Water adsorption on acetylene black carbon

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Abstract. Differential heat, isotherm, thermokinetics, and entropy of water adsorption on the black carbon were studied by the adsorption-calorimetric method at 303 K. The adsorption mechanism, type, and number of formed ion-molecular complexes were determined. Thermokinetics of adsorption on the black carbon and the law of migration of exchange cations were determined, and the adsorption energy of gases and vapors was calculated. The adsorption isotherm is described by the two- and three-dimensional mathematical equations of the volume-saturation theory of micro-pores (TVSM).

1 Introduction

Currently, several developed countries are researching the production of sorbents used in the purification and drying of natural gas and petroleum products. In particular, many scientific and practical innovations are being achieved in the production of effective sorbents, investigation of their adsorption and active properties, the carbon black of pores, determination of the number of active centers, strength and nature of the adsorption using the microcalorimetric device.

In the development of technology for obtaining adsorbents with high adsorption properties, it is necessary to solve the solutions of the following problems, including determination of the nanostructure of adsorbents and analysis of adsorption processes between them; study of the chemical structure of adsorbents using non-polar, polar and aromatic molecules; identification of functional groups in the sorbents, investigation of the thermodynamics of adsorption of ion-molecular complexes formed during adsorption.

On the base of black carbon, a broad group of materials, including graphite, coke, pyrocarbon, activated carbon and materials, alloy carbon materials, carbon fibers and composites, fibrous carbon, diamond, intercalated graphite, and glass carbon, were elaborated. The shift in scientific research from graphite, popular in the 1960s, coincided with relatively recently discovered carbon compounds - thermally expanded graphites, fullerenes, single-layer and multilayer carbon nanotubes, and graphene [1, 2], many of which are used as sorbents in the separation of molecules of different sizes including organic compounds. In addition, as a result of the replacement of active-focused functional groups within the structure, a form that is different in specificity is selected. Therefore there

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is a growing interest in studying the adsorption and catalytic properties of this type of carbon black. At the same time, small-sized carbon atoms increase the number of branched chain carbons due to the interconnection of long and thin channels in the structure and their intersections, resulting in a high number of micropores. In particular, the investigation of adsorption can explain the reason for such properties in the carbon black as hydrophobic-hydrophilic bifunctionality [3].

Carbon black crystallites as have consisted of 3-5 parallel hexagonal layers. Which slide high chaotically toward each other, forming a crystalized irregular three-dimensional structure k. In this case, they are called crystal lattice, two-dimensional synthesis, or turbostratic methods; that is, at this these layers are at a certain angle around the vertical axis [4].

Pyrolysis of hydrocarbons results in the formation of carbon black [5], which also formed during the combustion of hydrocarbon raw materials in furnaces at the temperature of $\sim 1400\ ^0C$ at limited air flow.

Carbon black is a widely used product with a special surface (1500 m^2/g) and porosity, and it is widely produced in the industry [6-8]. Carbon black is used as a conductive filler for various types of batteries and electrodes of condensate [9]. A carbon nanotube is a cylinder formed by a seamless layer of flat hexagonal graphite mesh. The upper ends of the tubes are covered with multi-layered hemispherical caps. Each of their layers consists of pentagons resembling six and a half of a fullerene molecule, which in a sense, is also reminiscent of part of its carbon black composition.

It is known [10] that carbon nanotubes can absorb both liquid and gaseous substances. Under the influence of external pressure or owing to capillary forces, the penetrating substances can be placed inside the tube, for example, liquids with surface tension less than 200 mn /m [10].

The energy of adsorption interactions is the sum of energies of specific (special-electrostatic polarization, dipole, and quadrupole interactions) and nonspecific (non-specific-dispersion) interactions. Adsorption of water vapors is energetically favorable only in the presence of hydrophilic groups (cations, OH-groups, Luce centers) in carbon black. Hydrocarbons are adsorbed nonspecifically; therefore, strong adsorption centers are not necessary for their adsorption. The main problem is studying the adsorption of various substances on carbon black, which depends on the functional groups present in carbon black: anions and cations. Because the distance between the adsorption centers is large, carbon black is very suitable as a model for investigating adsorption properties [10] of substances of different natures.

