[Chem. Pharm. Bull.
30(7)2555—2560(1982)]

Structure Analysis of Microporous Activated Carbon by Measurement of the Adsorption Isotherm of Hydrogen Sulfide

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(Received January 18, 1982)

The structures of micropores and supermicropores of activated carbon are discussed on the basis of the results of application of the two-term equation, $a=W_{01}/\nu^*\exp[-(A/\beta E_{01})^2]+W_{02}/\nu^*\exp[-(A/\beta E_{02})^2)]$ to the adsorption isotherms of hydrogen sulfide. The fact that the Dubinin–Radushkevich plots of the adsorption isotherms showed deviation from linearity whereas the two-term equation described them well seems to indicate that the activated carbon used possesses heterogeneous pores, that is, micropores and supermicropores with a flat slit shape. The distribution of radii of supermicropores seems to favor micropores rather than mesopores. It was suggested that the net differential heat of adsorption was more affected by the heterogeneity of pores than by the changes of lateral interactions of adsorbed hydrogen sulfide in relation to the increasing amount adsorbed.

Keywords——hydrogen sulfide; micropore; supermicropore; heterogeneous pore; flat slit-shaped pore; Dubinin-Radushkevich equation; two-term equation; net differential heat of adsorption

Hydrogen sulfide, which is often discharged into the atmosphere from paper-making factories, oil refineries, *etc.*, has a noxious odor and is toxic. We have studied the structural properties of various adsorbents which might be useful to remove hydrogen sulfide.[1)]

Dubinin[2)] pointed out that the pore structure of an adsorbate can be divided into three classes, *i.e.*, micropores (radius<15—16 Å), transitional pores (15—16 Å<radius<1000—2000 Å), and macropores (radius>1000—2000 Å). The theory of volume filling of micropores (TVFM)[3)] was applied to describe the physical adsorption of gases and vapors in micropores, and the fundamental equation is

$$a = W_0/\nu^* \exp[-(A/\beta E_0)^n] \qquad (1)$$

where a is the amount adsorbed at a relative pressure p/p_s, W_0 is the limiting volume of the adsorption space or the micropore volume, E_0 is the characteristic energy of adsorption, β is the similarity coefficient, n is an integer, and $A=\mathbf{R}T\, ln(p_s/p)$. The parameter n for microporous activated carbon is equal to 2, as a rule,[4)] and the case where $n=2$ corresponds to the Dubinin–Radushkevich (D–R) equation.[2)] As plots according to the D–R equation frequently show deviation from linearity at low equilibrium pressure, Rand[5)] proposed that the data could usually be linearized by adopting the constant parameter n of equation (1) as its variable parameter. However, this is not desirable[4)] because it changes the properties of equation (1) and its applicability for the characterization and description of the microporous structures of adsorbents. Later, the division of the finest pores of adsorbents with equivalent radii up to 15—16 Å into micropores (radius<6—7 Å) and supermicropores (6—7 Å<radius<15—16 Å) was proposed by Dubinin,[6)] and the following two-term adsorption equation[4,7)] was presented,

$$a = W_{01}/\nu^* \exp[-(A/\beta E_{01})^2]+ W_{02}/\nu^* \exp[-(A/\beta E_{02})^2] \qquad (2)$$

where W_{01} and W_{02} are the micropore volume and supermicropore volume, respectively, and

ν^* is the molar volume of an adsorbate. Dubinin[4] showed that the parameters (net differential heat of adsorption and adsorption volume) of the adsorption equation of TVFM at different n values for the adsorption of benzene on activated carbon gave relatively better agreement between the experimental results and the values calculated by using equation (2) when $n=2$.

In this paper, the applicability of the two-term equation to the adsorption isotherm of hydrogen sulfide and the structures of the microporous activated carbon are discussed.

