Description of the adsorption equilibrium of organic substances absorbed from a flow of moist air by a fixed bed of active carbon moistened to equilibrium

V. S. Kut'kov★ *and N. S. Polyakov*

Institute of Physical Chemistry, Russian Academy of Sciences, 31 Leninsky prosp., 117915 Moscow, Russian Federation. Fax: +7 (095) 952 7514

Isotherms of the adsorption of benzene vapor from moist air on active carbon (AC) moistened to equilibrium are obtained from dynamic experiments. The experimental data on the adsorption equilibrium of some organic substances from a flow of moist air by a fixed bed of AC moistened to equilibrium are obtained. The data on the equilibrium adsorption of benzene vapor is analyzed using the Dubinin—Radushkevich equation (the theory of volume filling of micropores). It is revealed that the characteristic adsorption energy of benzene vapor decreases as the filling of the microporous volume with water molecules increases. The characteristic adsorption energy depends on the following factors: polarizability of a substance in the adsorption field created by micropores, the number of carbon atoms in the adsorbate molecules, and parameters of the porous structure. The equation for the calculation of the parameters of equilibrium adsorption of organic substances from moist air on AC moistened to equilibrium are obtained.

Key words: adsorption equilibrium, active carbon, porous structure.

In the general case (when the parameters of the blend and the flow are constant) the dynamics of physical adsorption is determined by the adsorption ability of a sample under equilibrium conditions, the adsorption kinetics, and the adsorption heat. It is reasonable that the value of the equilibrium adsorption is a determining factor in the estimation of the dynamic activity of a blend.

The atmospheric moisture existing in air as vapor is a virtually constant component in the purification of industrial waste from organic substances. The environmental moisture considerably decreases the adsorption ability of AC and changes the adsorption kinetics.[1–6] A method for calculating the equilibrium adsorption of a mixture of water vapor and a water-insoluble substance that displaces almost none of the moisture sorbed has been proposed in Refs. 7 and 8. Mathematical models of the dependence of the adsorption of the vapor of organic substances on the parameters of a microporous adsorbent structure and the relative moisture content in air are considered in Refs. 9 and 10.

The adsorption of organic substances by the displacement of moisture from an adsorption microporous volume is the method most widely used in practice. An analysis of the literature[9–13] shows that descriptions of the adsorption equilibrium for "water—organic substance—AC moistened to equilibrium" systems are scarce.

This work is devoted to the experimental study of the adsorption of benzene vapor and the vapor of several organic substances on AC moistened to equilibrium from a moist air flow at different concentrations of the organic component and to the development of the mathematical apparatus for describing adsorption under these conditions.

Experimental

The main studies of the adsorption of organic vapor on AC moistened to equilibrium from a moist air flow were carried out with benzene. Hexane, cyclohexane, dioxane, *p*-xylene, perfluorobenzene (PFB), and tetrachloromethane (TCM) were studied in individual experiments.

Active carbon AC-40 was used. The adsorption isotherm of benzene vapor on AC-40 *in vacuo* was determined and the parameters of the porous structure of AC-40 were calculated: W_{01} = 0.214 cm^3/g; W_{02} = 0.056 cm^3/g; E_{01} = 22.73 kJ/mol; E_{02} = 9.5 kJ/mol; and V_{me} = 0.120 cm^3/g.

The experiments were carried out according to a procedure[1] that allows one to obtain individual output curves of the adsorption dynamics for each component of the mixture. Almost dry air with a relative moisture content up to 75% was used. Sorbents were pre-moistened to equilibrium with the water vapor at the specified moisture content. The moisture content in air during the adsorption of organic substances was the same as that used for pre-adsorption of water.