2 Methods

In JSC "Navoiyazot", in the process of obtaining acetylene by pyrolysis methane at 1500 ^0C, a large amount of carbon black (technical carbon) is formed. The interaction of carbon molecules with modified and active functional centers and channels of carbon black, which is a secondary product, has been studied. The modified carbon black was obtained from the secondary raw material - carbon black, by processing under special conditions. Based on it, adsorbents with different functional groups having high adsorption activity were obtained. Experiments were carried out on an adsorption-microcalorimetric device at a high vacuum to study the adsorption parameters. Before the experiment, the sample was heated for 10 h at 773K under a vacuum at 10–4 Pa before the pumped state [10]. Adsorption heat and isotherm parameters were calculated at 303 K.

3 Results and discussion

At 303K, the differential heat and isotherm parameters of water adsorption on carbon black were calculated [10]. From these values, the differential mole entropy of adsorption was derived. Adsorption on the black carbon consists of 6 steps; in the case of the modified carbon, it consists of 2 steps. At each step, stoichiometric compatibility between the active centers of the carbon black and the water vapors can be seen. The result of chemical analysis showed that each functional group in the modified carbon black corresponds to different proportions of water molecules, in which the general formula of each elementary cell was calculated, i.e., $(OH^- : 1H_2O)_{1,35}$; $(CO^-:2H_2O)_{3,25}$; $(COO^-:3H_2O)_{4,36}$. These figures indicate that water adsorption in the carboxyl groups was greater than in the other groups. Thus, an average number of 20.93 water molecules adsorbed on the total groups in the elementary cell was equal to 20.93 and an average of 6.97 - per group. Also, the formation of complex clusters was found explained by the strong basic properties of the carboxyl group.

As mentioned above (Figure 1), there are 6 steps in the adsorption heat graph; in the first step, water molecules with an active center are 100% adsorbed to form triaqua complexes. As the activity of the cations located in the active center increases, their adsorption rate also increases. However, small adsorption levels are observed in unmodified carbon black due to the almost complete absence of functional groups. For example, it was determined that 0.5 mmol / g of water molecules interact with a small number of active centers and a carbon frame. The degree of adsorption is also related to the hydrophilic properties of carbon black. Synthetic carbon black has a higher hydrophilicity level than most natural compounds, i.e., $1.5<X$. In carbon black, the initial isothermal point rises slightly due to the induction of the active centers in it, mainly by carboxyl, carbonyl, hydroxyl, and other hydrophilic groups, by the flow of electrons in different amounts of water molecules. This indicates that the centers tend to form aqua complexes due to carbon black adsorption, having a large number of functional groups which are strong centers for adsorption. In addition, the sharp rise of the isotherm, the formation of adsorbate-adsorbent systems in carbon pores, has reflected such interaction.
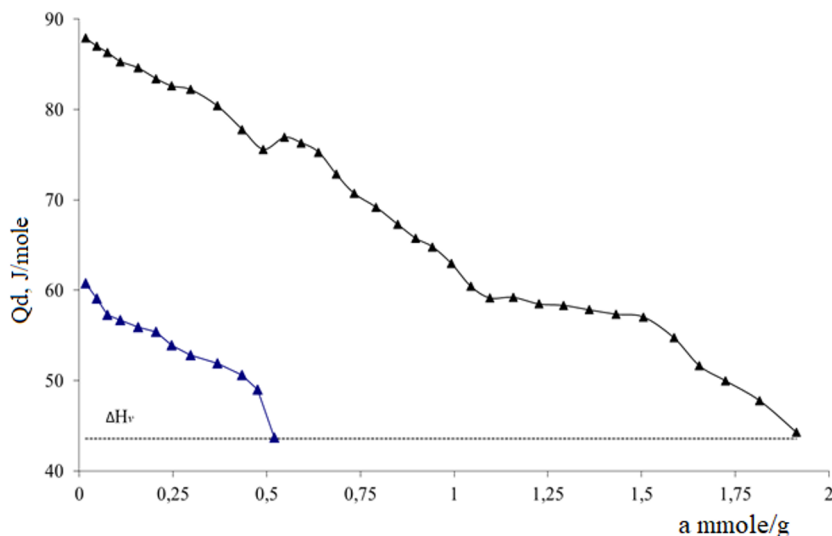
Fig. 1. Differential heat values of water vapor adsorption on ▲ - modified carbon black and ▲ - unmodified carbon black samples at 303 K.

The isothermal parameters of the adsorption processes in the small-scale region of the modified adsorbent were compared using the equation.

The adsorption isotherm of water was characterized by the three-dimensional equation of the theory of volumetric saturation of micropores (TVSM).

