The Application of a Modified Dubinin-Radushkevich Equation to Adsorption on Active Carbon with Heterogeneous Micropore Systems

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The Dubinin-Radushkevich plots of active carbons, curved concavely for a high value of $\log^2 P_0/P$, on methanol adsorption at 30 °C have been characterized by using a modified Dubinin-Radushkevich equation, *i.e.*:

$$V = CV_0 \exp[-B_0A^2] \exp[A^4\Delta^2/2]\,[1-\mathrm{erf}(X)]/2,$$

where $\mathrm{erf}(X)$ is the error function, $A=RT\ln P_0/P$, V_0 is the micropore volume, C is the correcting coefficient for fitting the equation to the experimental data, and $X=(A^2-B_0/\Delta^2)\Delta/\sqrt{2}$, with B_0 being the average value of a measure of the micropore size and Δ, the heterogeneity parameter of the micropore size. The significance of the equation was discussed, and it was shown that the equation can describe the heterogeneous micropore systems of active carbons with suitable parameters.

The Dubinin-Radushkevich equation,[1)]

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

has been used to characterize microporous carbons. In this equation, V is the volume adsorbed at a relative pressure of P/P_0; V_0 is the micropore volume, $A=RT\ln P_0/P$, and k and β are constants. The linear form of the Dubinin–Radushkevich equation,

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

where $D=2.303\,kR^2T^2/\beta^2$, is usually used to plot the adsorption data.

However, although the plot may show a linear range, it is rarely linear over a wide pressure range.[2–5)] Rand[4)] has recently reported three general types of Dubinin-Radushkevich plots which show deviations from linearity. These three types are designated as Type A, B, and C Dubinin-Radushkevich curves. The Type A, curve has two linear sections with a gentle slope for low values of $\log^2 P_0/P$. The Type B curve is curved concavely over the whole range of $\log^2 P_0/P$. The Type C curve shows two inflection points, indicating a bimodal distribution of the adsorption potential. Especially in the case of the Type B curve, the plots can be linearized by means of the Dubinin-Astakhov equation,

$$V = V_0 \exp[-k(A/\beta)^n], \tag{3}$$

with a suitable value of n, and the micropore volume is obtained by extrapolation of the plot.

However, the characterization of the Dubinin-Radushkevich plot by use of the Dubinin-Astakhov equation is contrary to the original nature of the Dubinin-Radushkevich equation, and the Dubinin-Radushkevich plot should be characterized by an equation maintaining the original nature of the Dubinin-Radushkevich equation.

Stoeckli[7)] has recently proposed an adsorption equation maintaining the nature of the Dubinin-Radushkevich equation. Assuming that the Dubinin-Radushkevich equation has a general validity, but applies to homogeneous systems of micropores, he has described adsorption by heterogeneous micropore systems by means of a sum of the Dubinin-Radushkevich equation:

$$V = \sum_j V_{pj} \exp[-B_jA^2], \tag{4}$$

where $B_j=k_j/\beta^2$.

Equation 4 may be replaced by the integral,

$$V(A^2) = \int_0^\infty V_p f(B) \exp[-BA^2]\,\mathrm{d}B, \tag{5}$$

where $f(B)$ is the normalized Gaussian distribution and is described as follows:

$$f(B) = \frac{1}{\sqrt{2\pi}\,\Delta}\exp[-(B-B_0)^2/2\Delta^2], \tag{6}$$

with B_0 being the avarage value of B, and Δ, the standard deviation, *i.e.*, the heterogeneity parameter.

Moreover, Eq. 5 leads to,

$$V(A^2) = V_p \exp[-B_0A^2] \times \exp[A^4\Delta^2/2]\,[1-\mathrm{erf}(X)]/2, \tag{7}$$

where $X=(A^2-B_0/\Delta^2)\Delta/\sqrt{2}$ and $\mathrm{erf}(X)$ is the error function. Equation 7 is expected to be applied to the Type B curve of the Dubinin-Radushkevich plot.

