1 (1955).
(2) S.G.Daniel : *Trans. Farad. Soc.*, 47, 1345 (1951).
(3) W.D.Schaeffer, M.H.Polley and W.R.Smith : *J. Phys. Coll. Chem.*, 54, 227 (1950).