Adsorption of vapor mixtures of water and organic substance on activated carbons

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The isotherms of water adsorption in the presence of an organic substance vapor with a specified concentration are calculated from experimental data on the joint frontal dynamics of adsorption of water vapor and several organic substances (benzene, hexane, cyclohexane, tetrachloromethane, and perfluorotripropylamine) on two samples of activated carbons. The influence of the organic substances on the equilibrium water adsorption decreases with an increase in the molecule size.

Key words: isotherm of adsorption of water, adsorption mixture, frontal dynamics of adsorption.

Experimental studies of equilibrium adsorption of gas—vapor mixtures are difficult tasks, especially for the water—organic substance—microporous sorbent systems. At the same time, these studies are of significant theoretical and practical interest. Activated carbons are widely used for air decontamination. Water vapor that is present in air usually decreases the adsorption capacity of sorbents with respect to an organic substance.

The equilibrium adsorption of the vapors of organic substances and water on activated carbons has been studied in several works.[1,2] In the past few years, the findings on the dynamics of adsorption of the vapors of an organic substance and water have been reported.[3—7] The major attention in these studies was paid to the effect of preadsorbed water on the organic substance adsorption and output dynamic curves for the organic substance.

A procedure for studying the adsorption dynamics[3] makes it possible to monitor changes in concentrations of both the vapors of an organic substance and water in time at the outlet of the sorbent layer. The system reaches equilibrium during the run because the concentrations of water vapor and the substance at the inlet and outlet of the sorbent layer become equal, whereas the weight of the sorbent layer remains unchanged. Therefore, the adsorption values at various concentrations of the organic substance and water can be calculated from the experimental data on the dynamics of adsorption.

In this work we studied the joint frontal dynamics of adsorption of vapors of water and organic substances (benzene, hexane, cyclohexane, tetrachloromethane, and perfluorotripropylamine) on two samples of activated carbons.

Experimental

Earlier,[4,5] the experimental findings on the dynamics of joint adsorption of vapors of water and organic substances (hexane, cyclohexane, benzene, tetrachloromethane, etc.) at various humidities of an air flow and different equilibrium wetting of a sorbent have been reported. The water adsorption values obtained in those studies are used in this work. The experiments with perfluorotripropylamine were carried out by us according to a known procedure.[3]

Two microporous samples of activated carbons, *viz.*, the commercial activated carbon after vapor-gas activation (AC) and carbon catalyst (CC) prepared from AC, were under study. The parameters of the pore structure of the sorbents are presented in Table 1.

The frontal dynamics of adsorption was studied on a Tsvet-100 chromatograph. A portion of a carrier-gas was bubbled through a vessel with an organic substance, and the concentration of the vapor of this substance after a sorbent layer (C_0) was monitored with a flame-ionization detector. The sensitivity of

Table 1. Parameters of the pore structure of sorbents

Sorbent	W_{01}	W_{02}	E_{01}	E_{02}	x_{01}	x_{02}	S_{me} /cm^2 g^{-1}
	cm^3 g^{-1}		kJ mol^{-1}		nm		
AC	0.178	0.122	26.7	11.6	0.37	0.86	0.134
CC	0.220	—	22.9	—	0.44	—	0.07

Note. The half-width of a micropore was calculated according to the literature data[8]; W_{01}, W_{02} are the volumes of micro- and supermicropores; E_{01}, E_{02} are the characteristic energies of micro- and supermicropores; x_{01}, x_{02} are the half-widths of micro- and supermicropores; S_{me} is the surface area of mesopores.

Published in Russian in *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 4, pp. 570—573, April, 2001.

measurements was $5 \cdot 10^{-5}$ mg L^{-1}. Water vapor was introduced into a flow by the same way, and the water concentration after the sorbent layer was monitored by a heat conductivity detector. The sensitivity of measurements was 0.2% of the flow humidity. The dry sorbent with the weight m_{sorb} was placed into a dynamic tube (L, length of sorbent layer). According to experimental conditions, a carrier-gas (air) was fed into the tube with the velocity V and the water vapor concentration φ_0. The sorbent was wet up to the appearance of water with the concentration φ_0 after it. The sorbent weight in the dynamic tube reached a constant value. An excess water in the sorbent (m_{w}) was estimated by weighting. In each run of the water preadsorption, the $m_{\text{w}}/m_{\text{sorb}}$ ratio corresponded to the equilibrium adsorption of water on the sorbent at $p/p_{\text{s}} = \varphi_0$. Figure 1 shows the adsorption isotherms (AI) for water on the samples studied, which were measured by the conventional evacuation-weighing method under dynamic conditions. As can be seen in the figure, the values of water adsorption determined by different methods virtually coincide. Some deviations can be explained by differences in the preparation of samples. In a standard procedure, carbon was dried and evacuated at 573 K, whereas in a dynamic experiment, carbon was dried in a drying box at 373 K for 5—6 h. Upon loading into the dynamic tube, the sorbent was purged with a dry air (dried with a zeolite) to a constant weight.