The experimental study of the adsorption of benzene vapor on AC moistened to equilibrium from a moist air flow was carried out at different concentrations of the substance in the gas-vapor mixture within the range of relative pressures (p/p_s) from $1 \cdot 10^{-5}$ to $2 \cdot 10^{-2}$. The volume velocity of the gas-vapor

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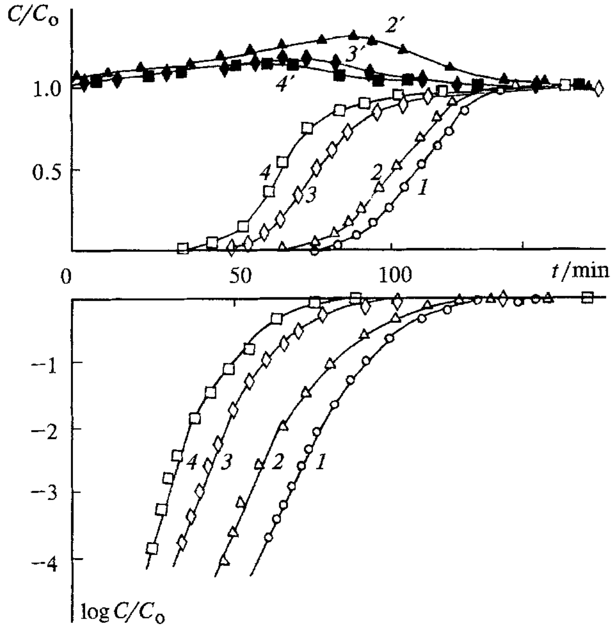

Fig. 1. Output curves of the combined adsorption of dioxane (*1, 2, 3, 4*) and water (*2′, 3′, 4′*) on AC-40 moistened to equilibrium (L = 20 mm; $\varphi = W_p$ (%)): 0 (*1*), 40 (*2, 2′*), 65 (*3, 3′*), 75 (*4, 4′*).

mixture and the temperature were constant (1.57 L/min and 293 K, respectively). The diameter of the adsorbent bed was 20 mm. The length of the AC bed, the surface area of the blend cross-section, and the amount of the sorbent were varied in order to obtain output curves of the adsorption dynamics, which allowed one to calculate the amounts of benzene adsorbed and water displaced and to rapidly achieve adsorption equilibrium.

The other organic substances were studied under the following conditions: the length of the AC bed was 20 mm, the concentration of a substance in a gas-vapor mixture was 3.8 mg/L, and the specific velocity of air was 0.5 L/min cm^2, 293 K.

The output curves of dioxane adsorption and water displacement on AC moistened to equilibrium at different relative moisture contents in the gas-vapor mixture are presented in Fig. 1.

Results and Discussion

The volume filling of the adsorption bed is typical of the physical adsorption of organic substances in micropores of both dry AC and AC moistened to equilibrium.[14,15] When the adsorption occurs on AC moistened to equilibrium from a moist air flow, the adsorption of the majority of substances is accompanied by the partial displacement of some amount of sorbed water from the microporous volume by an organic component. According to adsorption theory, in this process the adsorption ability of one of the components decreases in the presence of another component. This is supported by the calculations of the adsorption equilibria of the water—organic substance mixtures on AC-40 active carbon moistened to equilibrium at a 75 % moisture content in air (Table 1). The values of adsorption of organic substances on dry AC (a) and AC moistened to equilibrium (a') were calculated from the output curves of the adsorption dynamics. The value of water adsorption (a_{H_2O}) was determined as the difference between the amount of water preliminarily sorbed by AC at the moisture content of 75 % and the amount of water displaced in the course of the experiment. These amounts were calculated from the displacement curve. The summarized adsorption values of organic substances and water ($a^*_{eq} = a' + a_{H_2O}$), the results of the weight measurements of a^*_w, and the equilibrium adsorption values of organic substances on dry AC calculated by the Dubinin—Radushkevich equation from the theory of the volume filling of micropores (TVFM) (a_{D-R})[14] are presented in Table 1.

Table 1. Equilibrium values of the adsorption[a] of organic substances on AC-40 (a/mg g^{-1})

Substance	$\varphi \approx W_{eq} \approx 0\%$			$\varphi \approx W_{eq} \approx 75\%$		
	a	a_{D-R}	a'	a_{H_2O}	a^*_{eq}	a^*_w
Hexane	151	143	30(28)	233	263	267
Cyclohexane	162	156	35(31)	229	264	262
Benzene	178	179	74(80)	189	263	280
Dioxane	247	220	164(180)	160	324	324
PFB[b]	336	320	130(110)	186	316	320
TCM[c]	276	276	90(105)	203	293	295
p-Xylene	262	220	200(180)	83	283	289

[a] The calculated values are presented in parentheses.
[b] PFB is perfluorobenzene; [c] TCM is tetrachloromethane.

