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Determination of Micropore Volumes of Active Carbon Using Dubinin-Radushkevich Plots

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The adsorption of methanol on active carbons at 30 °C was carried out and a new method for determining the micropore volume in the Dubinin-Radushkevich plot is presented. From this method, it was found that the adsorption volume (V) corresponding to the adsorption potential ($A=RT\ln P_0/P$), at which the plot of $\mathrm{d}V/\mathrm{d}(-A)$ *vs.* A has its minimum value, is the value of the micropore volume in cases where extrapolation of the Dubinin-Radushkevich plot cannot be applied because of non-linearity of the Dubinin-Radushkevich plot.

The Dubinin-Radushkevich equation has been extensively used in studies of gas adsorption on microporous carbons. Its application has been reported in the determination of the micropore volume of heat-treated and activated carbons. For this application, the Dubinin-Radushkevich equation[1)] is written as

$$V = V_0 \exp[-k(A/\beta)^2], \tag{1}$$

where V is the volume adsorbed at relative pressure P/P_0, $A=RT\ln P_0/P$, and k and β are constants. Equation 1 is converted to its linear form

$$\log V = \log V_0 - D\log^2 P_0/P, \tag{2}$$

where $D=2.303\,k\,R^2T^2/\beta^2$, and the micropore volume (V_0) is obtained by extrapolation.

However, deviations from linearity can be observed at low values of $\log^2 P_0/P$ and great care must be taken in the extrapolation for the determination of the micropore volume.

Furthermore, the pore structure of carbon is customarily classified into three types, micropores (radii$<$ 15—16 Å), transitional pores (15—16 Å$<$radii$<$1000—2000 Å), and macropores (radii$>$1000—2000 Å).[1)]

Generally speaking, the lower limit of pore size for which the Kelvin equation is applicable is about 15 Å in radius.[1)] The pore-volume distribution in the transitional pore range (15 Å$<$radii$<\approx$100 Å) can usually be obtained by application of the Kelvin equation on the adsorption isotherm, and that in the transitional and macropore range ($\approx$100 Å$<$radii) using a mercury porosimeter. However, there is no satisfactory method for estimating the pore-volume distribution in the micropore range, although the micropore volume can be obtained by subtracting the cumulative pore volume (15 Å$\leq$radii$\leq$100 Å) from the volume adsorbed at the relative pressure corresponding to a radius of 100 Å in the Kelvin equation.

In this paper, the applicability of the proposed method for determining micropore volumes is discussed.

Experimental

Active Carbons. Commercially available Pittsburgh SGL- and PCB-type activated carbons were used. PCB-type activated carbons were treated with steam at 600 and 800 °C, respectively, for 6 h with supply of *ca.* 1.4 g-H_2O/g-carbon h. The percentages of burn-off of these treated PCB carbons were 5.3 and 33.3%, respectively, and can be described as PCB (5.3% burn-off) and PCB (33.3% burn-off).

Methanol Adsorption. The adsorption of methanol on active carbons at 30 °C was measured gravimetrically by means of a conventional quartz spring balance. Prior to the adsorption measurement, the active carbon dried overnight at 110 °C was outgassed at a pressure of 10^{-6} Torr at 30 °C for 14 h. In all cases, the time required for adsorption equilibrium was rapid and was established within 45 min.

Pore-volume Distribution. From the adsorption isotherms, the pore-volume distribution, lying in the radius range between 15 and 100 Å, was calculated employing the Kelvin equation.[2)]

In transitional pores, there occur monomolecular and multimolecular adsorption and filling of the free space between the adsorption layers by the capillary condensation mechanism. The Kelvin equation is applicable to the space of the capillary condensate.

In the desorption step, the volume, ΔV, of the capillary condensate is lost between the beginning and the end of a step between two relative pressures P_1/P_0 and P_2/P_0. When the capillary condensate is lost, monolayers and multilayers remain on the pore walls and, thus, the radius of the meniscus of the capillary condensate is less than the actual radius of the pores by the adsorption thickness t. Thus, the quantity ΔV must be multiplied by the factor $[\bar{r}/(\bar{r}-\bar{t})]^2$, where $\bar{r}=(r_1+r_2)/2$ and $\bar{t}=(t_1+t_2)/2$. Multiplication by $[\bar{r}/(\bar{r}-\bar{t})]^2$ is also used in the calculation for the adsorption side of the adsorption isotherm.