Meanwhile, as to the determination of the micropore volume from the non-linear Dubinin-Radushkevich plots, the present author[5,6)] has previously reported that the adsorption volume (V) corresponding to the adsorption potential (A), at which the plot of $\mathrm{d}V/\mathrm{d}(-A)$ *vs.* A has its minimum value, is the value of the micropore volume (V_0) in cases where the extrapolation of the Dubinin-Radushkevich plot cannot be applied because of the non-linearity of the plot.

In this paper, micropore systems of active carbon showing Type B curve by Rand's classification[4)] or plots gradually curved concavely for a high value of $\log^2 P_0/P$ on methanol adsorption have been characterized by means of the modified Dubinin-Radushkevich equation, and the significance of the modified Dubinin-Radushkevich equation discussed.

Experimental

Active Carbons. Commercially available Pittsburgh Filtrasorb 100- and SGL-type active carbons and Hokutan active carbon were used. For the SGL-type active carbon, the adsorption isotherm reported in a previous paper[5)] was used.

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, 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 adsorption equilibrium was established within 45 min.

Results and Discussion

Micropore Volume. The adsorption isotherms, Dubinin-Radushkevich plots, and characteristic curves are sown in Figs. 1—3.

The micropore volumes (V_0) of active carbons were obtained by the method[5,6] described above; they are listed in Table 1.

Modified Dubinin-Radushkevich Equation and Its Application to the Experimental Data. In this paper, following Stoeckli,[7] the micropore systems of active carbon are classified into "homogeneous" and "heterogeneous" micropore systems. Actually, active carbon with a homogeneous surface does not exist. However, when the structural constitution of micropores is considered as a system, the micropore system determined by a given constant, k, in Eq. 1 can be said to be a homogeneous micropore system, and, in this case, the Dubinin-Radushkevich plot is strictly linear in form. On the

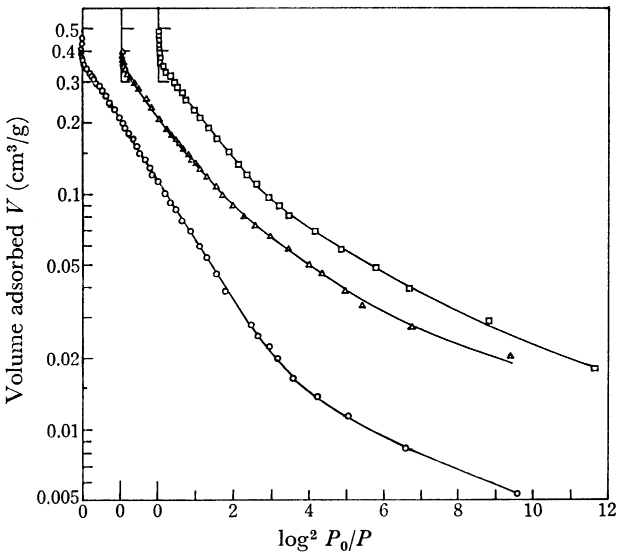

Fig. 2. Dubinin-Radushkevich plots of methanol adsorption at 30 °C on active carbons.
○ SGL, △ Filtrasorb 100, □ Hokutan.

