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A Theoretical and Experimental Study of Physical Adsorption of Gases on Uniform Flat Solid Surface

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In this work we have experimentally observed the physisorption isotherms for nitrogen, TMS, cyclohexane, benzene, and *n*-hexane adsorbed on flat aluminum foil surface and have analyzed them theoretically on the basis of the theory proposed by Chang *et al.* The results show that the theory by Chang *et al.* can provide a useful means to describe the physisorption of gases on uniform flat solid surface which is essentially important for analysis of the pore volume distribution in porous solid surface. We have also discussed the application of the results obtained in this work to the analysis of pore volume distribution in porous alumina we reported previously.

Introduction

In the process of analysis of pore volume distribution in porous solids the knowledge of statistical thickness of adsorbed gas on the uniform flat solid surface is required and this thickness plotted against the relative gas pressure forms the so-called "*t*-curve".[1] In other words one may say that the knowledge of *t*-curve is essential for analysis of pore volume distribution in porous solids by the gas adsorption method. Gaseous nitrogen has been the most popular adsorbate used for this purpose and its *t*-curves have been reported by several authors.[2] De Boer *et al.*[3] have noted that the shape of nitrogen *t*-curve is nearly independent of the adsorbent used and have suggested that such a universal feature of the nitrogen *t*-curve should be used for the study of pore volume distribution. Since then the universal *t*-curve for gaseous nitrogen has become the major tool with which one can investigate into the mesopore distribution problems.

In a previous paper[4] (hereafter, referred to as Paper I), however, the authors have demosntrated that the use of nonpolar and spherical molecules with relatively large molecular weight as adsobates is more advantageous and gives more reliable and consistent results in the analysis of pore volume distribution by the gas adsorption method. Unfortunately, for such molecules as TMS, CCl$_4$, and cyclohexane, which are recommended as more suitable than nitrogen as adsorbate, little is known about their flat-surface adsorption isotherms. Therefore, in Paper I we have used their adsorption-desorption isotherms measured for the porous alumina sample to estimate their flat-surface isotherms by fitting the former into the theoretical isotherms derived from the theory

due to Chang *et al.*[5] over the relative pressure range of 0.0-0.3 and thereby have obtained very encouraging results. Thus we have decided that it is worth following this route for further investigation of the aforementioned problems. Ultimate justification of the validity of this method requires the experimental measurement of the flat-surface isotherm for each adsorbate and its comparison with the corresponding theoretical isotherm. Thus the objective of this paper is to observe the experimental flat-surface isotherms for adsorbates such as TMS, CCl$_4$, and cyclohexane and compare them with those calculated from the Chang's theory.

The theoretical isotherm derived by Chang *et al.* contains four adjustable parameters that can be fixed in such a way that it gives the best fit into the experimental data over a wide range of relative pressure. Among these four parameters, a is the one that has the largest influence on the shape of isotherm over the relative pressure range of 0.8-1.0 which is the most crucial region for the analysis of pore volume distribution. In Paper I we have simply assumed $a = 0.95$ because from the adsorption-desorption isotherms observed for the porous alumina system the value of this parameter could not be determined directly. By observing the experimental flat-surface isotherm one may find a better way to determine the value of this parameter via direct comparison with the theoretical isotherm. In this work we have measured the flat-surface physisorption isotherms for nitrogen, TMS, cyclohexane, benzene, and *n*-hexane adsorbed on the uniform aluminum foil and the results have successfully been compared with the calculated ones. We have also recalculated the pore volume distribution curves for the porous alumina system we discussed in Paper I using the results ob-

tained in this work and have compared them with those esti-
mated by other methods.

