Adsorption of benzene and perfluorobenzene vapor from a flow of moist air by a layer of equilibrium moistened active carbon

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The equilibrium adsorption of benzene and perfluorobenzene vapor from a flow of moist air by a layer of active carbon (AC) hydrated to equilibrium were considered. It was ascertained that these organic substances partly displace the water from the adsorptive micropore volume of AC. The equilibrium adsorption values of benzene, perfluorobenzene, and water vapors on AC were calculated. The adsorption of benzene and perfluorobenzene from a flow of moist air by a layer of AC is characterized by volume filling of the micropore adsorption space. This work is part of the research devoted to the study of the dynamics of the adsorption of organic substances from a flow of moist air by a layer of AC hydrated to equilibrium.

Key words: adsorption, active carbon, porosity structure.

As a rule, the adsorption of organic substances by active carbon (AC) in the course of the purification and recuperation of solvents is accompanied by adsorption of the water vapor usually present in the gas flow. The presence of water in the air and sorbent for the most part reduces the amount and the rate of the adsorption of organic substances. The effect of water vapor on the adsorption of organic substances was investigated in Refs. 1—11. The adsorption of an organic substance as a function of its physicochemical properties can proceed with partial, full, or practically negligible displacement of water from the adsorptive micropore volume of AC.

The calculation of the equilibrium adsorption of a mixture of water vapor and substances insoluble in it (generally not displacing the sorbed moisture) on AC was developed in Refs. **7** and **8**. In the case of full displacement of moisture from the micropore volume, the Dubinin—Radushkevich (D—R) equation[12] is suitable for the calculation of the adsorption of organic substances. The adsorption of organic compounds with partial displacement of moisture is the case that most often occurs. However, only separate experimental data that does not allow one to elucidate the mechanism of filling of AC micropores are given in the works devoted to the adsorption of organic substances in the presence of water.

This work is devoted to the experimental study of the adsorption of benzene and perfluorobenzene from a flow of moist air by a layer of AC and is part of the research into the dynamics of the adsorption of organic substances in the presence of water.

Experimental

Benzene and its fluorinated analog, perfluorobenzene, were chosen as the adsorbates. Some physicochemical characteristics of these compounds are given in Table 1. The pressure of the saturated vapor of perfluorobenzene was experimentally determined. The affinity coefficients (β) were calculated relative to parachors of the substances under investigation and parachors of a standard; in this work benzene was used as the standard substance. The heats of adsorption of the substances under investigation on graphitized thermal carbon black (q_{st}) according to the data of Ref. **13** are presented.

The adsorption studies were carried out using the active carbon AU-40 which has the following parameters of the porosity structure: $W_{01} = 0.214$ cm$^3 \cdot$g^{-1}; $W_{02} = 0.056$ cm$^3 \cdot$g^{-1}; $E_{01} = 22.73$ kJ $\cdot$ mol^{-1}; $E_{01} = 9.50$ kJ $\cdot$ mol^{-1}; $V_{\rm me} = 0.120$ cm$^3 \cdot$g^{-1}.

The experiments were performed using a specially developed procedure[1] that made it possible to obtain the individual yield curves of the dynamics of the adsorption of each component of the mixture.

Practically dry air and air with relative humidity equal to 75% were used. The sorbents were preliminarily hydrated to equilibrium by water vapor at a given humidity. The adsorption of organic substances was carried out at the same humidity as the preadsorption of water. The concentrations of the substances in the water-air mixture, the specific flow rate, the length of the sorbent layer, and the temperature were constant and

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were equal to 3.8 mg $\cdot$ L^{-1}, 0.5 L min^{-1} $\cdot$ cm^{-2}, 20 mm, and 293 K, respectively.

Using the method developed, the yield curves of the adsorption of the substances under investigation were determined on dry AC and AC hydrated to equilibrium. The experimental results are given in Fig. 1.

Results and Discussion

Benzene and perfluorobenzene molecules have similar structures and are characterized by coplanarity. Comparative investigations of the adsorption and the intermolecular interactions of these compounds with graphitized thermal carbon black at low volume filling of the surface[14] using GC have shown that these molecules are oriented parallel to the basic graphite face[14] and are in contact with it *via* carbon atoms having a van der Waals radius equal to ~1.8 Å. The replacement of H atoms by F atoms does not change the distance from the surface since the polarizability of the CF sections is slightly larger than that of the CH sections. The heats of adsorption of benzene and perfluorobenzene on graphitized thermal carbon black determined by GC are similar (see Table 1), suggesting that the volume filling of the micropore adsorption space of AC by these substances has approximately the same character.

