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Porous structure and adsorption properties of active carbon

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Abstract - Theoretical basis for quantitative analysis of the pore structure of active carbons is considered. Active carbons are classified into four types, according to their variances and mesopore surface areas. The parameters of micro- and mesopores of active carbons produced in different countries are defined from the benzene vapour adsorption isotherms at 293 K. The parameters of the TVFM equation for different adsorbates differ slightly

At present there are some technologies of active carbons with various adsorption properties and structures in industry and there are also laboratory-prepared samples. The ever increasing level of production and types of carbonaceous adsorbents pose the task of developing rational techniques for obtaining quantitative characteristics of their pore structure.

To characterise porous structures of microporous activated carbons, the theory of volume filling of micropores(TVFM) has been accepted [1,3]. In comformity with TVFM the efficienoy of the equilibrium adsorption except physical chemical properties of adsorbed substances and conditions of adsorption is characterized by three parameters of microporous structure of active carbon: the micropore volume W_o, the characteristic energy of adsorption E_o or micropore half - width x_o and dispertion δ characterizing the distribution range.These parameters are determined from the vapour experimental adsorption isotherm.

The activated carbons are classified into four types, depending on the dispersion and surface area values:

1. Microp o rous active carbons without supermicropores and mesopores.

2. Micro - mesoporous active carbons which practically without supermicropores and where the adsorption on mesopore surfaces is compared with the adsorption in micropores.

3. Active carbons, which contain micro- and supermicropores, but mesopores are absent.

4. Active carbons with micro-, supermicropores and mesopores with commensurable adsorption on the mesopores surfaces.

Good representation of experimental data for benzene and other substances adsorption in the heterogeneous micropore

activated carbons is given by adsorption isotherm equation (1):

$$W = \frac{W_o^o}{2\sqrt{1 + 2m\delta^2A^2}} \exp\left[- \frac{mx_o^2 A^2}{1 + 2m\delta^2A^2} \right]\left[1 + \mathrm{erf}\left[\frac{x_o}{\delta\sqrt{2}\sqrt{1 + 2m\delta^2A^2}}\right]\right] \quad (1)$$

where β - is a similarity coeffitient; $m = 1/\beta k$ is a coefficient constant for a given vapour and $k = x_o E_o$ is the energy caracteristic of micropores.

For the active carbons of the first and the second types when $\delta \to 0$ we obtain the DR adsorption equation (2) for adsorbents with homogeneous micropore structure:

$$W = W \exp\left[- \left(\frac{A}{\beta E_o}\right)^2 \right] \quad (2)$$

For the active carbons of the third and the fourth types we can calculate the total volume of micropores and the characteristic energy of adsorption from equation (1) and from the two - terms TVMF equation (3):

$$W = W_{01} \exp\left[- \left(\frac{A}{\beta E_{01}}\right)^2 \right] + W_{02} \exp\left[- \left(\frac{A}{\beta E_{02}}\right)^2 \right] \quad (3)$$

Equation (3) contains four parameters: W_{01}, E_1, W_{02} and E_2. For the homogeneous microporous structure $W_{02}=0$ and (3) reduced to the single term DR equation. The parameters of the both equations (1) and (3) are connected as follows:

$$W_o^o = W_{01} + W_{02} \quad (4)$$

$$x_o = \frac{x_{01}W_{01} + x_{02}W_{02}}{W_{01} + W_{02}} \quad (5)$$

$$\delta = \left[\frac{(x_{01}-x_0)^2 W_{01} + (x_{02}-x_0)^2 W_{02}}{W_{01} + W_{02}}\right]^{0.5} \quad (6)$$

When we determine the parameters of the active carbon of the second and the fourth types with high level of mesopores we have to correct the experimental isotherm for the adsorption on the mesopore surfaces, applying eqn (7) to each point of the experimental isotherm within the p/p_s range from 10^{-5} to 0.3 [5].

$$a_{mi} = a_{exp} - \gamma a_{me} \quad (7)$$

where a_{mi} is adsorption in micropores, a_{exp} is experimental adsorption, S_{me} is specific surface area of mesopores in square meters per gram, γ is benzene adsorption on mesopore surfaces according to eqn (8) in millimoles per square meter:

$$\gamma = 9.16 \times 10^{-3} \exp\left[- A/6.35 \right] \quad (8)$$

It should be noted that in [4] the more general equation was derived for various organic substances in the same range of $p/p_s = 1x10^{-5} - 0.3$

$$\gamma = 8.14x10^{-4}/v \exp\left[- A/\beta E_o\right] \quad (9)$$

where v is the molar volume of the adsorbate.