The Kelvin equation, giving the relationship between the relative pressure P/P_0 and the pore radius r(Å), can be expressed as follows:

$$\ln P/P_0 = -2\gamma v\cos\theta/RT(r-t), \tag{3}$$

$$\begin{aligned}\log P/P_0 &= -2\times 21.7\times 41.0\times 1/2.303\times 8.31\times 10^7\\ &\quad\times 303.2\times(r-t)\times 10^{-8}\\ &= -3.07/(r-t),\end{aligned} \tag{4}$$

and

$$t = 4.6\times(-\ln P/P_0)^{-1/6}, \tag{5}$$

where γ is the methanol surface tension, v the molar volume of methanol, θ the contact angle between the methanol and the carbon ($=0$), R the gas constant, and t the thickness of the adsorbed methanol layer.[3)]

Discussion

In his early work, Dubinin[1,4)] demonstrated the linearity of the Dubinin-Radushkevich plots for gas adsorption on active carbon, however, afterward many investigators[5—7)] frequently observed deviations from linearity.

Marsh and Siemieniewska[8)] have suggested that the linearity of the Dubinin-Radushkevich plots occurs because the distribution of the adsorption potential with adsorption volume follows the Rayleigh distribution. On the other hand, Gregg and Sing[9] and Sutherland[10] have considered that the apparent wide applicability of the Dubinin-Radushkevich equation arises because the log V *vs.* $\log^2 P_0/P$ plot is inherently insensitive and that the distribution of adsorption potential with adsorption volume need not be of the Rayleigh-distribution type.

Since, there have been many discussions of the determination of micropore volumes using Dubinin-Radushkevich plots.

Dubinin[1] suggested that upward deviations from linearity for low values of $\log^2 P_0/P$ can be attributed to the filling of transitional pores and that extrapolation in the Dubinin-Radushkevich plots of the linear section for high values of $\log^2 P_0/P$ can be used to predict the micropore volume. Chiche, Marsh, and Prégermain[5] have adopted extrapolation in the second section of the Dubinin-Radushkevich plots for estimations of the micropore volume when the Dubinin-Radushkevich plot is composed of two linear sections with downward deviations for low values of $\log^2 P_0/P$. In a recent paper, Rand[7] has applied the more generalized Dubinin-Astakhov equation

$$V = V_0 \exp\left[-k(A/E)^n\right], \tag{6}$$

with E being a constant, in order to linearize the data. In this case, the micropore volume was obtained by the extrapolation of the linearized Dubinin-Astakhov equation.

If the Dubinin-Radushkevich plot can be shown to be strictly linear in form, a plot of $\mathrm{d}V/\mathrm{d}(-A)$ must be of the Rayleigh-distribution type. Thus, the plot of $\mathrm{d}V/\mathrm{d}(-A)$ *vs.* A can be considered to give more important information about the micropore volume using the Dubinin-Radushkevich plot.

Assuming the micropore volume to be equivalent to the V_0 obtained by extrapolating the Dubinin-Radushkevich plot only in cases when the Dubinin-Radushkevich plot is strictly linear and when the plot of $\mathrm{d}V/\mathrm{d}(-A)$ *vs.* A follows the Rayleigh distribution, upward deviations of $\mathrm{d}V/\mathrm{d}(-A)$ *vs.* A from the Rayleigh distribution for low values of A can be considered to indicate filling of the transitional pores. The adsorption volume corresponding to the adsorption potential A at the point of the upward deviation from the Rayleigh distribution, which is really of Rayleigh-like distribution, can be evaluated as the micropore volume.