The conditions of dynamic experiments were the following: temperature 293 K, $V = 1.1$ L min^{-1}, the relative humidity of a flow was varied in the range $\varphi_0 = p/p_{\text{s}} \cdot 100\% = 15$—92%. The concentration of organic substances in a carrier-gas flow was maintained constant and equal to 4.0 ± 0.2 mg L^{-1}.

The organic substances under study are well adsorbed. As can be seen in Fig. 2, during the run on the frontal adsorption, these substances displace the adsorbed water from the sorbent layer. During the run, when the equilibrium-moistened sorbent was purged with a humid air flow with the organic admixture, the water vapor concentration after the sorbent layer, φ, initially exceeded that at the inlet of the sorbent layer, φ_0. A fraction of preadsorbed water was displaced. In some experiments with benzene, the water vapor concentration after the carbon layer exceeded the initial H_2O concentration by 10—12%, and the concentration of perfluorotriethylamine was 3—5%. Then the process was stabilized, and the water vapor concentration after the sorbent layer became equal to φ_0. As in any experiment on the frontal adsorption dynamics, the concentration of the organic substance (C) after the sorbent layer increased to C_0. The amount of the organic substance adsorbed during the run (q_{ad}) was calculated from the output curve for this substance $C/C_0 = F(t)$. The amount of the displaced water (m_{dw}) was calculated from the area under the curve of the evolution of water vapor $\varphi/\varphi_0 = f(t)$ (down to the φ_0 straight line). The q_{ad} and m_{dw} values were estimated by weighing the dynamic tube before and after the run. The weight of the sorbent after the run coincided with the $m_{\text{sorb}} + m_{\text{w}} - m_{\text{dw}} + q_{\text{ad}}$ value within the limits of experimental error (10—15%).

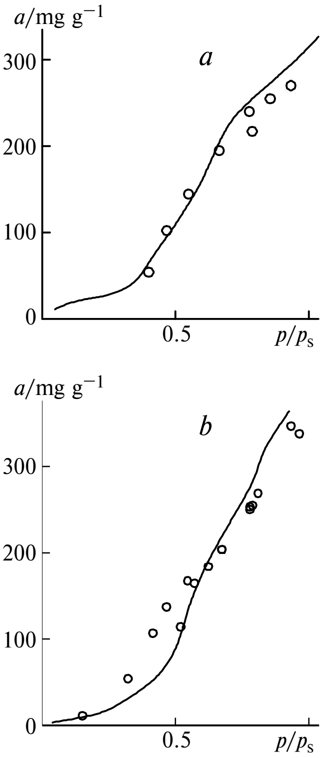

Fig. 1. Adsorption isotherms for pure water on sorbents CC (*a*) and AC (*b*) measured by the evacuation-weiging method. Points designate previous moistening of sorbents in the dynamic regime.

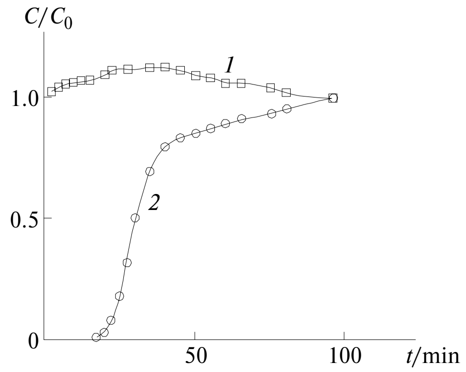

Fig. 2. Frontal output curves for dynamics of joint adsorption of water (*1*) and C_6H_6 (*2*). Conditions: $V = 1.1$ L min^{-1}, $C_0 = 4$ mg L^{-1}, $\varphi_0 = 75\%$.

Results and Discussion

When the concentrations of the organic substance and water in an air flow after the sorbent layer reach the C_0 and φ_0 values, respectively, an equilibrium between the water-organic mixture in the interpore space and in the adsorbed layer is likely established. The water adsorption on the sorbent under the conditions of equilibrium adsorption of the mixture at the C_0 and φ_0 (p/p_{s}) concentrations, respectively, was estimated from the $(m_{\text{w}} - m_{\text{dw}})/m_{\text{sorb}}$ ratio. The values of pure water adsorption were found in experiments on the preliminary moistening of samples.

The effect of water sorption on the adsorption isotherms for organic substances has been studied in detail previously.[3,4] Let us consider the effect of the organic substance adsorbed on the equilibrium adsorption of water on the microporous sorbent (Fig. 3).