Theory

The capillary condensation phenomena in an open-ended
cylindrical pore can be described by the following Kelvin
equation:[6]

$$\ln (p_a/p_o) - \ln (p_\infty/p_o) = - \frac{\gamma_\infty V_m}{(r-t-\delta)RT} \qquad (1)$$

where p_a is the vapor pressure of adsorbed phase of thick-
ness t on the inside wall of an open-ended cylindrical pore
with radius r, p_o the saturation vapor pressure, and p_∞ the
vapor pressure that the adsorbed phase of the same thick-
ness t would have if it were adsorbed on the flat surface. γ_∞
is the surface tension of the adsorbed phase on the flat sur-
face and δ may be interpreted as the monolayer thickness.
V_m and R are the molar liquid volume of adsorbed phase and
the gas constant, respectively.

The stability conditions for equilibrium, $(dG)_{p,T} = 0$ and
$(d^2G)_{p,T} \geq 0$, require that there exists a critical thickness t_{cr} at
which the adsorbed phase in a cylindrical pore just becomes
unstable. The critical thickness t_{cr} is determined by the fol-
lowing equation:[4]

$$[\frac{d\ln (p_\infty/p_o)}{dt}]_{t=t_{cr}} = \frac{\gamma_\infty V_m}{RT(r-t-\delta)^2} \qquad (2)$$

At this point capillary condensation takes place and the pore
fills up spontaneously. Thus, from Eqs.(1) and (2) we can cal-
culate the critical values for r and t for any given value of
p_a/p_o if we know $\ln(p_\infty/p_o)$ as a function of t. Because of dif-
ficulty of expressing $\ln(p_\infty/p_o)$ as a single continuous func-
tion of t, de Boer *et al.*[7] have divided the entire pressure
range into two and have used different expression for $\ln(p_\infty/
p_o)$ for each region. However, as we have already pointed
out[4], this kind of approximation violates the stability con-
dition $(d^2G)_{p,T} \geq 0$; that is, at a certain value of p_∞/p_o the deri-
vative $d \ln(p_\infty/p_o)/dt$ does not exist and Eq.(2) fails to hold.
As for now the theory due to Chang *et al.* appears to provide
the most compact and useful way to express $\ln(p_\infty/p_o)$ as a
continuous function of t over a wide range of pressure.

In the theory by Chang *et al.* t may be set equal to $\omega\delta$
where ω is the average number of molecules per adsorption
site on the adsorbent surface and δ, as before, may be regar-
ded as the monolayer thickness. Chang *et al.* showed that ω
can be calculated as follows:

$$\omega = x + \frac{x^n y}{1 - y^n} \qquad (3)$$

where x and y can be obtained by solving the following equa-
tions for a given relative pressure p_∞/p_o.

$$y = \frac{ap_\infty/p_o}{ap_\infty/p_o + f(y)} \qquad (4)$$

and

$$x = \frac{ap_\infty/p_o}{ap_\infty/p_o + \frac{q}{q_1} g(x, y)} \qquad (5)$$
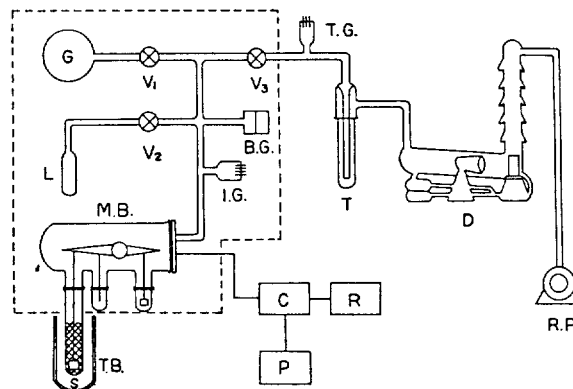
where

Figure 1. Adsorption Apparatus. M.B. Cahn microbalance, C
balance control unit, P Uninterrupted Power Supply, R recorder, S
hang-down sample tube, T. B. temperature control bath, G gas sam-
ple tube, L liquid sample tube, T trap, D oil diffusion pump, R. P.
rotary pump, I. G. ionization gauge, B. G. Baratron gauge, T. G.
thermocouple gauge, V_1, V_2, V_3 vacuum valves.