Experimental

Materials——Hydrogen sulfide gas was of certified grade (Seitetsu Kagaku Co.) and its purity was indicated to be 99.9%. Activated carbon was obtained commercially, and the particle sizes were 4—20 mesh. The specific surface area of activated carbon was measured with the BET apparatus by using nitrogen gas at liquid nitrogen temperature, and the procedure for measurement of pore volume was described previously.[8] The specific surface area and the pore volume of activated carbon used are shown in Table I.

Procedure for Adsorption of Hydrogen Sulfide——Adsorption isotherms of hydrogen sulfide on activated carbon were determined in an all-glass vacuum system similar to that described previously.[1] The adsorbent was dried at 110°C for 1 h at 1×10^{-3} Torr before use, and the decrease in the weight of adsorbent due to heating was corrected for. The equilibrium amounts adsorbed at pressures up to 500 Torr were measured by a gravimetric method by using a BET adsorption apparatus with a spring balance.

Results and Discussion

1. Application of the Two-Term Equation to the Adsorption Isotherm of Hydrogen Sulfide

Figure 1 shows the adsorption isotherms of hydrogen sulfide on activated carbon at 30°C. The open symbols denote the experimental adsorption data, and the equilibrium amounts adsorbed at different pressures were determined within an error of 0.5%. The adsorption isotherms rose gradually up to 500 Torr.

TABLE I. Physical Properties of Activated Carbon used

Activated carbon No.	Specific surface area (m^2/g)[a]	Pore volume(ml/g)[b]
1	1141.4	0.650
2	906.0	0.557
3	1384.5	0.790

a) N_2-BET method.
b) Pore volume is the volume from the adsorption isotherm of nitrogen at $p/p_s=1.0$.

The physical adsorption of gases on a microporous adsorbent is described by the TVFM[3] and the adsorption isotherm is given by the D–R equation

$$a = W_0/\nu^* \exp[-B(T/\beta)^2 \log^2(p_s/p)] \tag{3}$$

where B is the structural constant, and $\beta=P/P_0$ (in this case, P and P_0 are the parachors of hydrogen sulfide and benzene, respectively, and the value of β is 0.39).

The curves in Figs. 2, 3, and 4 show the application of the D–R equation to the adsorption isotherms of hydrogen sulfide on activated carbon Nos. 1, 2, and 3, respectively. The D–R plots were curved over the whole range of adsorption, and they corresponded to type B in the classification of Rand.[5] It seems that the activated carbon Nos. 1—3 possess heterogeneous surfaces[9] because of the absence of linearity of the D–R plots. Izotova and Dubinin[7] showed that the deviation from linearity of the D–R plots could be explained in terms of the sum of two equations, corresponding to the contributions of two different types of micropores. The existence of two types of micropores was confirmed by an independent method based on small-angle X-ray scattering.[10] The two-term adsorption equation[4,7] is expressed by equation

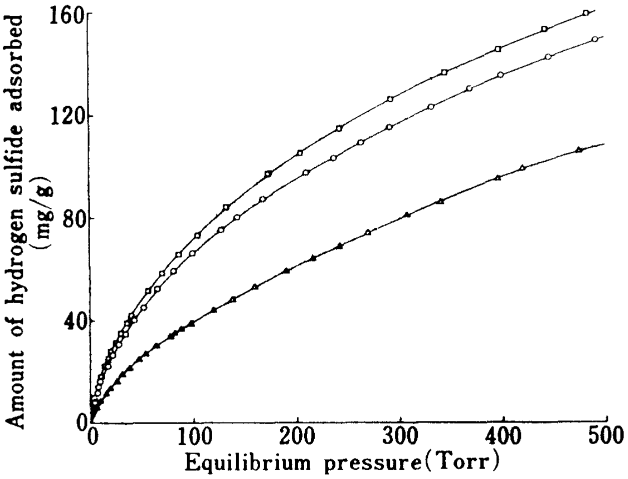

Fig. 1. Adsorption Isotherms of Hydrogen Sulfide on Activated Carbon at 30°C

□: No. 1; ○: No. 2; △: No. 3.