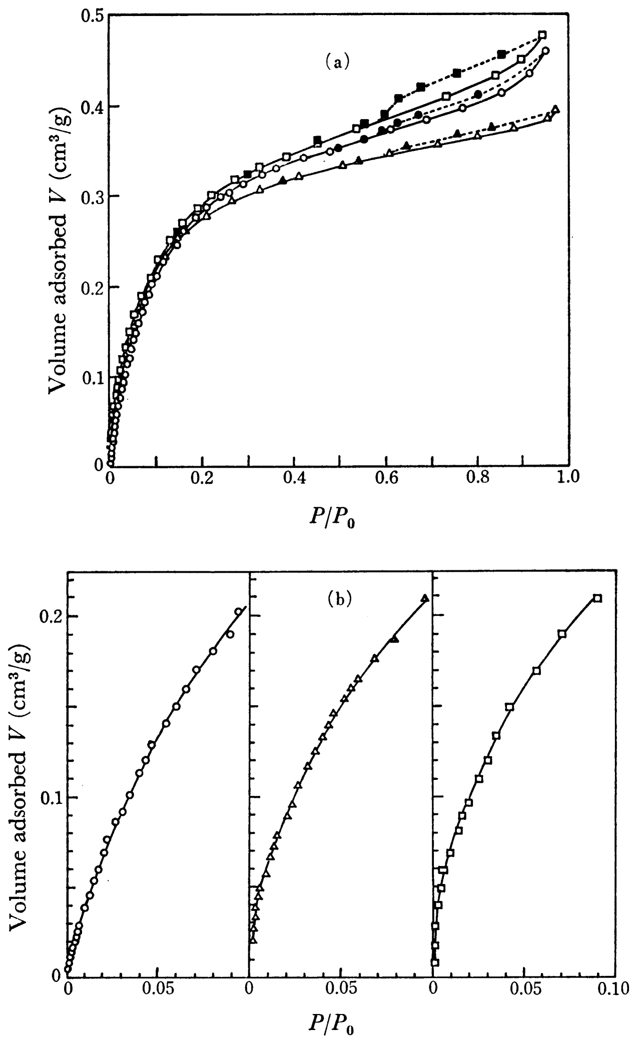

Fig. 1. Adsorption isotherms of methanol at 30 °C on active carbons.
○ SGL, △ Filtrasorb 100, □ Hokutan.
Filled symbols indicate desorption.

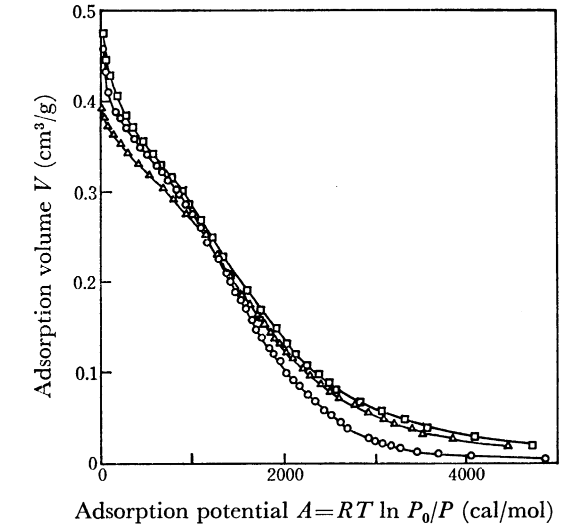

Fig. 3. Characteristic curves of methanol adsorption at 30 °C on active carbons.
○ SGL, △ Filtrasorb 100, □ Hokutan.

TABLE 1. PARAMETERS IN EQS. 10, 11, AND 11′

Active carbon	V_0 (cm^3/g)	$B_0\times10^6$ (mol^2/cal^2)	$\Delta\times10^6$ (mol^2/cal^2)	C	C'
SGL	0.305	0.35	0.10	1.19	1.001
Filtrasorb 100	0.305	0.27	0.135	1.17	1.023
Hokutan	0.325	0.27	0.15	1.27	1.037

The micropore volume, V_0, is the experimental value determined from the adsorption volume (V) at the $dV/d(-A)$=minimum on the distribution curve of the adsorption potential ($A=RT\ln P_0/P$). The parameters, B_0, Δ, and C, are values so determined that Eq. 11 fits the adsorption data obtained using V_0.

other hand, in the case of the non-linear Dubinin-Radushkevich plot, k is not constant and the micropore system can be designated as a heterogeneous micropore system.

According to Dubinin,[1] the k constant in Eq. 1 is a measure of the average micropore size, while the β constant is the relative differential molar work of vapor adsorption with the chosen standard substance, often called the affinity coefficient of the characteristic curve. Therefore, as to the heterogeneous micropore systems, the $B_j = k_j/\beta^2$ expression in Eq. 4 has validity. However, B_j is a positive value; therefore, using the distribution function, $f(B)$ (Eq. 6), in Eq. 5 is not adequate. In order to integrate the distribution function over $B>0$, we must use a new distribution function, $g(B) = C'f(B)$, instead of $f(B)$; C' is defined by the following equation:

$$\int_0^\infty g(B)\mathrm{d}B = \int_0^\infty C'f(B)\,\mathrm{d}B = 1 \tag{8}$$

and Eq. 7 is written as follows:

$$V(A^2) = C'V_0 \exp\left[-B_0A^2\right] \times \exp\left[A^4\Delta^2/2\right]\left[1 - \mathrm{erf}(X)\right]/2. \tag{9}$$