$$f(y) = (1 - y)^{\frac{ny^{n-1}}{1 + (n-1)y^n}} \exp[\frac{cw}{2kT} (2y - \frac{ny^{n-1}}{1 + (n-1)y^n} y^2)] \qquad (6)$$

and

$$g(x, y) = (1 - y)^{\frac{nx^{n-1}}{1 + (n-1)y^n}} \exp[\frac{cw}{2kT} (2x - \frac{nx^{n-1}}{1 + (n-1)y^n} y^2)] \qquad (7)$$

For the meanings of the four parameters n, a, q/q_1, and $cw/
2kT$ we would like to refer the readers to our earlier publica-
tions.[5,8,9] Although the physical meanings of these para-
meters are obvious, at present there seems to be no simple
way of relating them to experimentally measurable quan-
tities such as heat of condensation, isosteric heat of adsorp-
tion, etc. Thus we have to determine these parameters by di-
rectly fitting the theoretical isotherm obtained from Eq.(3) in-
to the experimentally observed flat-surface isotherm. To find
theoretical isotherms we first calculate y from Eq.(4) by suc-
cessive iteration and thus obtained y value is substituted into
Eq.(5) and then solve this equation for x again by successive
iteration for a given set of values of four parameters. For
more detailed calculation process the readers are again refer-
red to our previous publications.[5,8,9]

Experimental

The apparatus we have used in this experiment is shown
in Figure 1. One can easily see that the details of the appa-
ratus are very similar to those we have already reported[10] ex-
cept for the fact that a quartz beam balance was replaced by
the Cahn 2000 electrobalance (Ventron Corp., Calif., U. S.
A.). The amount of gas adsorbed on the uniform flat surface
of an adsorbent is usually much smaller than that for the
porous adsorbent and we need to use the balance with higher
sensitivity. Previously used quartz beam balance correctly
indicates weight only to ± 10 micrograms while the preci-
sion of the Cahn balance is accurate down to ± 0.2 micro-
gram. A considerable amount of electrostatic charge was
detected around the outside wall of hang-down sample tube
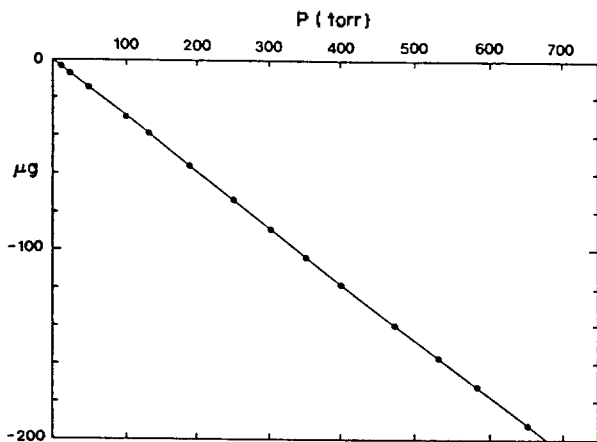whenever heating mantle or temperature control bath was

Figure 2. Buoyancy curve for aluminum foil sample measured by making use of argon gas.

Figure 3. Adsorption isotherm of nitrogen on aluminum foil at 78 °K. o: experimental data —: calculated isotherm.

removed. Such static electricity could be removed by covering the sample tube with copper stockings connected to the electrical ground.

The aluminum foil used as the adsorbent was a domestic product with 7 μm thickness and was employed in the form of a bundle of ten rectangular sheets round-hooked together with a fine tungsten wire. The size of each sheet was 70 mm × 32 mm. This bundle of aluminum sheets was thoroughly washed by immersing it in acetone for 24 hours and then was oxidized at 100 °C in the atmosphere for 24 hours. It then was vertically hung on the one arm of the Cahn balance. After being set in the balance, this sample adsorbent was outgassed at 10^{-5} torr and 200 °C for 24 hours before being used for our adsorption experiments.

As adsorbates, Matheson, Coleman & Bell chromatoquality TMS, cyclohexane, benzene, and Merck spectroquality *n*-hexane were used without further purification. These adsorbates were dehydrated by making use of the Linde 4X molecular sieve and were degassed by repeating the freeze-pump-thaw cycle.