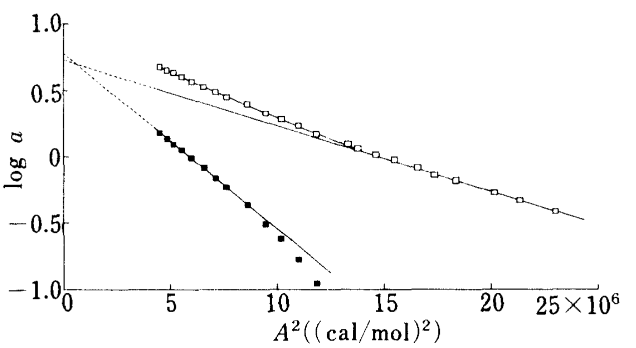

Fig. 2. Application of the Dubinin-Radushkevich Equation and the Two-Term Equation to the Experimental Adsorption Isothermof Hydrogen Sulfide on Activated Carbon No. 1

a: amount of hydrogen sulfide adsorbed (mmol/g); *A*: the decrease of free energy of adsorption.

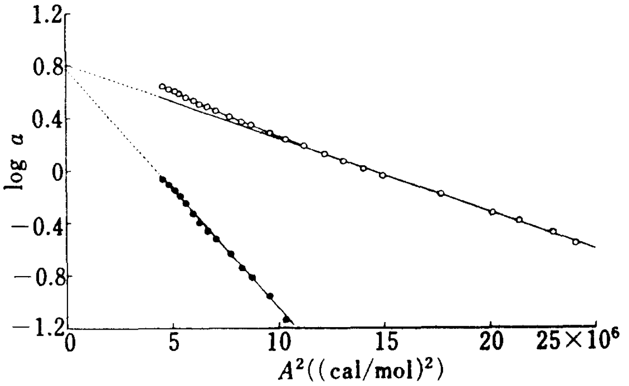

Fig. 3. Application of the Dubinin-Radushkevich Equation and the Two-Term Equation to the Experimental Adsorption Isotherm of Hydrogen Sulfide on Activated Carbon No. 2

a: amount of hydrogen sulfide adsorbed (mmol/g); *A*: the decrease of free energy of adsorption.

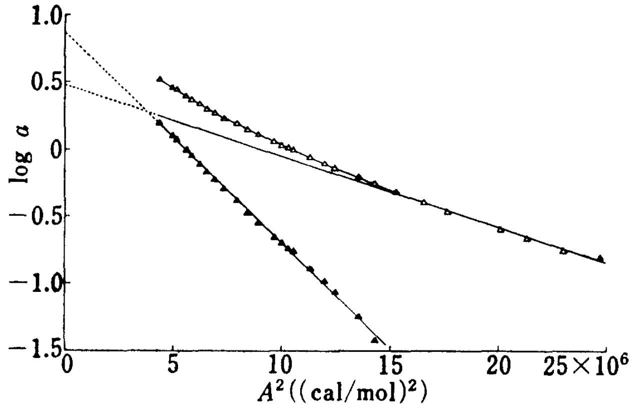

Fig. 4. Application of the Dubinin-Radushkevich Equation and the Two-Term Equation to the Experimental Adsorption Isotherm of Hydrogen Sulfide on Activated Carbon No. 3

a: amount of hydrogen sulfide adsorbed (mmol/g); *A*: the decrease of free energy of adsorption.

(2). The micropore volume (W_{01}) and the characteristic energy of adsorption of micropores (E_{01}) were estimated by extrapolation of the intercept to $A^2=0$ and from the slope, respectively, of the straight line with open symbols. The difference between the ordinates of curves with open symbols and of the straight line with open symbols for the same values of A^2 ($A^2<10$—15×10^6) is expressed by the second term of equation (2), that is ,the straight line with closed symbols represents, in linear form, its second term. The supermicropore volume (W_{02}) and the characteristic energy of adsorption of supermicropores (E_{02}) were calculated from the straight line with closed symbols. The parameter B is expressed[3] through E from equations (1) and (3),

$$B=(2.303R/E)^2 \qquad (4)$$

where R is the gas constant. The structural constant has an intimate relation with the average dimensions of the micropores and supermicropores.[10] The values of B_2 were about three times those of B_1. The applicability of the two-term equation to the adsorption isotherms of hydrogen sulfide on activated carbon Nos. 1—3 indicates that the samples contain micropores and supermicropores.