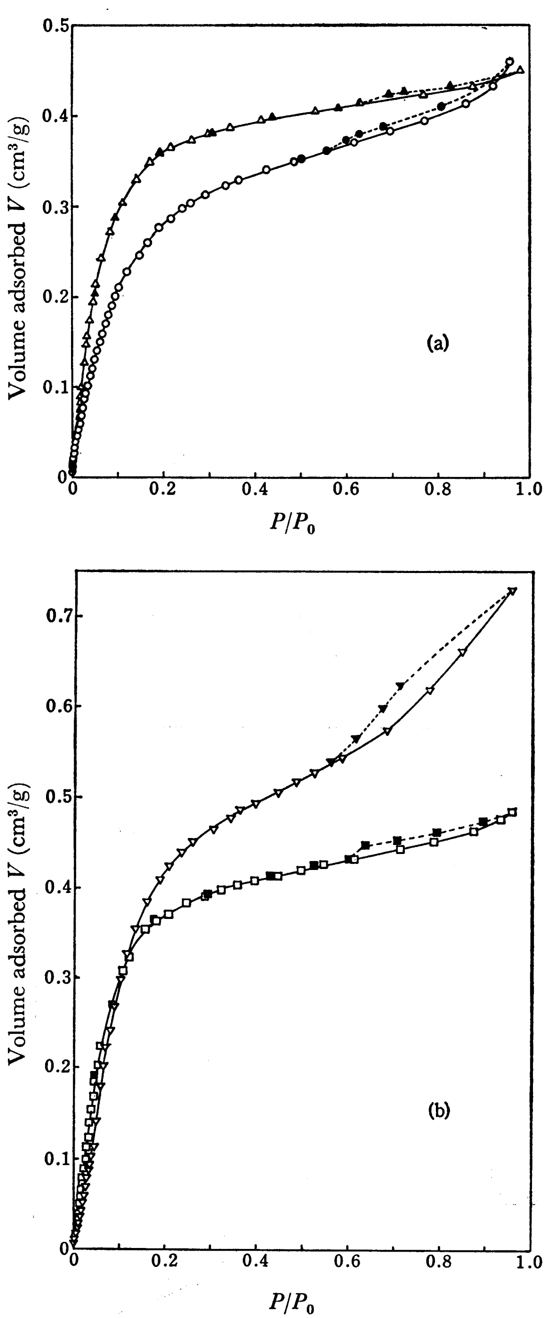

Fig. 1. Adsorption isotherms of active carbons.
(a) △ PCB, ○ SGL.
(b) ▽ PCB(33.3% Burn-off), □ PCB(5.3% Burn-off).
Filled symbols indicate desorption.

Results

The adsorption isotherms, Dubinin-Radushkevich plots, characteristic curves, distribution curves of the adsorption potential, and pore volume distributions of the activated carbons are shown in Figs. 1—5.

The Dubinin-Radushkevich plot of SGL-type activated carbon is linear for low values of $\log^2 P_0/P$, as is shown in Fig. 2. If the plot is extrapolated, the micropore volume is evaluated to be 0.370 cm^3/g, which is considerably higher than that calculated using the Kelvin equation (Table 1). This means that the Dubinin-Radushkevich plot is insensitive and great care must be taken in extrapolation. However, as shown in Figs. 4(a) and 5 and in Table 1, the value of the adsorption volume corresponding to the adsorption potential at which the plots of $\mathrm{d}V/\mathrm{d}(-A)$ *vs.* A deviate upward, *i.e.*, at the minimum value of $\mathrm{d}V/\mathrm{d}(-A)$, occur coincides with that of the micropore volume obtained using the Kelvin equation.

In the cases of PCB, PCB (5.3% burn-off) and PCB (33.3% burn-off), the Dubinin-Radushkevich plots are curved and the conventional method of extrapolation cannot be applied (see Figs. 2(a)—(b)). However, the