The sample tube containing the aluminum foil was immersed into the temperature control bath which can control the temperature between –30.0 °C and + 70.0 °C automatically with accuracy ± 0.1 degree. On the opposite arm of the Cahn balance a weight was hung to counterbalance the weight of the sample. The whole balance system plus a part of the vacuum system was placed in an insulating box with transparent acryl walls and the inside of the box was maintained at a rather high temperature of 30.0 °C.

When the amount of vapor adsorbed on the adsorbent is measured using the Cahn balance which has the balance arms with unequal length, one must not forget that the amount of vapor adsorbed on the balance body and the buoyancy effect due to th vapor introduced into the balance room should carefully be taken into account. To eliminate the former effect we first evacuate the balance room and adjust the balance to the zero point. Then we introduce the adsorbate vapor at a known pressure and measure the gain of weight. Let this gain of weight be m_1. Then we replace the sample adsorbent by a gold wire with roughly same weight as that of the sample, evacuate and newly adjust the balance to the zero point. Next, we introduce the adsorbate vapor at the same pressure as before and measure the gain of weight
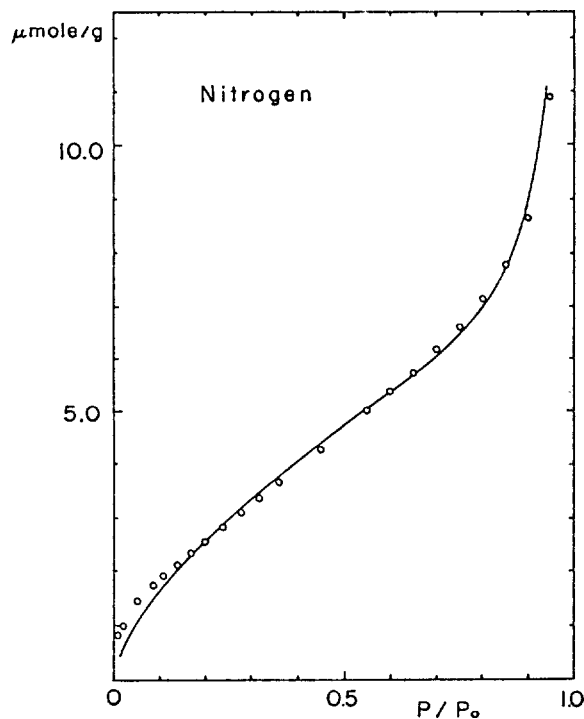
again. Let us denote this gain of weight by m_2. Taking the difference m_1-m_2 we obtain the apparent weight of vapor adsorbed at a given pressure uncorrected for the buoyancy effect. We denote this apparent weight by $m(p)$. In order to make correction for the buoyancy effect we again evacuate the balance room and adjust the balance to the zero point with the aluminum foil in the sample tube. Then we introduce pure argon gas into the balance room and measure the gain of weight as a function of the argon gas pressure. In this way we have obtained the buoyancy correction curve for our aluminum foil sample, as shown in Figure 2. With the buoyancy effect taken into account the true mass of adsorbed gas can be calculated as follows:[11]

$$m_a(p) = m(p) + ApT_oM_a / TM_o \qquad (8)$$

where T_o is the temperature at which the buoyancy effect is measured using the argon gas, M_o the molecular weight of the argon gas, T the temperature at which the adsorption experiment is performed using the adsorbate gas, p the pressure of adsorbate vapor used for the adsorption experiment, M_a the molecular weight of the adsorbate. A is the specific buoyancy for argon gas, that is, the rate of change in $m(p)$ with change in the pressure of argon, $\Delta m(p)/\Delta p$, which can easily be calculated from the buoyancey curve shown in Figure 2.