2. Structural Analysis of Activated Carbon

The values of the parameters of equations (2) and (4) are shown in Table II. The micropore volumes (W_{01}) of activated carbon Nos. 1 and 2 were almost equal to their supermicropore volumes (W_{02}), and their micropore volumes were twice that of No. 3. Although the pore volume and the specific surface area of No. 3 were considerably larger than those of Nos. 1 and 2 (Table I), the amount adsorbed on No. 3 was small in comparison with those of Nos. 1 and 2. The amount adsorbed seems therefore to be mainly determined by the micropore volume in view of the results in Fig. 1 and the values of W_{01}, W_{02}, specific surface area, and pore volume.

Table II. Parameters of the Adsorption Equation based on the Theory of Volume Filling of Micropores for Adsorption of Hydrogen Sulfide on Activated Carbon

Activated carbon No.	W_{01}(ml/g)	W_{02}(ml/g)	W_0(ml/g)	E_{01}(kJ/mol)	E_{02}(kJ/mol)
1	0.1930	0.2176	0.4106	31.65	19.36
2	0.2253	0.2055	0.4308	29.79	16.57
3	0.1067	0.2598	0.3665	30.65	17.95

The activated carbon Nos. 1—3 showed clear departure from the D–R equation (3), which[9] was found to apply strictly only to homogeneous systems of micropores. They therefore seem to possess heterogeneous structure, that is, to contain micropores and supermicropores. Dubinin *et al.*[4,10] pointed out that the parameters of the adopted model of micropores and supermicropores as flat slit shapes formed between circular bases were in agreement with both the adsorption and X-ray data. The model of flat slit-shaped micropores was also suggested by Perret *et al.*[11] on the basis of the results that the energies of adsorption of simple gases in microporous carbons were always smaller than twice the corresponding value for adsorption on graphitized carbon blacks. A more elaborate model of cylindrical micropores was suggested by Gurfein *et al.*,[12] but this model has been questioned by Stoeckli *et al.*[13] on energetic grounds as well as from a structural viewpoint. The direct observations by Fryer[14] by transmission electron microscopy support the view that a large proportion of the micropores may be flat slit-shaped. It is therefore concluded that activated carbon Nos. 1—3 are heterogeneous and that their micropores and supermicropores may be flat slit-shaped on the basis of the applicability of the two-term equation to the adsorption isotherms.

The parameters of an idealized model of slit-like micropores are the radius of the circular base r and the half-width of the flat slit l, and the inertia radius R_{I} of a flat slit-shaped pore is expressed[15] by

$$R_{\mathrm{I}} = \sqrt{62B \times 10^6} \qquad (5)$$

where B is the constant of the D–R equation. The relationship between the inertia radii of the micropores and supermicropores and their characteristic sizes x is expressed [4] by the following equation

$$x = 0.878R_{\mathrm{I}} \qquad (6)$$

The characteristic sizes express the linear dimensions, which are of decisive importance for the properties of the micropores, and they are average values which correspond to the characteristic points of the adsorption isotherm.[4] The characteristic size x of the slit-shaped pore is equal to the half-width of the slit l.[4] Table III shows the values of B, R_{I}, x obtained from the adsorption data. The pores of the carbonaceous adsorbents are divided, according to their sizes, into micropores (radius<6—7 Å), supermicropores (6—7<radius<15—16 Å), mesopores (15—16<radius<1000—2000 Å), and macropores (radius>1000—2000 Å).[3] The fact that the characteristic sizes of supermicropores of activated carbon Nos. 1—3 were 6.7—7.8 Å indicates that the distribution of half-width of the slit-shaped supermicropores favors micropores rather than mesopores.