To choose the true technique for determining of the mesopore surface area we compare results of the analysis on data in the mercury porosimetry and of the experimental benzene vapore adsorption isotherm. Two ways for determining S_{me} are connected with the capillary evaporation theory from adsorbent mesopores and Kelvin - type equation. In the first case one takes into account the effect of the adsorption field in mesopores on the adsorption layer thickness and the meniscus liquid curvature. In the second case one takes into account the dependence of the surface strain on the meniscus liquid curvature. The third way for determining S_{me} from adsorption isotherms is a variety of the t - method:

$$\gamma' = 9.11/ A^{0.5645}{}_x\ 10^{-3} \quad (10)$$

We did not use S_{me} obtained from BET plots in active carbons with a great deal of micropores because of its rather high value. This method (10) is in good agreement with the results of the mercury porosimetry.

In all cases this method was used to determine the specific surface area of the mesopores because of its high precision and not requiring of additional experiments. So to obtain the value for a quantitative characterization of the adsorbent micropore structure the experimental adsorption isotherm must be corrected taking into account adsorption in mesopores according to eqn. (7), (8) and (10).

The proposed methods of characterization of the adsorption properties and microporous structure were used for a number of industrial activated carbons from Russia, Germany, Poland, CSFR. Experimental data were kindly supplied for investigation by Dr.O.Kadlec.

Table 1 lists the real micro-mesoporous structure parameters of these samples.

According to the data of table 1, the investigated industrial active carbons are the nonhomogeneous adsorbents. The AP -3, HS -4 and P -4 specimens belong to the third type, and FB-4, RKD-3, H to

TABLE 1. Parameters of the porous structure of the industrial active carbons.

Country	AC	S (m^2/g)	W_o^o (cm^3/g)	δ (nm)	E (kJ/mol)	ξ %	ξ %
CSFR	FB-4	120	0.294	0.263	32.9	3.5	6.0
RUSSIA	AP-3	30	0.324	0.210	18.4	0.9	-1.9
GERMANY	PKD-3	84	0.536	0.216	18.0	1.1	3.6
POLAND	H	134	0.435	0.218	17.6	1.4	-3.5
CSFR	HS-4	40	0.444	0.224	15.7	0.4	1.2
GERMANY	P-4	61	0.429	0.284	13.8	0.5	1.0

the fourth type. It should also be noted that the mean absolute deviations and maximum deviation, presented in table 1 for the eaoh active carbon show high accuracy of TVFM equation because deviations are not considerably in excess of 10%.

Table 2 presents the parameters of equation of the adsorption isotherm TVFM defined from experiments with C_2H_2CL, CCl_4 and C_6H_6 for the active carbons of the first and the fourth types. The values of the characteristic adsorption energies for the standard vapour E_o in all oases are calculated as the ratio of the characteristic adsorption energies to the similarity factors of corresponding vapours.

TABLE 2. The parameters of TVFM equation

Active carbon	Vapour	W_o (cm^3/g)	δ (nm)	E_o (kJ/mol)
AC-1	C_6H_6	0.426	0.0033	29.9
	C_2H_5Cl	0.450	0.0033	25.5
	CCl_4	0.395	0.0033	29.9
AC-4	C_6H_6	1.022	0.462	9.82
	C_2H_5Cl	0.861	0.298	11.3
	CCl_4	0.937	0.236	11.6

From table 2 it is seen that for the active carbon of the first type the total micropore volumes determined from experiments with different vapours differ. In the case of adsorption of ethyl chloride the value E_o is lower than for benzene once carbon tetracloride. For active carbon AC-4 the values of variances differ greatly for different vapours. It may be caused by two factors. On the one hand the method for determining β as the ratio of the parachors or the molar volumes of vapours is not universal(2).On the other hand, for the substances which molecules differ in sizes it should be displacement of the boundaries of adsorptive pore sizes. For studying these peculiarities we investigated the equalibrium vapour adsorption with range of the molecule sizes from 0.27 to 0.75 nm . The results of these studies will be published soon.

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