Since the adsorption equilibrium is attained almost within 10 minutes after introduction of the adsorbate vapor, each adsorption experiment was performed at every 15 minutes after vapor introduction. The overall error in the precision of the adsorption balance was ± 0.2 μg on the recording chart. For the purpose of comparison the nitrogen adsorption on the aluminum foil was also measured at the liquid nitrogen temperature. In this case the adsorbent sample was hung as a horizontally-laid pile made of 80 aluminum foil sheets with dimension 17.5 mm × 16 mm. The adsorption experiments

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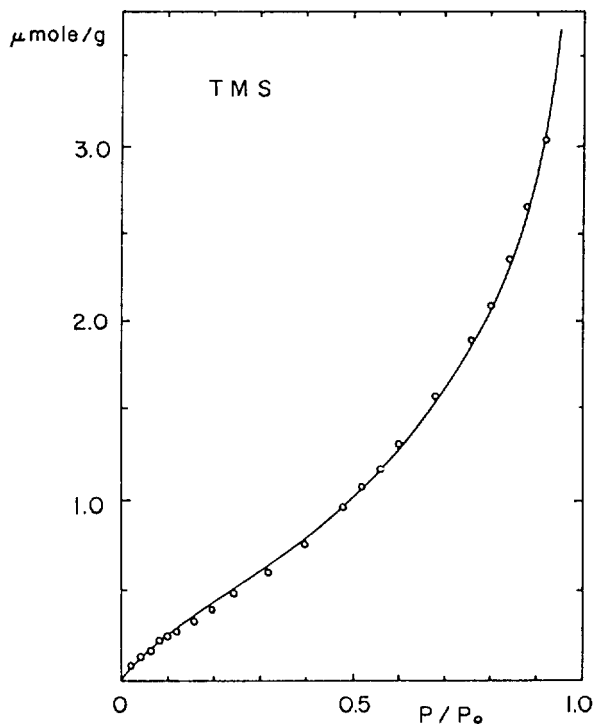

Figure 4. Adsorption isotherm of tetramethylsilane on aluminum foil at 291° K. o: experimental —: calculated.
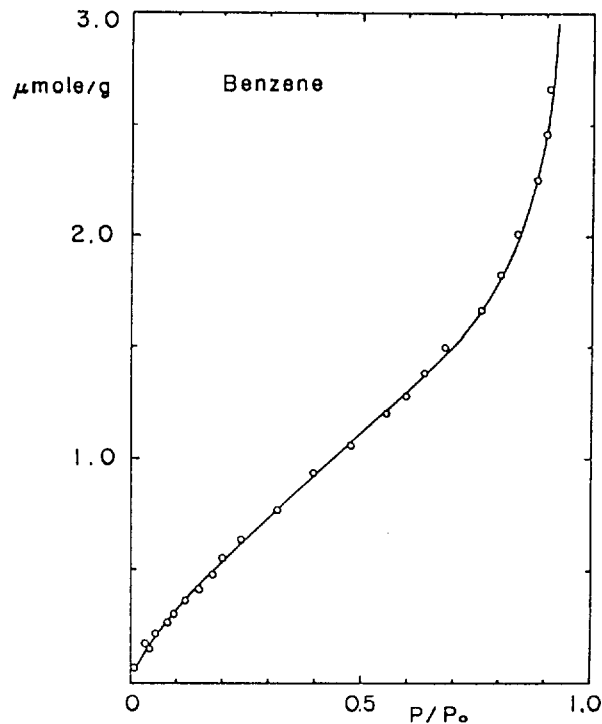