The coefficient C''s are listed in Table 1. However, in order to fit Eq. 9 to the experimental data of the micropore-volume range, the C' coefficient must be multiplied by the correcting coefficient, C'', to give

$$C = C' \times C''. \tag{10}$$

The following equation is written in order to describe the experimental data:

$$V(A^2) = CV_0 \exp\left[-B_0A^2\right] \times \exp\left[A^4\Delta^2/2\right]\left[1 - \mathrm{erf}(X)\right]/2 \tag{11}$$

or

$$\log V = \log V_0 - 2.303\,B_0R^2T^2 \log^2 P_0/P + \frac{1}{2}2.303^3\Delta^2R^4T^4 \log^4 P_0/P + \log\frac{1-\mathrm{erf}(X)}{2} + \log C,$$

where

$$X = (2.303^2R^2T^2 \log^2 P_0/P - B_0/\Delta^2)\Delta/\sqrt{2}. \tag{11'}$$

The application of the modified Dubinin-Radushkevich equation (Eq. 11′) with the best-fit parameters, listed in Table 1, to the experimental data is shown in Fig. 4. The value of B_0 is a measure of the average value of the micropore size, and at the same time, a measure of the higher adsorptive capacity for a smaller value of B_0 at a low relative pressure (see Figs. 1(b), 2, and 3). The heterogeneity parameter, Δ, is the standard deviation of B, and also a factor influencing the pore-size distribution at a given value of B_0, with a larger value of Δ giving a broader shape of the pore-size distribution. Moreover, both parameters, B_0 and Δ, are responsible for the pore-size distribution and for the adsorptive capacity on the Dubinin-Radushkevich plots at a high value of $\log^2 P_0/P$.

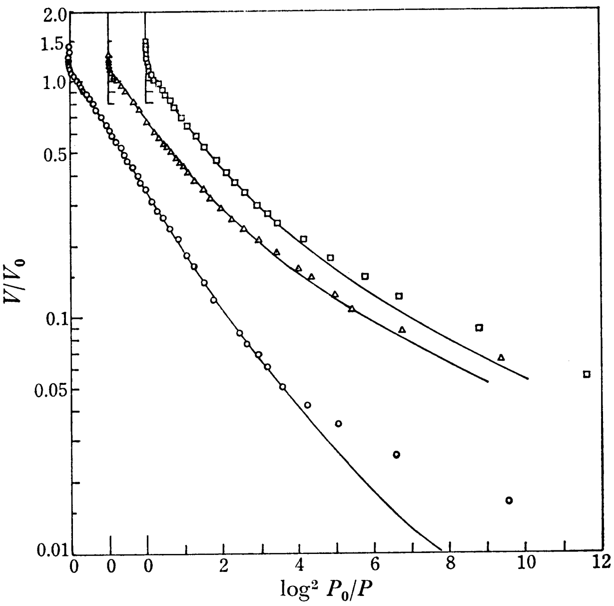

Fig. 4. Application of the modified Dubinin-Radushkevich equation (Eq. 11′) to the Dubinin-Radushkevich plots.
○ SGL, △ Filtrasorb 100, □ Hokutan.
The solid curves were calculated by use of Eq. 11′.

From these results, the modified Dubinin-Radushkevich equation can be said to have the following characteristics:

Equations 11 and 11′ are based on the original Dubinin-Radushkevich equation, and they maintain their general validity. Although the Dubinin-Astakhov equation is successful in linearizing the Dubinin-Radushkevich plots, it is empirical, and so it is more difficult to make a physical interpretation of the Dubinin-Radushkevich plots compared with the use of Eqs. 11 and 11′. On the other hand, the modified Dubinin-Radushkevich equation enables us to describe the heterogeneous micropore systems of active carbon on the Dubinin-Radushkevich plots by means of 4 parameters, V_0, B_0, Δ, and C.

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