ON THE QUESTION OF THE STRUCTURAL CHARACTERIZATION OF ACTIVE CARBONS

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Abstract

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ON THE QUESTION OF THE STRUCTURAL CHARACTERIZATION OF ACTIVE CARBONS

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The surface of active carbons is energetically heterogeneous, owing to the disordered arrangement of elementary graphite crystallites and to the effect of an increase in the adsorption potentials from opposite pore walls in narrow pores. This effect can be quantitatively evaluated by the indicator of degree n, with which the adsorption potential enters into the characteristic equation of M. M. Dubinin and L. V. Radushkevich ([1,2]). For nonporous carbon preparations and maximally activated active carbons with a burn-off of more than 75%, in which this effect is practically absent, $n = 1$, while for carbons with a burn-off of less than 50%, $n = 2$. For active carbons of moderate activation (burn-off 50–75%), which contain micropores of average dimensions, the value of n lies within the limits from 1 to 2. Then the equation of the vapor sorption isotherm on any active carbon may be written in the form:

$$a = \frac{w_0}{v} \exp\left[-B\frac{T^n}{\beta^n}\left(\lg\frac{P_s}{P}\right)^n\right]. \tag{1}$$

The determination of the structural characteristics of an active carbon—the limiting volume of the adsorption space w_0, the constants B and n—can be carried out by the method of successive approximations, using experimental data on the adsorption values a for different relative pressures P/P_s at a given temperature T, affinity coefficient β, and specific molar volume of the liquefied vapor v.

Taking in the first approximation the value $n = n_1$, let us write equation (1) for two neighboring experimental points i, $i+1$ and, after logarithmizing, dividing the first equation by the second, determine from the resulting relation the quantity $B(T/\beta)^{n_1} = \alpha_i^{(1)}$:

$$\alpha_i^{(1)} = \frac{\lg\dfrac{a_i}{a_{i+1}}}{0.434\left[\left(\lg\frac{P_s}{P}\right)_{i+1}^{n_1} - \left(\lg\frac{P_s}{P}\right)_i^{n_1}\right]}. \tag{2}$$

Substituting $\alpha_i^{(1)}$ into equation (1), from the experimental data a and P_s/P at the i-th point we find the quantity $\delta_i^{(1)} = w_0/v$. In the same way we determine $\alpha^{(1)}$ and $\delta^{(1)}$ for the remaining pairs of experimental points ($i+1$, $i+2$, etc.)

and calculate their arithmetic mean values $\alpha_{\text{av}}^{(1)}$, $\delta_{\text{av}}^{(1)}$ in the specified interval of relative pressures P/P_s. Knowing the quantities $\alpha_{\text{av}}^{(1)}$, $\delta_{\text{av}}^{(1)}$, from equation (1) we determine the theoretical values of the adsorption a_{T} at all m points and, comparing them with the experimental a_{op}, find the arithmetic mean relative error ε_1 of approximation of the experimental data by equation (1) at $n = n_1$

$$\varepsilon_1 = \frac{\sum_{i=1}^{i=m} \left(\frac{|a_{\text{op}} - a_{\text{T}}|}{a_{\text{op}}} \right)_i}{m}. \tag{3}$$

Changing the value $n = n_1$ to $n = n_2$, we determine the new values $\alpha_{\text{av}}^{(2)}$, $\delta_{\text{av}}^{(2)}$, ε_2. If $\varepsilon_1 > \varepsilon_2$, we proceed to the calculation at $n = n_3$; if, however, $\varepsilon_1 < \varepsilon_2$, the calculation is stopped, and from the values $\alpha_{\text{av}}^{(1)}$ and $\delta_{\text{av}}^{(1)}$ the values w_0 and B are calculated.