Figure 6. Adsorption isotherm of benzene on aluminum foil at 293°K. o: experimental —: calculated.
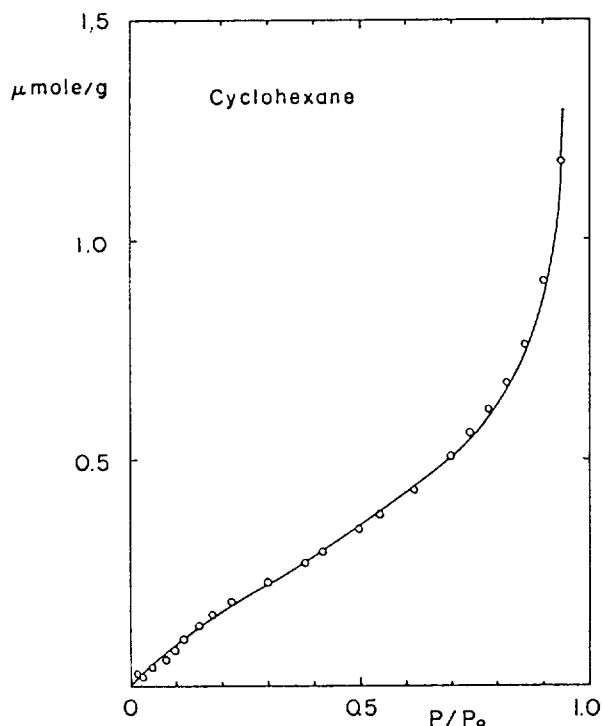

Figure 5. Adsorption isotherm of cyclohexane on aluminum foil at 288°K. o: experimental —: calculated.
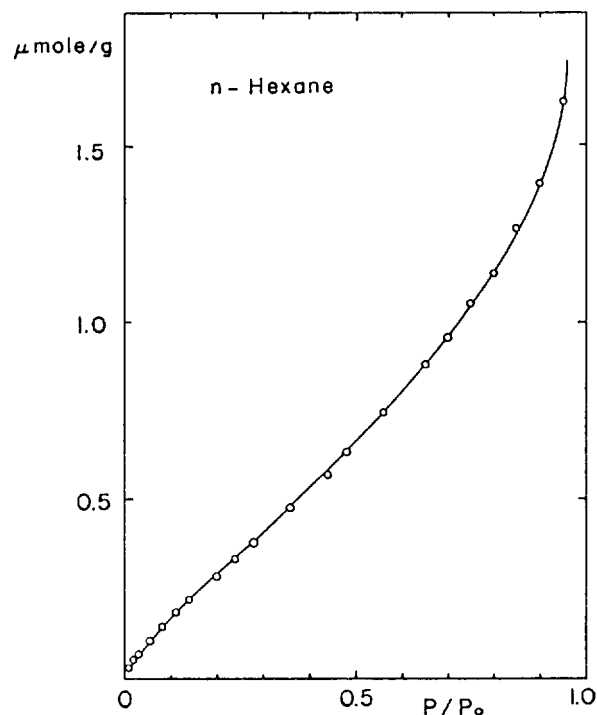

Figure 7. Adsorption isotherm of *n*-hexane on aluminum foil at 291°K. o: experimental —: calculated.

for TMS and *n*-hexane were carried out at 291 K while those for benzene and cyclohexane were performed at 293 and 298 K, respectively.

