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The Composition and Thermodynamic Properties of Pyrolytic Carbon Black

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Abstract The secondary product of acetylene production from methane pyrolysis was purified from soluble salts and oxides by acidic, alkaline and thermal treatment of carbon black, processing. Differential heat, isotherm, thermokinetics and entropy of benzene adsorption in acetylene black carbon were studied using the adsorption-calorimetric method at a temperature of 303 K. The mechanism of adsorption of molecules and the type and number of formed ion-molecular complexes were determined. The adsorption isotherm was characterized by a three-dimensional mathematical equation of the volumetric saturation theory of micro-pores from the initial field to the saturation field.

Keywords Pyrolysis process, Structure, Acid, Acetylene, Solubility, Isotherm, Adsorption heat, Entropy, Thermokinetics, Ion-molecular complexes, Benzene, Adsorption calorimeter

1. Introduction

The acetylene carbon black occupies a special place among other structures. The carbon black has high electrical conductivity and a secondary structure. Its particles are connected to each other by strong branched chains.

Not only is the high electrical conductivity of the carbon black but also its secondary structure is important. In terms of its activity, the acetylene carbon black is close to the P-1250 furnace gas carbon black. Carbon black is produced on an industrial scale and is also produced in large quantities as a by-product in the process of high-temperature processing of carbon sources. Used in the manufacture of rubber, various cables, ebonite, and insulating materials [1]. It is also used in the adsorption treatment of aqueous solutions, in medicine as a drug to prevent poisoning, and as a fuel source. The composition of the carbon black especially its properties varies, and its properties depend on the process of formation of the carbon black, the initial raw material, technological processes and temperature. In addition to carbon, carbon black also contains some other elements, including hydrogen and oxygen, which form a strong bond with the individual atoms of carbon. On average, for every fifteenth atom of carbon, there is one atom of hydrogen. Oxygen is bound to the outer atoms of carbon by strong chemical bonds [2]. Although the properties of the carbon black have been sufficiently studied, the mechanisms of interaction in its application have not been studied.

The growing importance of carbon materials in several chemical processes is due to the importance of these materials in their use as adsorbents and catalysts. The surface area, porosity, chemical inertness, and presence of oxygen in carbon materials affect not only the adsorption properties but also the catalytic activity and selectivity of the catalyst [3]. The mechanism of phenol adsorption in microporous carbon adsorbents and non-carbon samples has been studied and shown to be similar to the benzene adsorption mechanism [4-5]. The use of different types of carbon adsorbents in gas chromatography (activated carbon, carbon molecular sieves, graphitized carbon adsorbents, etc.) is analyzed and their general surface properties, methods of preparation, modification, and application are studied.

2. Materials and Methods

The secondary product of acetylene extraction from methane pyrolysis is carbon black. It was treated with hydrochloric acid of different concentrations at different time intervals and the solubility of the resulting product was determined. Determination of the composition of samples of raw materials and purified products under acidic conditions was carried out using a scanning electron microscope SEM - EVO MA 10. The literature contains information on the adsorption of benzene in various carbon black, which were obtained by various physicochemical research methods [9]. The adsorption energy and mechanism of benzene as a sorbent in the processed carbon black have not been studied. Adsorption of benzene at a temperature of 303 K was studied

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in the carbon black (a). Differential heat values of adsorption (kJ) were determined using a high-precision adsorption-calorimeter device [10]. The device is a high vacuum-resistant glass device equipped with a micro burette and symbol transmissions. It consists of an adsorbent ampoule, a measuring part, a storage system, a gas and liquid collector and a vacuum system. The high-precision differential microcalorimeter DAK 1-1A was used in the study. Initially, the sample was heated under vacuum at 10^{-4} Pa for 10 h, in the closed state at 1023 K. The experiment was performed on an adsorption-calorimetric device [11]. Adsorption heat and isotherm values were calculated at 303 K.

3. Results and Discussion

The composition of acetylene carbon black was analysed for macro- and microelements by optical emission spectrometry. The results of the analysis are presented in Table 1.