The theory of the volume filling of micropores has become the most popular for describing the physical adsorption of gas and vapor in micropores of non-moistened AC. The main equation of this theory has the following form:[14]

$$W = W_0 \exp\{-[A/(\beta E_0)]^2\}, \quad (1)$$

where W is the equilibrium adsorption value for an organic substance at relative pressure p/p_s and temperature T; W_0 is the limiting volume of the adsorption microporous space; A is the change in Gibb's free energy; E_0 is the characteristic adsorption energy for the standard vapor; β is the affinity factor determined from physical constants of determined and standard substances. For AC with the bidispersed structure the TVFM equation takes the form:

$$W = W_{01} \exp\{-[A/(\beta E_{01})]^2\} + W_{02} \exp\{-[A/(\beta E_{02})]^2\}, \quad (2)$$

where W_{01} and W_{02} are the limiting volumes of micro- and supermicropores, respectively, and E_{01} and E_{02} are the characteristic adsorption energies of the standard vapor for the first and second structures. The linear form of Eq. (2) can be presented as follows:

$$\log W = \log W_{01} - 0.434\,[(2.3\,RT)/(\beta E_{01})]^2 \cdot [\log(C_s/C)]^2 + \log W_{02} - 0.434\,[(2.3\,RT)/(\beta E_{02})]^2 \cdot [\log(C_s/C)]^2, \quad (3)$$

where R is the universal gas constant, C_s is the concentration of the saturated vapor of the organic substance, C is the concentration of an organic substance in the experiment. Using the Dubunin—Radushkevich equation in form (3), the experimental data on the adsorption of benzene vapor by AC (dry and moistened to equilibrium at relative moisture contents of benzene vapor in air, C_s/C, from $1 \cdot 10^{-5}$ to $2 \cdot 10^{-2}$) are analyzed. The experimental results are presented in Fig. 2. It can be seen that the values of benzene vapor adsorption obtained *in vacuo* and from a flow of virtually dry air coincide. The data obtained for both dry AC and AC moistened to equilibrium are well approximated by straight lines intersected at the point corresponding to the volume of the adsorption microporous space W_{01}. An increase in the relative moisture content in air and equilibrium moistening of AC results in a change in the slope of the isotherm of benzene vapor adsorption. As shown by the experimental data obtained when the relative moisture content in air and the equilibrium moistening of AC were $\varphi = W_{eq} = 75\%$ (see Fig. 3), a decrease in the concentration of benzene vapor in air is accompanied by a decrease in the amount of displaced water. The total volume occupied by benzene and water during adsorption on AC remains almost unchanged within the studied range of the relative concentrations of the organic component, and corresponds to filling of the total volume of the adsorption microporous space W_0 (0.27 cm^3/g).

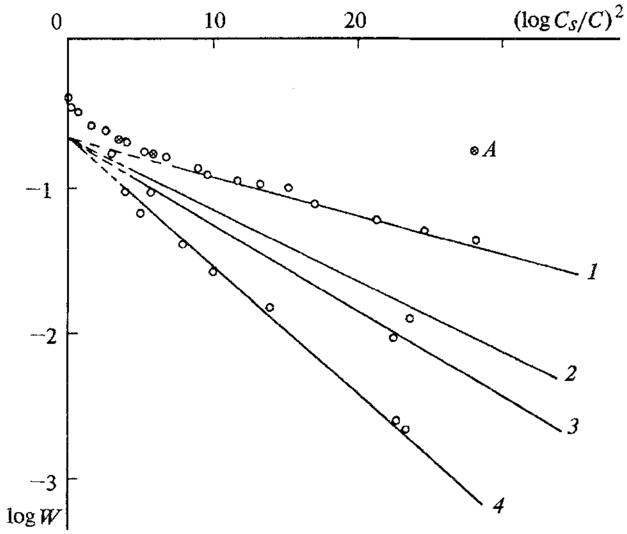

Fig. 2. Adsorption isotherms of the adsorption of benzene vapor *in vacuo* on dry AC (*1*) and from a flow of moist air on AC-40 moistened to equilibrium at the relative humidities (%): 45 (*2*), 65 (*3*), 75 (*4*). The experimental data are indicated by points, *A* is the adsorption of benzene vapor from a flow of virtually dry air on dry AC. The calculated data are indicated by lines.