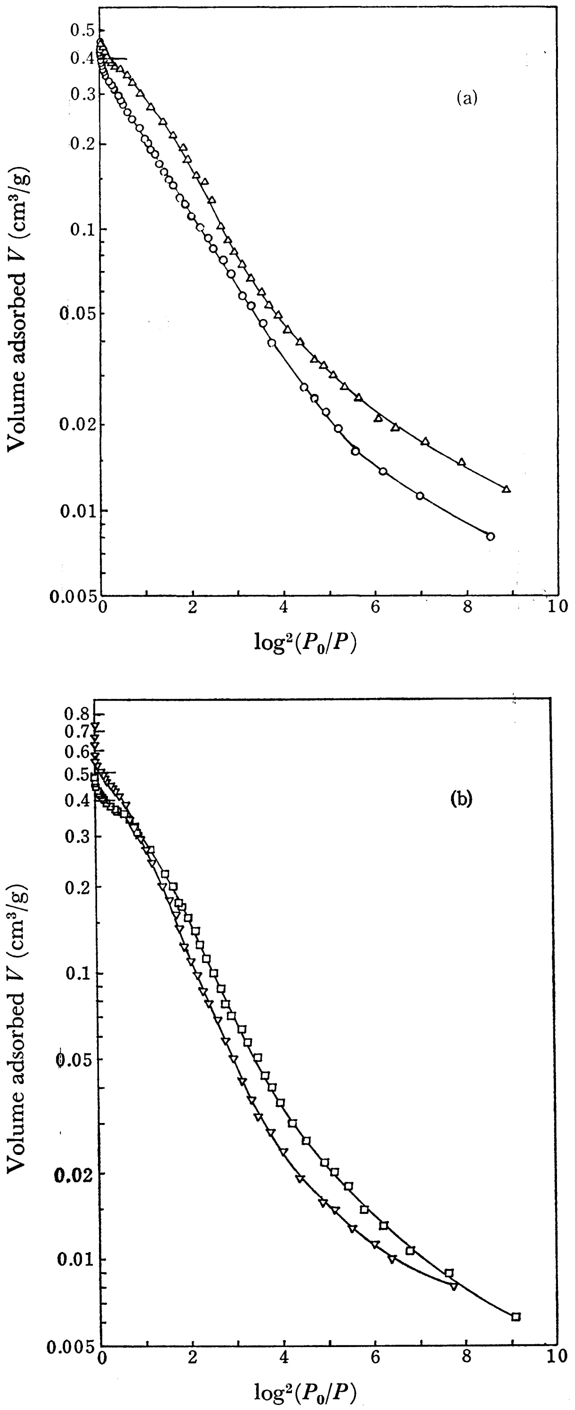

Fig. 2. Dubinin-Radushkevich plots of active carbons.
(a) △ PCB, ○ SGL.
(b) ▽ PCB(33.34% Burn-off), □ PCB(5.3% Burn-off).

distribution curves of the adsorption potential clearly show upward deviations for low values of A. As in the case of SGL-type activated carbon, the values of the adsorption volume corresponding to the adsorption potential at which the upward deviations occur in the distribution curves coincide with those of the micropore volume calculated using the Kelvin equation, as shown in Figs. 4(a)—(b) and 5 and in Table 1.

There are three points to be discussed concerning the applicability of the new method proposed for deter-

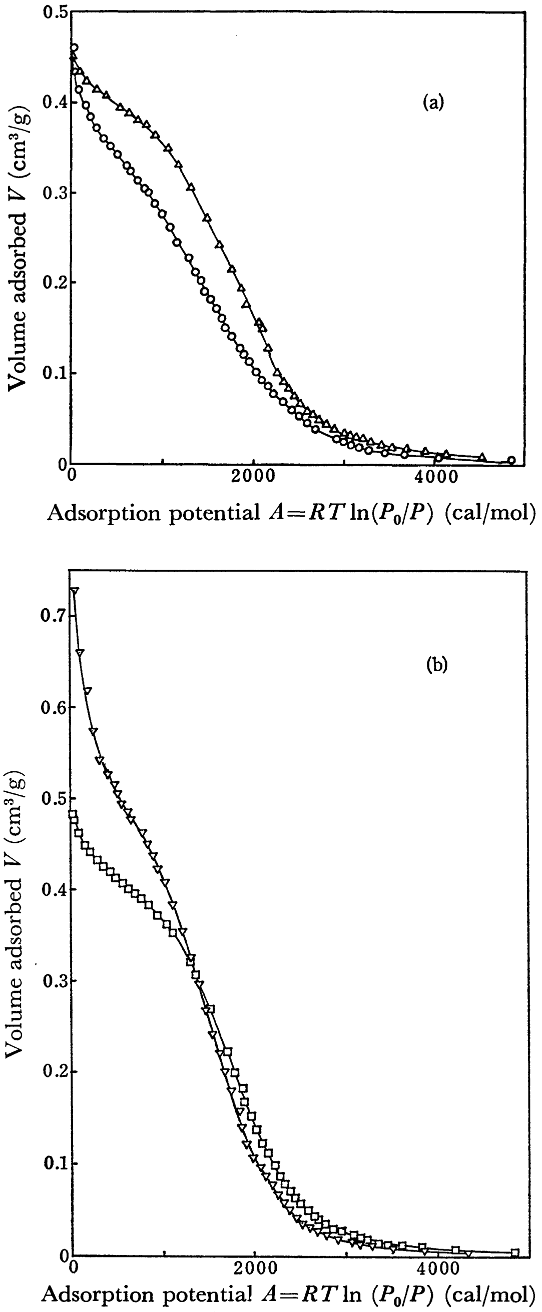

Fig. 3. Characteristic curves of active carbons.
(a) △ PCB, ○ SGL.
(b) ▽ PCB(33.3% Burn-off), □ PCB(5.3% Burn-off).