A dotted line in the figures represents the adsorption isotherm for water on the sorbent under study. As can be

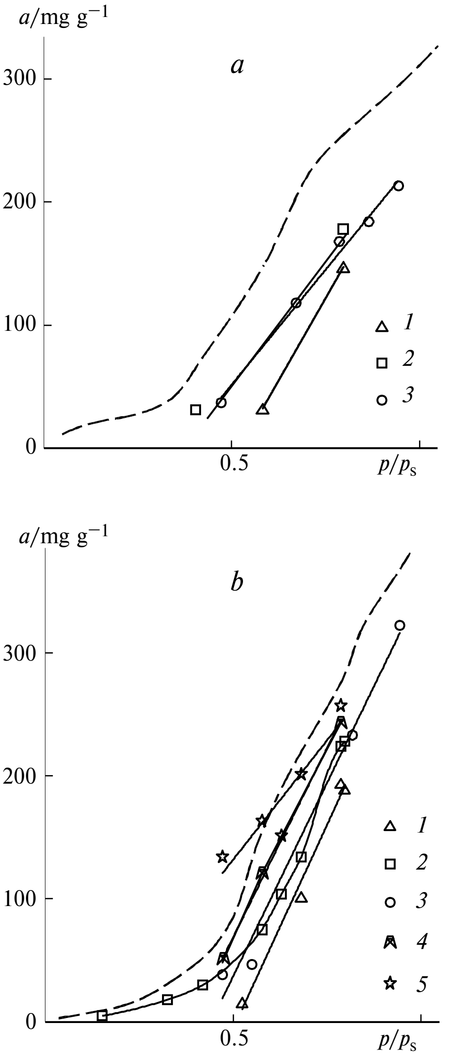

Fig. 3. Adsorption isotherms for water on sorbents CC (*a*) and AC (*b*) calculated from the results of dynamic experiments in the presence of *1*, benzene, *2*, cyclohexane, *3*, hexane, *4*, tetrachloromethane, and *5*, perfluorotripropylamine at C_0 = 4 mg L^{-1}. The dotted line is the AI for pure water.

seen in Fig. 3, *a*, the presence of adsorbed benzene, hexane, and cyclohexane affects substantially the water adsorption on sorbent CC. The water adsorption isotherms shift to the right relatively to that for pure water, and this manifests itself most clearly for water in the presence of benzene. Benzene partially displaces water from the adsorption volume. The adsorption isotherms for water in the presence of cyclohexane and hexane coincide within the limits of experimental error. These substances also displace preadsorbed water but to a lesser extent.

Similar results were obtained for sorbent AC (Fig. 3, *b*). The AI for water in the presence of benzene is most clearly shifted to the right with respect to the AI for pure water. The adsorption isotherms for water in the presence of cyclohexane and hexane also shift to the right and coincide in fact. The effect of tetrachloromethane adsorbed on the water adsorption is significantly less than that of benzene, cyclohexane, and hexane. Noteworthy, the perfluorotripropylamine adsorbed does not influence the water adsorption. The AI for pure water coincides in fact with that for water in the presence of this substance. The accuracy of the above calculations is at least 10%.

It has been shown earlier[1] that at relatively low concentrations of organic substances in a mixture with water vapor, these substances displace water from the adsorbent. In our experiments, this effect was not found for all the substances under study. Small amounts of perfluoropropylamine ($C/C_s = 2 \cdot 10^{-2}$) do not affect the water adsorption. The adsorption of perfluoropropylamine changes from 55 to 5% when p/p_s changes from 0.4 to 0.8. Meanwhile, one can suggest that the water adsorption will decrease with increasing the concentration of the substance vapor in a mixture.[1] This suggestion is confirmed by the findings of experiments on embedding the samples of sorbents with the preadsorbed water into liquid organic substances.[9,10] An excess organic substance can displace all preadsorbed water from the sorbent. This concerns primarily the substances with small molecules, for example, benzene. The molecules of the organic substance displace the preadsorbed water from the accessible volume of sorbent micropores. Not a whole volume of the sorbent micropores is accessible to larger molecules of perfluorotripropylamine, and a fraction of preadsorbed water remains in the sorbent upon its complete embedding into this substance.

A different effect of the organic substances on the water adsorption in our experiments can likely be explained by inequal accessibility of the adsorbent pores to the organic substances. The molecule size of the adsorbates used increases on going from benzene to perfluorotripropylamine. The smaller the molecule, the greater volume of micropores is accessible to this substance, and the the greater amount of water will be displaced by this organic substance from the adsorption volume. The water adsorption is nearly independent of the presence of the adsorbed molecules of tetrachloromethane and perfluorotripropylamine. Apparently, in our experiments the molecules of water and these organic substances adsorb in different micropores: water adsorbs in smaller micropores and the organic substance adsorbs in larger micropores.

The adsorption isotherms for vapor mixtures of water with organic substances can coincide with the AI for pure water. As a rule, this is found at small relative concentrations of the organic substance and is due to the fact that the water molecules adsorb in the pores inaccessible to the molecules of the organic substance. However, in most cases, the AI for water in a mixture with the organic substance deviate from the AI for pure water.

This work was financially supported by the Russian Foundation for Basic Research (Project No. 98-03-32397a).

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Received May 25, 2000;
in revised form November 15, 2000