According to which the basic equation for investigating adsorption processes can be presented by the following equation:

$$a = a_0 \cdot \exp\{-[A/E]^n\} \tag{1}$$

where "a" is the adsorption amount in mmol / g; a_0 is the detected adsorption in mmol/g, A = PTln (R / Ro) is the amount of 1 mole of gas (kJ / mol), E is the characteristic energy of the adsorbent (kJ / mol); parameter related to the carbon black of the porous area n-adsorbent. The adsorption isotherm of water in on modified adsorbent is described by the three-dimensional equation of TVSM:

$$a = 0.82 \exp[-(A/22.94)^5]+0.365 \exp[-(A/14.36)^3]+0.117 \exp[-(A/2.4)^1] \tag{2}$$

The adsorption isotherm of water on unmodified adsorbent is described by the three-dimensional equation of TVSM:

$$a = 0.148 \cdot e^{-\left(\frac{A}{14.18}\right)^2} + 0.074 \cdot e^{-\left(\frac{A}{5.26}\right)^2} + 0.078 \cdot e^{-\left(\frac{A}{0.99}\right)^1} \tag{3}$$

where:

$$a = a_{01} \exp[-(A/E_{01})^{n_1}] + a_{02} \exp[-(A/E_{02})^{n_2}] + a_{03} \exp[-(A/E_{03})^{n_3}]$$

and : a01 = 0.148 mmol / g, E01 = 14.18 kDj / mol i n1 = 2; for the second member a02 = 0.074 mmol / g, E02 = 5.26 kDj / mol and n2 = 2; the third member values a03 = 0.078 mmol / g, E02 = 0.99 kDj / mol, and n3 = 1. It is shown that adsorption is almost not observed in the microstructure within the secondary structure.
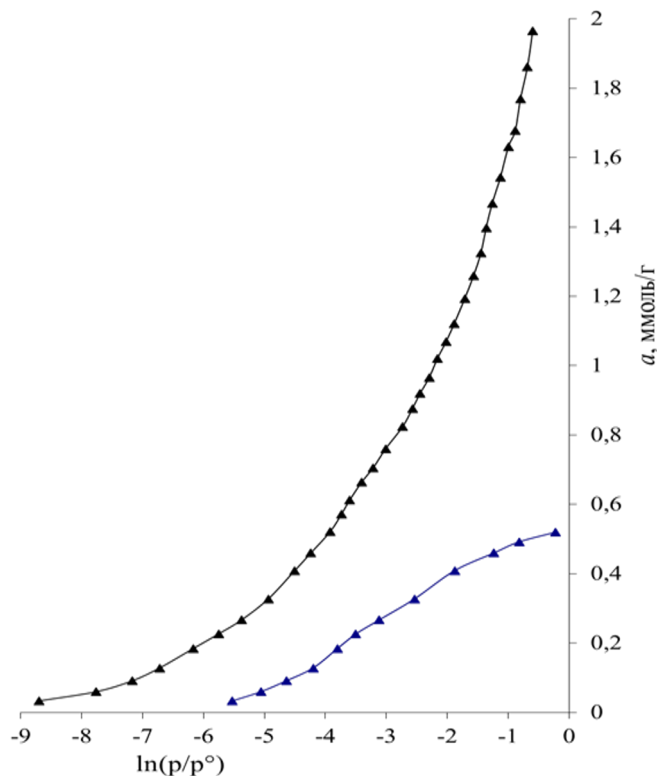
Fig. 2. Isothermal values of water vapor adsorption on ▲ -modified and
▲ - unmodified samples at 303 K

From Figure 3, it is shown that the molar differential entropy of water adsorption has increased from -220 to 0 J / mol · K, i.e., from a minimum to a sharply higher value, as mentioned above. ion-molecular mono-, di- and tri-aquacomplex formation Molar differential entropy of water adsorption ΔSd Isotherms according to the Gibbs-Helmholtz equation and adsorption differential heat are calculated on the base of the following equation:

$$\Delta S_a = \frac{\Delta H - \Delta G}{T} = \frac{-(Q_a - \lambda) + A}{T} \qquad (4)$$