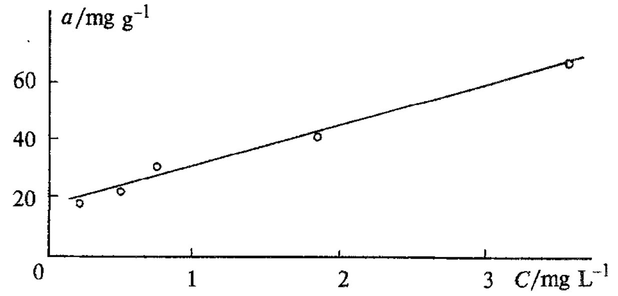

Fig. 3. The dependence of the amount of water (*a*) displaced by benzene from the adsorption volume of micropores of AC-40 moistened to equilibrium at the relative moisture content in air $\varphi = W_{eq} = 75\%$ on the concentration of the organic component in the flow.

The tangents of the slopes of the benzene vapor adsorption isotherms were determined from the experimental results. The characteristic energies of benzene vapor adsorption (E_{01}) on AC moistened to equilibrium at different moisture contents in air were calculated by the formula:

$$\tan\alpha = 0.434\,[(2.3\,RT)/(\beta E_{01})]^2 \quad (4)$$

The value of E_{01} is 22.73 kJ/mol for the dry sorbent and dry air, while for AC moistened to equilibrium and moist air at $\varphi = W_{eq}(\%) = 45$, 60, and 75 these values are 16.18, 14.61, and 12.41 kJ/mol, respectively. The results obtained attest to a substantial decrease in the characteristic energy of benzene vapor adsorption and a change in the size distribution function of the microporous volume as the adsorption microporous volume of the AC studied is filled with water. The dependences of the change in the characteristic energy of benzene vapor adsorption (E'_{01}/E_{01}, where E'_{01} is the characteristic energy of benzene vapor adsorption on AC moistened to equilibrium) on the extent to which the adsorption microporous space is filled (θ_{H_2O}) are presented in Fig. 4. It can be seen that the dependence is almost linear and can be approximated by the following equation:

$$E'_{01}/E_{01} = 1 - \xi\theta_{H_2O}, \quad (5)$$

where ξ is the angular coefficient equal to 0.5. In the previous work devoted to the study of the adsorption kinetics,[4] an equation was obtained that relates the change in the value of the effective mass-exchange kinetic coefficient β_{eff} for the range of relatively low concentrations to the change in the extent to which the adsorption microporous space is filled with water:

$$\beta'_{eff}/\beta_{eff} = 1 - \xi\theta_{H_2O}\,. \quad (6)$$

Here ξ is the angular coefficient, whose value depends on the properties of the water—organic substance—AC

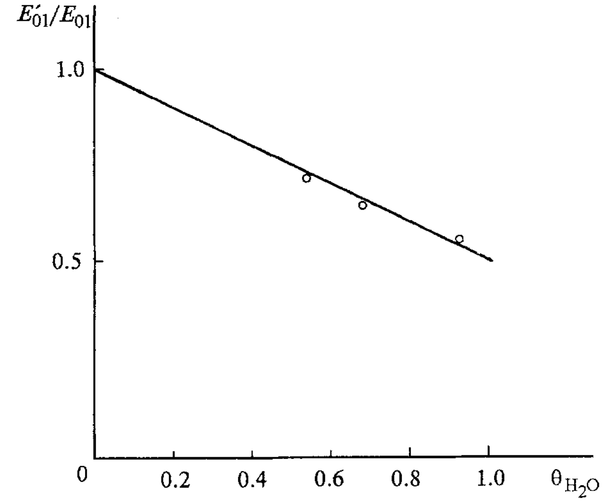

Fig. 4. Dependence of the characteristic energy of benzene vapor adsorption (E'_{01}/E_{01}) on the extent to which the adsorption microporous volume of AC-40 is filled with water.