Results and Discussions

In Figure 3 through Figure 7 are shown the adsorption

isotherms oberved experimentally for nitrogen, TMS, cyclohexane, benzene, and *n*-hexane. Each data point shown in these figures represents the average of several independent measurements under the same conditions. From these we see that the resultant isotherms are virtually free of hysteresis over the whole range of pressure and can be classified as Type II having a rounded kneebend. Also shown in the
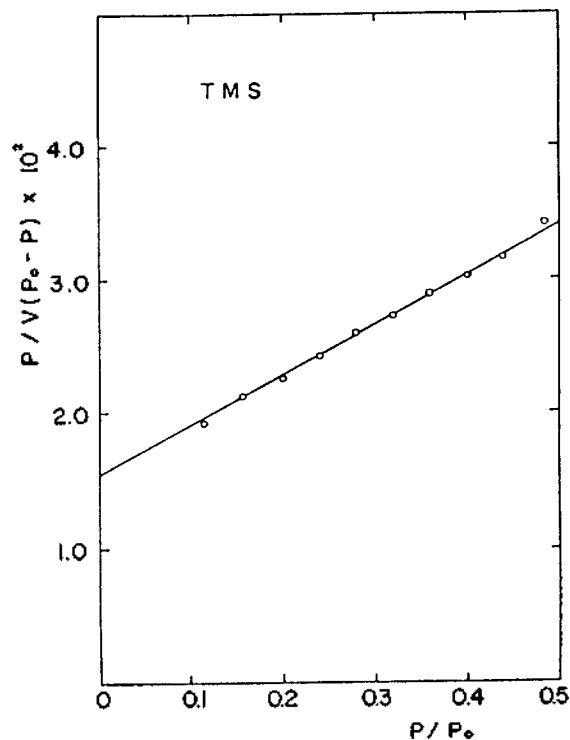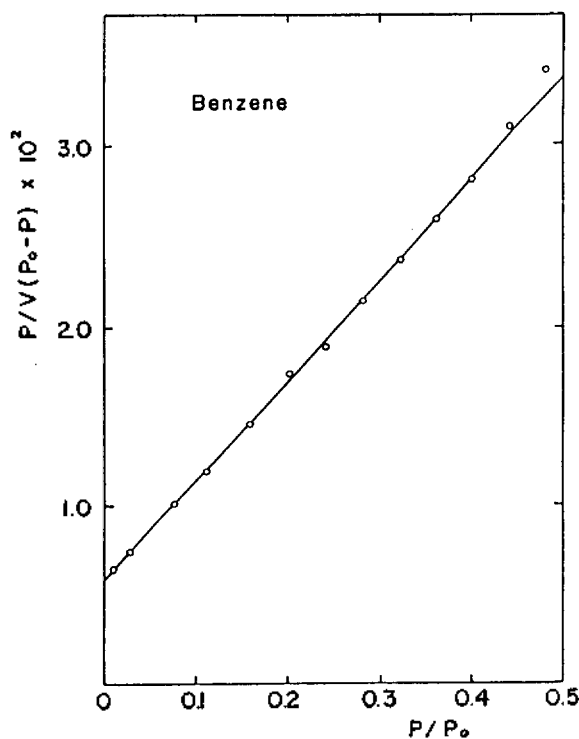
Table 1. Physical Constants and Parameters

	N_2	CCl_4	TMS	C_6H_{12}	C_6H_6	C_6H_{14}
n	3.0	3.0	3.0	3.0	3.0	3.0
a	0.921	—	0.906	0.950	0.949	0.864
$cw/2kT$	0	—	-0.003	-0.006	-0.002	-0.001
q/q_1	0.162	—	0.545	0.305	0.245	0.372
δ (Å)	3.54	4.73	5.40	5.04	4.62	5.24
γ_∞ (dyne/cm)	8.72	27.00	17.81	25.30	28.02	18.40
V_m(cm³/mol)	34.68	96.51	130.86	108.04	88.06	130.76
$\gamma_\infty V/RT$	4.663	10.691	10.454	11.215	10.123	10.220
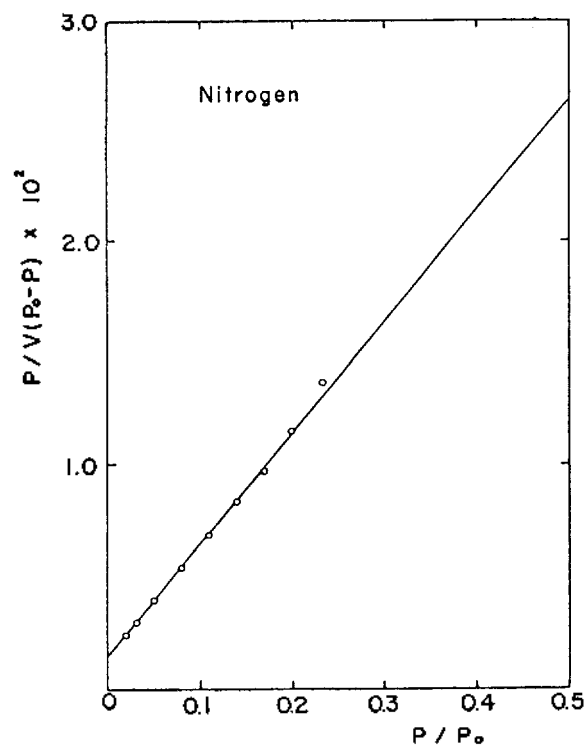
Figure 8. BET linear plot of nitrogen adsorption on aluminum foil at 78 °K.