Table III. Structural Constant, Inertia Radius, and Characteristic Size of Micropores and Supermicropores

Activated carbon No.	Micropores			Supermicropores		
	$B_1\times10^6(K^{-2})$	R_{l1}(Å)	x_1(Å)	$B_2\times10^6(K^{-2})$	R_{l2}(Å)	x_2(Å)
1	0.37	4.8	4.1	0.98	7.8	6.7
2	0.41	5.2	4.4	1.33	9.1	7.8
3	0.39	5.1	4.2	1.14	8.4	7.2

3. Thermodynamics of Adsorption of Hydrogen Sulfide

The net differential heat of adsorption q was obtained in order to elucidate the relationship between the heterogeneity of pore structure and the lateral interaction of hydrogen sulfide adsorbed. According to the TVFM,[3] q is expressed by,

$$q = A + \frac{\alpha T E_0}{n}(\ln a_0/a)^{\frac{1}{n}-1} \tag{7}$$

where a is the amount adsorbed, a_0 is the limiting amount adsorbed, and α is the thermal coefficient of limiting adsorption. The following equation (8) is obtained for the case of adsorbents containing both micropores and supermicropores from equation (7),

$$q = A + \frac{\alpha T}{nA^{n-1}} \times [\gamma E_{01}^n + (1-\gamma)E_{02}^n] \tag{8}$$

where

$$\gamma = W_{01}/(W_{01}+W_{02}) \tag{9}$$

Beebe and co-workers[16] suggested that two factors contribute to the heat curves; these are (1) physical heterogeneity of the surface, and (2) lateral interaction between adsorbed molecules. In the adsorption of nitrogen on carbons at −195°C they found a marked difference between the heat-coverage curves within the BET monolayer on Spheron Grade 6 and on Graphon produced by sintering at 3200°C, and showed that the difference of 1600 to 700 cal per mol could be accounted for by the nature of the heterogeneity in the surfaces of the former carbon rather than by the lateral interaction between adsorbed nitrogens. The value of A is equal to the difference between the chemical potentials of a substance in the bulk liquid state and in the adsorbed state at the same temperature,[2] and it therefore implies the lateral interaction between adsorbed molecules. The monotonous decrease of A with increasing amount adsorbed is clear from the relationship between log a and A^2 in Figs. 2—4. On the other hand, the values of q decrease with increasing amount adsorbed, but then pass through minima and increase somewhat with greater amount adsorbed, as shown in Fig. 5. The difference between the dependence of A and that of q upon the amount adsorbed on activated carbon Nos. 1—3 can be explained by assuming that the heterogeneity in their pores has a large effect on the change of lateral interaction with increase in amount adsorbed. The minima of q of activated carbon Nos. 1—2 and 3 correspond to degrees of filling of micropores of 0.5—0.6 and 0.9, respectively.

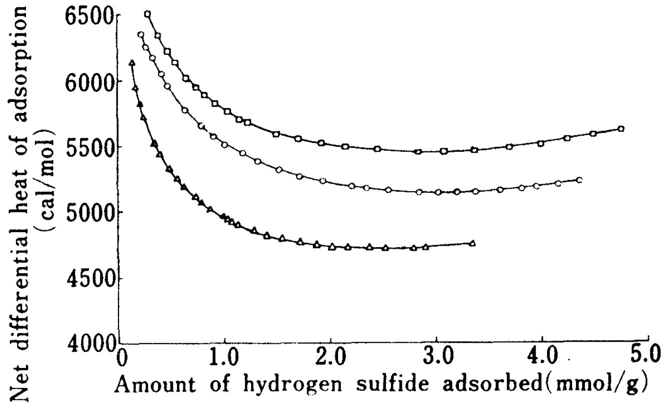

Fig. 5. Dependence of Net Differential Heat of Adsorption on Amount of Hydrogen Sulfide adsorbed

□: No. 1; ○: No. 2; △: No. 3.

The above results seem to indicate that the heterogeneity in micropores of activated carbon Nos. 1—2 is greater than in the case of No. 3.

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