Table 1. Micropore volumes of active carbons

Active carbon	Methods of determination		
	Kelvin equation		Adsorption volume at $dV/d(-A)=$ mininum (cm^3/g)
	Adsorption side (cm^3/g)	Desorption side (cm^3/g)	
SGL	0.313	0.305	0.315
PCB	0.384	0.381	0.390
PCB (5.3% burn-off)	0.393	0.386	0.405
PCB (33.3% burn-off)	0.417	0.411	0.480

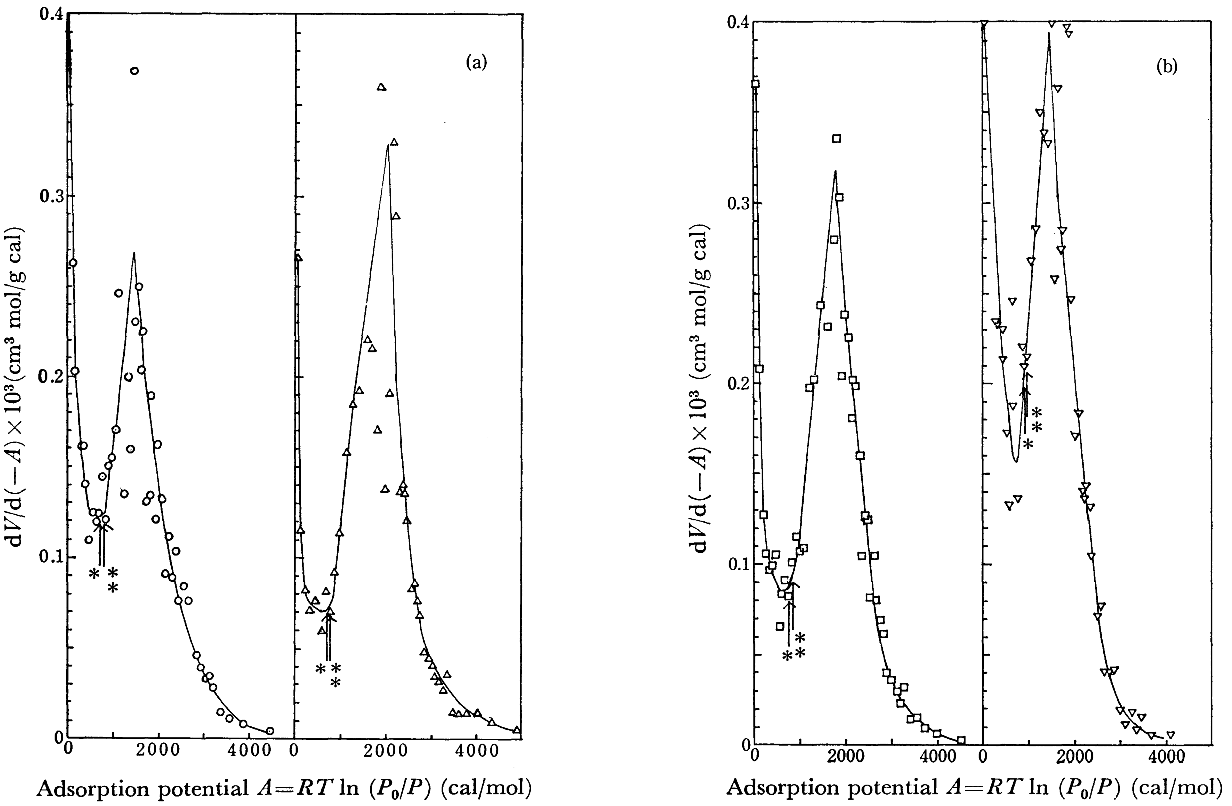

Fig. 4. Distribution curves of adsorption potential of active carbons.

(a) ○ SGL, △ PCB.

(b) □ PCB(5.3% Burn-off), ▽ PCB(33.3% Burn-off).

Marks, * and ⁑, indicate the points of the adsorption potential which correspond to the adsorption volume, the values of which are equal to the micropore volume (radii≦15.5 Å) calculated by the Kelvin equation from the adsorption and desorption sides of the isotherms, respectively.

mining micropore volumes.