Table 1. Physicochemical properties of the compounds under investigation

Substance	M g $\cdot$ mol^{-1}	B.p./K	V cm^3/mol	P_s^{293} Torr	β	q_{st} kJ/mol
Benzene	78.0	353.0	89	75.2	1.00	40.6
Perfluoro-benzene	186.1	353.0—354.0	115	129.1	1.25	53.6

The analysis of the experimental results (see Fig. 1) shows that when the combined adsorption of benzene and perfluorobenzene and water vapor occurs, displacement of the water from the adsorptive micropore volume by the organic components is observed. The presence of moisture in the gas flow and AC leads to a significant decrease in the retention time of identical pass through concentrations of the organic component. In this case, the preliminarily adsorbed water has a noticeable effect on the kinetic characteristics of the process, resulting in an increase in the retention time of given compound concentrations before equilibrium.

Taking into account the data obtained we calculated the equilibrium values of the adsorption of benzene and perfluorobenzene on dry AC (a) and AC in equilibrium hydrated up to 75% (a'), water (a_{H_2O}), as well as the values $a^*_{cal} = a' + a_{H_2O}$ which were then compared with the results of weight measurements (a^*_W) (see Table 2). The values of a and a' were calculated taking into account the output curves of the adsorption dynamics. The value of a_{H_2O} was determined as the

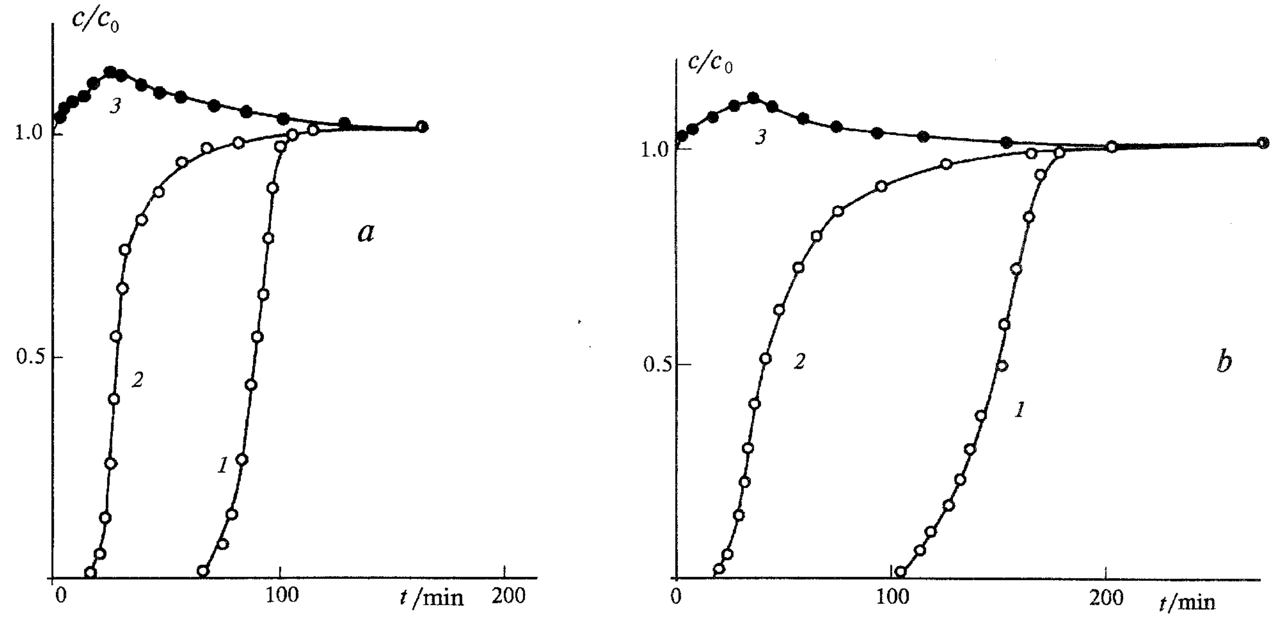

Fig. 1. The yield curves of the adsorption dynamics of benzene (a) and perfluorobenzene (b) and of the displacement of water during adsorption on activated carbon AU-40; *1*, adsorption of benzene (perfluorobenzene) by a layer of dry AC from the flow of dry air ($\varphi = W_{eq} = 0$); 2, adsorption of benzene (perfluorobenzene) by a layer of AC hydrated to equilibrium from a flow of humid air ($\varphi = W_{eq} = 75$ %); *3*, the displacement of water during adsorption of organic substances from a flow of humid air by AC hydrated to equilibrium ($\varphi = W_{eq} = 75$ %).