Table 1. Elemental analysis of dry ash of acetylene carbon black

Element	Mg/l	Element	Mg/l	Element	Mg/l
Mn	0.366	Co	0.265	Sn	0.014
Cr	0.002	Ni	91.62	Sb	0
As	3.157	Cu	2.67	Pb	0.053
Mg	13.56	Zn	0.145	Hg	0.115
Na	17.96	Al	22.94	V	0.029
Li	0.031	B	0.392	Ba	0.201
K	3.77	P	10.43	Mo	0.071
Ca	55.31	S	0.074	Cd	0
Fe	102.3	Se	0	Ag	0.006

In the composition of the solution formed as a result of hydrochloric acid treatment, macro- and microelements were also determined by optical emission spectrometric method. The results of the analysis are presented in Table 2.

Table 2. Composition of the solution after treatment

Element	Mg/l	Element	Mg/l	Element	Mg/l
Mn	0.182	Co	1.017	Sn	0
Cr	0.013	Ni	0.016	Sb	0
As	0	Cu	0.009	Pb	0.0004
Mg	2.062	Zn	0.528	Hg	0.011
Na	3.07	Al	4.663	V	0.023
Li	0.008	B	0.047	Ba	0.051
K	1.628	P	0.793	Mo	0
Ca	39.67	S	0.416	Cd	0.026
Fe	14.26	Se	0	Ag	0

Analysis of the results showed the presence of metal salts, soluble and insoluble in hydrochloric acid. The sol level of carbon black was determined relative to ASTM D 1506 and its value was 15.8%. The effect of acid concentration on acid black treatment on carbon black quality was determined. The results obtained are presented in Table 3.

The process took 1 hour. The analysis of the results shows that the sol of the treated carbon black decreases from 15.8 to 0.5% as the hydrochloric acid concentration increases in the range of 1-30%.

Increasing the acid concentration by 34% (concentrated) has virtually no effect on the sol of level. Hence, the optimum concentration of hydrochloric acid in the acid treatment of carbon black is 30%. Under these conditions, the carbon black of sol of rate reached to be 0.5%. So, the sol level of the studied institution is high and is considered unsuitable for use as an additive in the rubber industry. To improve its quality, acid processing is required.

Morphological examination of the surface of carbon black samples was performed using a scanning electron microscope. In general, a sharp decrease in the level of sol of was observed in acidic treatment when 15% acid was used for 1 hour.

Table 3. Hydrochloric acid to the degree of sol of the carbon black effect of concentration

S. n	Sample mass (g)	HCl concentration (%)	The amount of HCl (ml)	Processing time (hours)	The mass of the sample left after heating (g)	degree of sol (%)
1	1.9715	-	-	-	0.3114	15,8
2	2.0154	1	50	1	0.2035	10.1
3	1.9642	3	50	1	0.1001	5.1
4	2.0028	5	50	1	0.0921	4.6
5	1.9345	7	50	1	0.0675	3.4
6	2.3033	10	50	1	0.0612	2.6
7	1.9982	15	50	1	0.0302	1.5
8	1.9504	20	50	1	0.0121	0.6
9	2.2540	30	50	1	0.0108	0.5
10	2.3921	34	50	1	0.0109	0.5

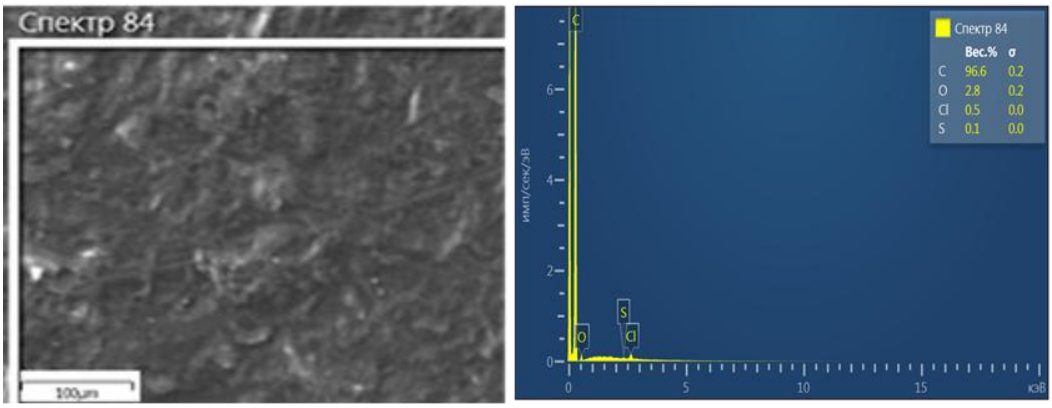

Figure 1. SEM image and analysis of carbon black sample: a) Image of carbon black processed in 15% acid; b) The elemental composition of the carbon black treated with 15% acid