1) The effective radius at the beginning of hysteresis loop is considered to be 15 Å and the hysteresis is attributed to the filling of transitional pores by the mechanism of capillary condensation.[1]

However, in both the adsorption and desorption steps, monolayers and multilayers exist on the walls of pores larger than those filled due to capillary condensation. The adsorption volume, V_h, at the beginning of hysteresis loop is considered to be the sum of the adsorption volume in the micropore and that of monolayers and multilayers on the walls of transitional pores. The values of the adsorption volume, V_h, for SGL, PCB, PCB (5.3% burn-off), and PCB (33.3% burn-off) activated carbons are 0.360, 0.415, 0.430, and 0.535 cm³/g, respectively, as shown in Figs. 1(a) and (b). These are somewhat higher than the micropore volume determined by the method proposed in this paper, as shown in Table 1.

2) Concerning the calculation of the pore-volume distribution, there are two assumptions.

a) The shapes of the pores are assumed to be cylindrical, although the true shapes are complicated and not necessarily cylindrical.

b) The walls of active carbon pores are heterogeneous surfaces and it is impossible to observe the actual thickness, *t*, of the adsorption layers on active carbons. The thickness, *t*, observed for substances with nonporous and homogeneous surfaces is assumed to be equal to the actual thickness on active carbon.

Due to these assumptions, discrepancies between the actual micropore volume and the volume calculated using the Kelvin equation will occur.

3) According to the theory of Dubinin,[1] if the Dubinin-Radushkevich plot is strictly linear, V_0 in Equation 1 is the micropore volume. In this case, the potential-distribution curve $dV/d(-A)$ *vs.* A is really a type of Rayleigh distribution.

The shape of the Rayleigh distribution is shown in Ref. 6 with a maximum value at $A=\beta/\sqrt{2k}$ below which $dV/d(-A)$ decreases to zero.

If active carbons were ideally composed only of micropores, the shape of the plot of $dV/d(-A)$ *vs.* A would have the form of a Rayleigh distribution. However real active carbons have transitional pores, in addition to micropores. Due to the filling of the transitional pores, the Dubinin-Radushkevich plot deviates upward from linearity, and at the same time the plot of $dV/d(-A)$ *vs.* A also deviates upward from the Rayleigh distribution. It can be assumed that the point of deviation, *i.e.*, the point of the $dV/d(-A)$ minimum represents the end of micropore filling and, at the same time, the beginning of transitional-pore filling by capillary condensates and, strictly speaking, the beginning of the adsorption of mono- and multilayers on

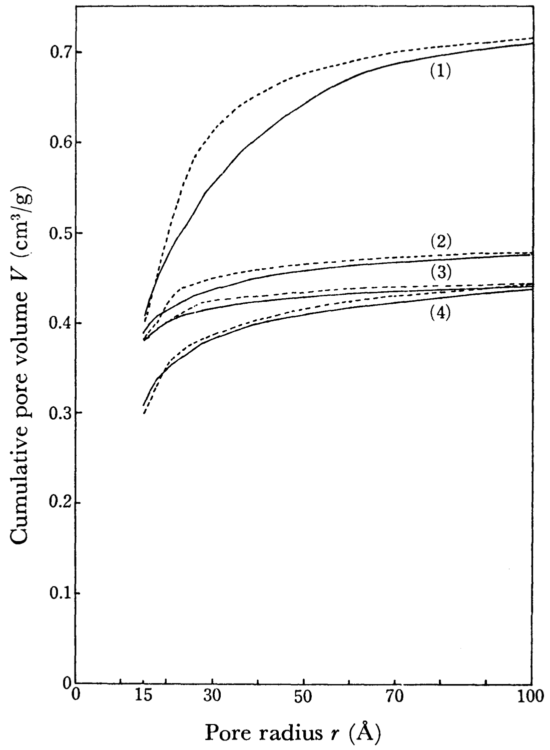

Fig. 5. Pore volume distributions of active carbons.
(1) PCB(33.3% Burn-off), (2) PCB(5.3% Burn-off), (3) PCB, (4) SCL.
---- Calculated from the desorption side of the isotherms.
—— Calculated from the adsorption side of the isotherms.

the transitional pores. The present experimental results show that the proposed method is applicable to the determination of micropore volumes.

From these results, the micropore volume can be estimated by plotting the values of $\mathrm{d}V/\mathrm{d}(-A)$ *vs.* A and by finding the adsorption volume corresponding to the adsorption potential at which the plots of $\mathrm{d}V/\mathrm{d}(-A)$ *vs.* A show a minimum value, in cases where extrapolation of the Dubinin-Radushkevich plot cannot be applied because of non-linearity of the Dubinin-Radushkevich plot.

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