Table 2. Equilibrium values of benzene and perfluorobenzene adsorption on dry and activated carbon hydrated to equilibrium

Substance	$\varphi \approx W_{eq} = 0$		$\varphi \approx W_{eq} = 75$ %			
	a	a_{D-R}	a'	a_{H_2O}	a^*_{cal}	a^*_W
Benzene	178	179	74	189	263	280
Perfluorobenzene	336	320	130	186	314	320

Table 3. The volumes ($cm^3 \cdot g^{-1}$), occupied by benzene and perfluorobenzene when adsorbed on dry activated carbon and activated carbon hydrated to equilibrium

Substance	$\varphi \approx W_{eq} = 0$	$\varphi \approx W_{eq} = 75$ %		
	a	a'	a_{H_2O}	a^*_{cal}
Benzene	0.204	0.084	0.189	0.273
Perfluorobenzene	0.208	0.081	0.186	0.267

difference between the quantity of water preliminarily adsorbed by AC when the moisture of the air was 75 % and the water quantity displaced during the experiment, calculated from the yield curve of displacement. The equilibrium values of the adsorption (a_{D-R}) of benzene and perfluorobenzene on dry AC calculated using the data of Table 1 according to the D—R equation of the theory of volume filling of the micropores (TVFM)[12] are given in Table 2. Analysis of the data presented shows that there is a good coincidence between the results calculated taking into account the adsorption dynamics and those measured using the weight method, implying the validity of the method developed.

TVFM[12] considers micropores to be volumes in a solid comparable in size with the adsorbed molecules. In this case, there is an adsorption field produced by the solid over the whole area of the micropores. Adsorption in micropores is characterized by volume filling of the adsorption space. The results of the calculation of the amount of the substances under investigation adsorbed on practically dry AC (see Table 2) show that the equilibrium adsorption values obtained from the experiment correlate well with the adsorption values calculated according to the of TVFM equation. This fact makes it possible to consider the equilibrium adsorption of benzene and perfluorobenzene on AC in the context of TVFM and to suggest the volume mechanism of filling of adsorption micropore space of AC with these substances and the governing importance of dispersion forces in adsorption interaction. Table 3 presents the results of the calculation of benzene and perfluorobenzene adsorption expressed in the volume units ($cm^3 \cdot g^{-1}$) providing the densities of the chosen organic substances in the liquid and adsorption states are approximately the same and are equal to the densities of the liquids at 293 K. The results obtained indicate that in the case of adsorption according to the volume mechanism the organic compounds under investigation occupy equal volumes of micropore adsorption space of dry AC at the given concentration (3.8 $mg \cdot L^{-1}$).

The hydration of AC (see Tables 2, 3) leads to a decrease in the equilibrium adsorption of benzene and perfluorobenzene, and partial displacement of the water vapor occurs. As the results of the calculation show, benzene and perfluorobenzene displace the equal quantities of sorbed water during adsorption on equilibrium hydrated AC and, therefore, release approximately the same volumes of micropore adsorption space of dry AC where the adsorption of the organic component occurs. As can be seen from Table 3, the volume filled by benzene during adsorption on AC hydrated to equilibrium is approximately equal to that perfluorobenzene. The results obtained testify that the adsorption of benzene and perfluorobenzene on micropores of AC hydrated to equilibrium as well as of practically dried sorbents is characterized by volume filling of the adsorption space, although, in this case the displacment and redistribution of water vapor occur simultaneously. The total volume occupied by the organic component and water during adsorption is in full accord with the filling of the total adsorption micropore volume of AC.

Knowledge of the equilibrium adsorption value of organic compounds on adsorbents is required to describe the adsorption dynamics because this value and the adsorption isotherm significantly influence the curve of the concentration distribution in the adsorbent layer. The results obtained will be used further for the development of the mathematical apparatus for calculating the appearance time of pass through concentrations of organic substances behind a layer of AC hydrated to equilibrium.

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