where λ is the condensation heat, ΔH and ΔG are the enthalpies of adsorption in the standard state, and the change in free energy. The mean integral values of entropy are correspondingly lower than the liquid value - 47.19 J / mol K. Thus, differential and integral entropies have indicated the state of motion of each adsorbed water on carbon black.
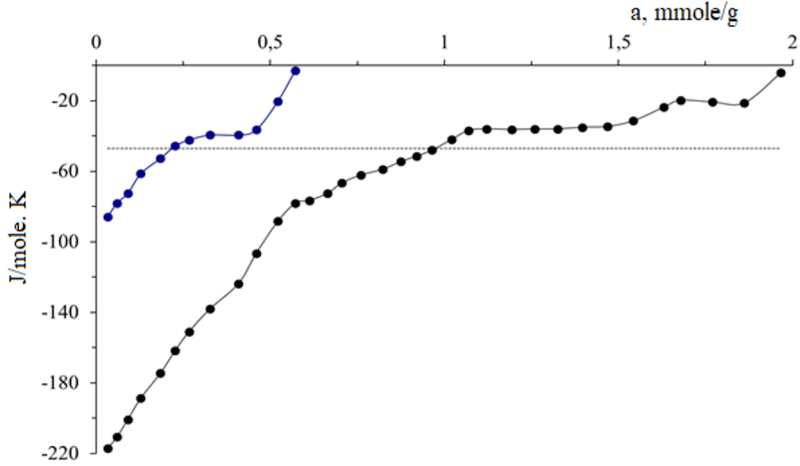
Fig.3. Entropy of water vapors adsorption at 303 k: ▲ -modified structure, ▲-unmodified structure samples. Dashed lines are the mean integral entropy values.

Therefore, the entropy curve is below the entropy of liquid water, indicating that the entropy changes from a liquid state to water vapors as the saturation rate has increased.

In modified carbon black, the equilibrium of adsorption at the intersections of water molecules in the initial pores is very slow, then accelerates. At the same time, the equilibrium time is reduced from 11 5.6 h, to 1.1 and a half h (Fig. 4). In the initial time of adsorption, a long time is necessary for the water molecules to bond firmly with the active centers. In the later stages, the time between cation (3-4 h) and adsorbate-adsorbate bonds between water molecules is less (1-2 h). The reduction of the adsorption equilibrium time to ~ 30 min in the final stage is explained by the fact that they remain in the vapor state due to the interaction of fully adsorbed molecules with non-adsorbed molecules in the adsorption volume.
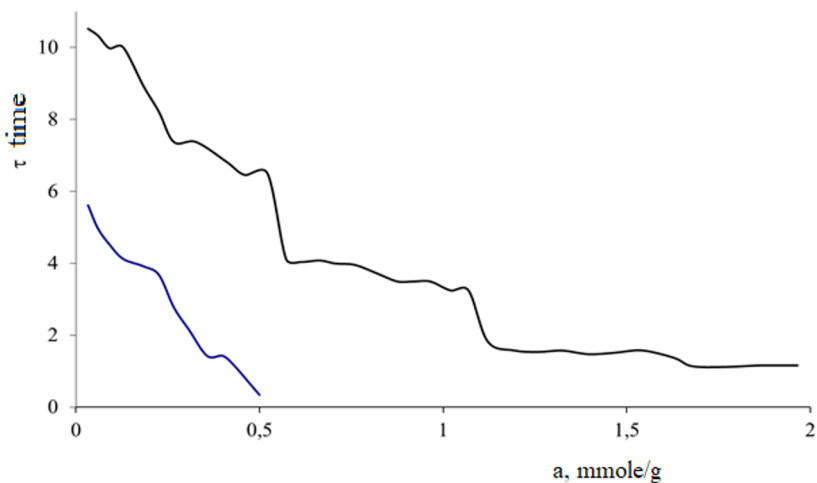
Fig. 4. Thermokinetics of water vapor adsorption on ▲ -modified structure, ▲-unmodified structure samples at 303 K

4 Conclusions

Investigating the adsorption energy of gases allows understanding the laws and practically complex processes that occur in the adsorbent at absorption of various adsorbents, as well as to identify, systematize and standardize the most important thermodynamic properties of heterogeneous systems.

Data by the adsorption isotherms and thermodynamic properties (ΔH, ΔG, and ΔS) of H_2O on carbon black are presented; the adsorption heat of the studied systems with small fillings was determined stepwise, and the adsorption properties were determined. Molecular mechanisms of water adsorption and interrelationships between adsorption-energy properties were determined. Due to the groups in the active centers, water adsorption on the modified carbon black was almost four times higher than on the unmodified form. The differential heat of adsorption was in the form of a curvilinear step, and in all experiments, it was found that the adsorption was carried out stepped. Water molecules are immobile in carbon black pores, motionless, i.e., in the solid state entropy. It was shown that adsorption has carried out very slowly in the primary micropores. On the base, the adsorption of water molecules, the hydrophilic properties, and the incrementality of carbon black were proved.

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