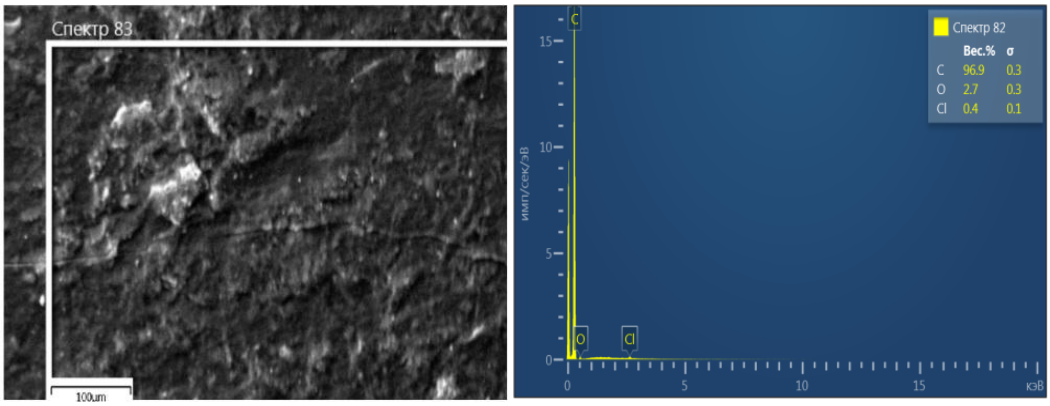

Figure 2. SEM image and analysis of carbon black sample: a) Image of carbon black processed in 20% acid; b) The elemental composition of the carbon black treated with 20% acid

Table 4. Composition of the residual mass of carbon black heating process

Appearance of the sample	Mineral composition
odorless,, powder of red color	Total: 15.8%, including: 7.9% SiO_2, 2.7% Al_2O_3, 2.3%, Fe_2O_3, 1.9% CaO, 0.6% MgO, 0.4%Na_2O,

Analysis of the results shows that when a carbon black sample treated with 15% hydrochloric acid is examined under a scanning electron microscope, it has a porous structure. SEM analysis showed that the composition of carbon black is 96.6% carbon, 2.8% oxygen, 0.5% chlorine, and 0.1% sulphur (Fig.1.b). A sharp decrease in the level of sol was observed in acidic treatment when 20 % acid was used for 1 hour [12-14].

A carbon black sample treated with 20% hydrochloric acid has a higher degree of porosity than a sample treated with 15% hydrochloric acid. SEM analysis showed that the composition of carbon black is 96.9% carbon, 2.7% oxygen, 0.4% chlorine (Fig.2.b).

The differential heat of benzene adsorption studied in carbon black is shown in Figure 3. In the initially adsorbed modified and unmodified carbon black, the benzene adsorption temperatures ranged from 70 kJ/mol to 63 kJ/mol at 0.55 mmol/g, respectively; At 1.43 mmol/g it decreased from 63 kJ/mol to 44 kJ/mol. Then the adsorption in both carbon black was 0.56 and 8.12 mmol/g; At 1.43 and 4.2, 2 clearly visible phases are formed: the first is adsorbed at a heat value of ~60 and ~46 kJ/mol, and the second at a heat value of ~51 and ~44 kJ/mol.

