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An Additional Discussion of the Micropore-volume Determination of Active Carbon Using Dubinin-Radushkevich Plots

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Synopsis. The validity of the recently presented method for determining the micropore volume (V_0) from the distribution curve of the adsorption potential based on the Dubinin-Radushkevich plot is further discussed in terms of the relationship between the V_0 and the adsorption volume (V_h) at the beginning of the hysteresis loop on the adsorption isotherm.

In a recent paper,[1] the present author reported that the adsorption volume (V) corresponding to the adsorption potential ($A=RT\ln P_0/P$), at which the plot of $dV/d(-A)$ *vs.* A has its minimum value, is the micropore volume (V_0) when the extrapolation of the Dubinin-Radushkevich plot cannot be applied because of its non-linearity. However, the relationship between the micropore volume (V_0), determined by the new method described above, and the adsorption volume (V_h) at the beginning of the hysteresis loop on the adsorption isotherm was not clarified quantitatively. In this report, this relationship is clarified on the basis of the experimental data on 6 types of active carbons.

The adsorption of methanol on active carbons at 30 °C was measured gravimetrically by means of a conventional quartz spring balance. The active carbons examined were Pittsburgh CAL-, Filtrasorb 100-, SGL-, PCB (5.3% burn-off)-,[1] and PCB (33.3% burn-off)[1]-type activated carbons; for the latter 4 carbons, the experimental data shown in the previous paper[1] were used. The conditions of the experiment were the same as those reported previously.[1]

The effective radius at the beginning of hysteresis is considered to be 15 Å,* and the hysteresis is attributed to the filling of transitional pores by the mechanism of capillary condensation.[2] The point of the beginning of hysteresis is also the boundary point dividing micropores from transitional pores according to the customary classification of pores.[2] Furthermore, this point is the end of the filling of micropores and, at the same time, that of the beginning of the capillary condensation of transitional pores, but monolayers and multilayers exist on the walls of the transitional pores. Moreover, the adsorption volume (V_h) at the hysteresis must be the sum of the micropore volume (V_0) and the volume (V_l) of adsorption layers on the transitional-pore walls.

The surface area (S_{trans}) of the transitional pores can be calculated by means of the equation

$$S_{trans} = \sum 2\Delta V/\bar{r}, \tag{1}$$

from the curve of the pore-volume distrubution,[1] here, $\Delta V = V_i - V_{i-1}$, and $\bar{r} = (r_i + r_{i-1})/2$, and with r_i lying from 15 to 100 Å. (The shapes of the pores are assumed to be cylindrical, and the surface area of the large pores (radii>100 Å) may be neglected compared with that of the small pores (15 Å≦radii≦100 Å).) Moreover, the volume (V_l) of the adsorption layers on the walls of the transitional pores at the beginning of hysteresis is obtained by the multiplication of S_{trans} by the thickness of the adsorption layers, 4.9 Å, corresponding to the radius of 15 Å in the Kelvin equation;[1]

$$V_l = 4.9 \times S_{trans}. \tag{2}$$

The values of V_0, V_l, and V_h are shown in Table 1. The sum of the V_0 and V_l coincide with V_h. These results show that the adsorption volume at $dV/d(-A)$=minimum on the distribution curve of the adsorption potential corresponds to the micropore volume; the validity of the method for determinimg the micropore volume of active carbon from the adsorption-potential distribution is thus further confirmed.

References

1) R. Tsunoda, *Bull. Chem. Soc. Jpn.*, **50**, 2058 (1977).

2) M. M. Dubinin, "Chemistry and Physics of Carbon," ed by P. L. Walker, Jr., Vol. 2, Mercell Dekker, N. Y. (1966), p. 51.

TABLE 1. RELATIONSHIPS BETWEEN MICROPORE VOLUMES AND ADSORPTION VOLUMES AT THE BEGINNING OF HYSTERESIS

Active carbon	V_0[a] (cm^3/g)	$V_{l,ads}$[b] (cm^3/g)	$V_{l,des}$[b] (cm^3/g)	$V_0+V_{l,ads}$ (cm^3/g)	$V_0+V_{l,des}$ (cm^3/g)	V_h[c] (cm^3/g)
SGL	0.315[d]	0.047	0.055	0.362	0.370	0.360[d]
PCB	0.390[d]	0.012	0.015	0.402	0.405	0.415[d]
PCB (5.3% burn-off)	0.405[d]	0.031	0.039	0.436	0.444	0.430[d]
PCB (33.3% burn-off)	0.480[d]	0.104	0.124	0.584	0.604	0.535[d]
Filtrasorb 100	0.305	0.033	0.039	0.338	0.344	0.340
CAL	0.355	0.048	0.052	0.403	0.407	0.382

a) V_0 is the micropore volume corresponding to the adsorption volume at $dV/d(-A)$=minimum on the adsorption-potential distribution. b) V_l is the volume of adsorption layers on the transitional-pore walls at the relative pressure corresponding to the radius of 15 Å in the Kelvin equation.[1] The subscripts, ads and des, indicate the calculation branch on the adsorption isotherm. c) V_h is the adsorption volume at the beginning of hysteresis on the adsorption isotherm. d) Ref. 1.

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* Throughout this paper 1 Å=0.1 nm.