Figure 9. BET linear plot of TMS adsorption on aluminum foil at 291 °K.

Figure 10. BET linear plot of benzene adsorption on aluminum foil at 293 °K.

same figures are the corresponding theoretical isotherms calculated from Eq.(3) by adjusting the four parameters involved therein. Among these four parameters n is normally set equal to 3 and other three parameters are adjusted in such a way that the calculated isotherm can best fit into the experimental isotherm over the whole range of relative pressure in the sense of nonlinear least square fitting. Thus determined values of parameters are listed in Table 1 for each adsorbate. Also listed in the same table are the other relevant data such as γ_∞, the surface tension of adsorbate, V_m, the molar liquid volume of the adsorbate, and δ, the monolayer thickness calculated as in our previous work.[4]

To estimate the smoothness of the surface of aluminum foil sample used in this experiment we have used the adsorption data for nitrogen, TMS, and benzene to calculate the standard BET area, S_{BET}. The BET linear plots for adsorption of nitrogen, TMS, and benzene are given in Figure 8 through Figure 10. The roughness factor of the surface, which is the ratio of S_{BET} to the geometrical surface area, was found to be 1.56 for nitrogen, 1.35 for TMS, and 1.18 for benzene. These values

are comparable to those reported by other authors[12,13] for the flat aluminum foil surface considering that the uncertainty in the magnitude of measured S_{BET} is ± 20%.[14] Hence we may regard the surface of aluminum foil sample used in our experiment as nearly flat.

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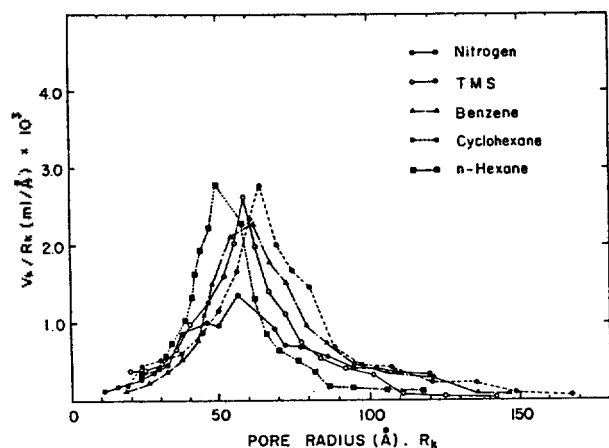*Bull. Korean Chem. Soc., Vol. 10, No. 3, 1989* 297

Figure 11. Pore volume distribution curves for porous alumina sample reported in Paper 1 obtained by making use of the flat-surface isotherms described in this work.

From the results shown in Figure 3 through Figure 7 we can again confirm that the theory by Chang *et al.* provides a (at least semiempirical) means to reproduce experimental adsorption data observed for the flat surface over a wide range of pressure. One disadvantage of this theory is that it contains the parameters that cannot be directly measured experimentally. If, one way or another, these parameters can be expressed in terms of experimentally measurable quantities such as heat of condensation, isosteric heat of adsorption, etc., the theory will provide a powerful means with which the pore volume distribution problems can be routinely analyzed. From the listed values for these parameters we see that they are substantially different from those estimated roughly from the adsorption-desorption data as in Paper I. This is probably due to the fact that the effect of the presence of micropores is not negligible in case we estimate the flat-surface isotherm from the adsorption-desorption data for porous systems. Finally, we have recalculated the pore volume distribution curves for the porous alumina sample reported in Paper I by making use of the flat-surface isotherms we ob-

tained in this work and the results have been shown in Figure 11. As can be seen from this, the pore volume distribution curves all display better-defined profiles and more conspicuous maxima compared to the cases reported previously[4] and this can be attributed to better-defined forms of isotherms we obtained in this work.

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