Table 1

Calculation of benzene adsorption values on active carbons:
A-6. $w_0 = 0{,}872$ cm^3/g; $B = 1{,}591 \cdot 10^{-4}$; $n = 1{,}32$; $\varepsilon = 0{,}986\%$
AR. $w_0 = 0{,}565$ cm^3/g; $B = 1{,}53 \cdot 10^{-5}$; $n = 1{,}65$; $\varepsilon = 4{,}1\%$

p/P_S	Active carbon A-6	P/P_S	Active carbon AR								
	a_{exp} adsorption, mm/g	a_T by (1)	a_T by (4)	$\lvert\Delta a\rvert/a_{\text{exp}}$, % by (1)	Δa, % by (4)		a_{exp} adsorption, mm/g	a_T by (1)	a_T by (4)	$\lvert\Delta a\rvert/a_{\text{exp}}$, % by (1)	Δa, % by (4)
$3{,}36 \cdot 10^{-6}$	0,66	0,66	0,66	0,0	0,0	$7{,}63 \cdot 10^{-6}$	0,44	0,44	0,50	9,3	2,0
$8{,}42 \cdot 10^{-6}$	0,85	0,85	0,87	0,0	2,3	$1{,}68 \cdot 10^{-5}$	0,68	0,59	0,68	12	0,0
$2{,}12 \cdot 10^{-5}$	1,10	1,10	1,14	0,0	3,64	$9{,}75 \cdot 10^{-5}$	1,10	1,07	1,17	2,5	6,3
$5{,}32 \cdot 10^{-5}$	1,40	1,40	1,45	0,03	3,5	$1{,}77 \cdot 10^{-4}$	1,29	1,29	1,39	0,03	7,8
$1{,}33 \cdot 10^{-4}$	1,75	1,77	1,83	1,27	4,57	$2{,}51 \cdot 10^{-4}$	1,43	1,43	1,53	0,0	7,0
$3{,}36 \cdot 10^{-4}$	2,20	2,23	2,26	1,4	2,7	$3{,}57 \cdot 10^{-4}$	1,61	1,58	1,63	1,3	1,24
$8{,}42 \cdot 10^{-4}$	2,74	2,78	2,78	1,5	1,5	$6{,}65 \cdot 10^{-4}$	1,91	1,89	1,95	0,9	2,1

p/P_S	Active carbon A-6	P/P_S	Active carbon AR								
$2{,}12\cdot 10^{-3}$	3,41	3,44	3,36	0,9	1,5	$4{,}7\cdot 10^{-3}$	2,92	3,08	3,02	5,4	3,42
$5{,}32\cdot 10^{-3}$	4,16	4,21	4,10	1,1	1,4	$1{,}25\cdot 10^{-2}$	3,61	3,78	3,55	4,7	1,7
$1{,}33\cdot 10^{-2}$	5,08	5,09	4,99	0,2	1,8	$3{,}21\cdot 10^{-2}$	4,33	4,49	4,14	3,6	4,4
$3{,}36\cdot 10^{-2}$	6,14	6,09	6,18	0,8	0,65	$4{,}6\cdot 10^{-2}$	4,62	4,76	4,37	2,9	5,4
$8{,}42\cdot 10^{-2}$	7,50	7,17	7,78	4,4	3,7	0,115	5,15	5,4	5,02	4,9	2,5
0,212	8,32	8,28	10,2	4,29	22	0,290	5,69	5,96	5,72	4,8	0,5
						0,687	6,06	6,30	6,37	4,0	4,92

This algorithm for calculating the structural characteristics of active carbon can be readily implemented on any digital computer.

To verify the applicability of equation (1) to calculations of adsorption values on moderately activated carbons, we shall use the experimental data of M. M. Dubinin et al. ([1]) on benzene adsorption at 20° on active carbon A-6 made from sugar with a burn-off of 60% and on recuperation carbon AR. The results obtained (Table 1) are compared with the calculation by equation (4), which is commonly used in determining vapor adsorption values on active carbons with a burn-off of 50-75% ([1]):

$$a = \frac{\alpha w_\varepsilon}{v} \exp\left[-B\frac{T^2}{\beta^2}\left(\lg\frac{P_S}{P}\right)^2\right] + \frac{(1-\alpha)w_\varepsilon}{v}\exp\left[-A\frac{T}{\beta}\lg\frac{P_S}{p}\right]. \qquad (4)$$

Equation (1), which contains only three constants instead of four, describes the sorption isotherm on carbons of any activation sufficiently well and is more convenient for practical calculations. To determine the structural characteristics ($w_0,\ B,\ n$), a program was compiled for the BESM-2 digital computer.

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CITED LITERATURE

1. M. M. Dubinin, E. D. Zaverina, ZhFKh, **23**, no. 10, 1129 (1949).

2. L. V. Radushkevich, ZhFKh, **23**, no. 12, 1410 (1949).

Note: Figure translations are in progress. See original paper for figures.