system and is determined by the following equation:

$$\xi = (W_0/V_{me}) \exp\{[(2.3\ RT)/E_{01}]^2 \cdot (R^*/R^*_H) - (\psi/2)\}, \quad (7)$$

where W_0 is the limiting volume of the adsorption microporous volume of AC; V_{me} is the volume of AC mesopores; R^* is the refraction of the organic substance; R^*_H is the refraction of the H atom; ψ is the total number of carbon atoms and unpaired electrons for Cl, O, N, and other atoms. The value of ξ for benzene in Eq. (5) is close to the value of ξ calculated by Eq. (7). Substituting formulas (5) and (7) into Eq. (2) and assuming that for the second structure the characteristic adsorption energy is changed according to formula (4), we obtain an equation for calculating the equilibrium adsorption of organic vapor on AC moistened to equilibrium from a flow of moist air:

$$W = W_{01} \exp\{-[A/(E_{01}(1 - \xi\theta_{H_2O}))]^2\} + W_{02} \exp\{-[A/(E_{02}(1 - \xi\theta_{H_2O}))]^2\}, \quad (8)$$

The adsorption isotherms of benzene vapor for AC at various relative humidities and with equilibrium moistening of sorbents were calculated using Eq. (8), as were equilibrium adsorption values for several organic substances when the air moisture content and the equilibrium moistening of AC were $\varphi = W_{eq} = 75\%$ (Table 1). A comparison of the experimental values of the equilibrium adsorption of the organic substances (see Table 1 and Figs. 2 and 5) shows that the equation obtained satisfactorily describes the experimental data (taking into account that the usual range of the acceptable deviation of the equilibrium adsorption values of organic substances is ± 20 % in dynamic experiments) and can be used for engineering calculations.

Thus, the studies performed show that dispersion forces are crucial in determining the adsorption interaction both for dry AC and for AC moistened to equilibrium. The value of the dispersion forces depends on the electron polarizability (refraction) of the organic molecules in the adsorption field created by micropores, the orientation of the atomic framework relative to the micropore surface, the existence of atoms with unpaired electrons, the value of the adsorption field in the micropores determined by the value of the characteristic energy of the adsorption of the standard vapor, and the extent to which the adsorption volume of the micropores and mesopores, which are transport arteries in AC, are filled with water.

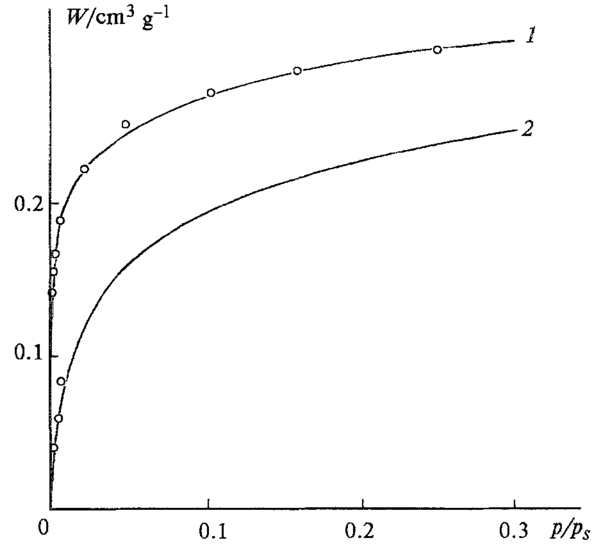

Fig. 5. Adsorption isotherms of benzene vapor adsorbed from a flow of dry air onto dry AC-40 (*1*) and onto AC-40 moistened to equilibrium (*2*) ($\varphi \approx W_{eq} \approx 75\%$). The experimental data are indicated by points, the calculated data are presented by lines.

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