In the final stage of adsorption (8.43 and 4.2 mmol/g), the heat is reduced to the heat of condensation (up to 35.9 kJ/mol). In the first high-energy phase, the active centres with benzene form π-complexes, and the localization of the formed complexes are observed at the intersections of micro-pores of appropriate size. Subsequently, adsorption takes place in the vertical (second stage) and horizontal (third stage) structural pores of carbon black, because in terms of the level of adsorption heat they correspond to the adsorption heat of benzene in these pores. In the third stage, with another molecule of benzene, the rest of the active centre's form π-complexes in the form of sandwiches, which are located along the width of the pores.

The decrease in the adsorption heat value along the curve during the transition from high energy to low energy indicates the adsorption of one benzene molecule into two functional groups. The adsorption heat going up in the pores in the perpendicular position is high in both sections. The high differential heat of adsorption indicates the formation of p-complexes (C_6H_6/(functional group)) in cations containing carbon black. In the second section, the formation of

C_6H_6/(functional group) complexes through the p-bond in adsorption also goes through the pores. After benzene is adsorbed in the pores, carbon black is adsorbed in very small amounts in the form of adsorbate-adsorbate in the pores. As the porosity increases, the differential heat value of benzene adsorption gradually decreases. In carbon black, the mechanisms of benzene adsorption isotherms from the initial state to saturation were studied (Fig. 4). The isotherm is characterized by graphical coordinate axes and the amount of adsorption (a, mmol/g). Adsorption isotherms initially start at 0.01-0.02 mmol/g, with an isotherm value of 9.9-8.3 ln (P/Ps). With small changes, the isothermal lines gradually rise. These changes in the isothermal lines are explained by the adsorption of carbon black into pores of different structures. No migration of functional groups into the connecting cavity was observed in the pores in the vertical and horizontal positions, ion-molecular complexes are formed in the pores of carbon black. Adsorption isotherms were described using the three-dimensional saturation theory of volumetric saturation. The mobility of benzene is reduced in carbon black pores. In this way, the adsorption mechanisms from the initial saturation to the final saturation were studied.

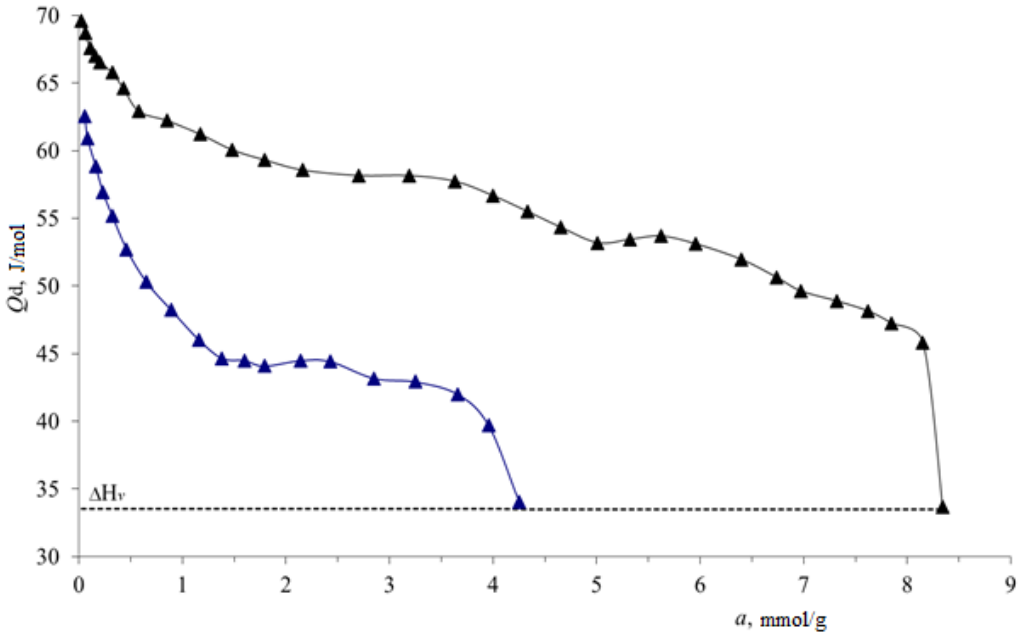

Figure 3. Differential heat values (Qd) of benzene adsorption are given in ▲ -modified carbon black, ▲ -unmodified carbon black samples at 303 K. Barcodes Condensation value of benzene at 303 K

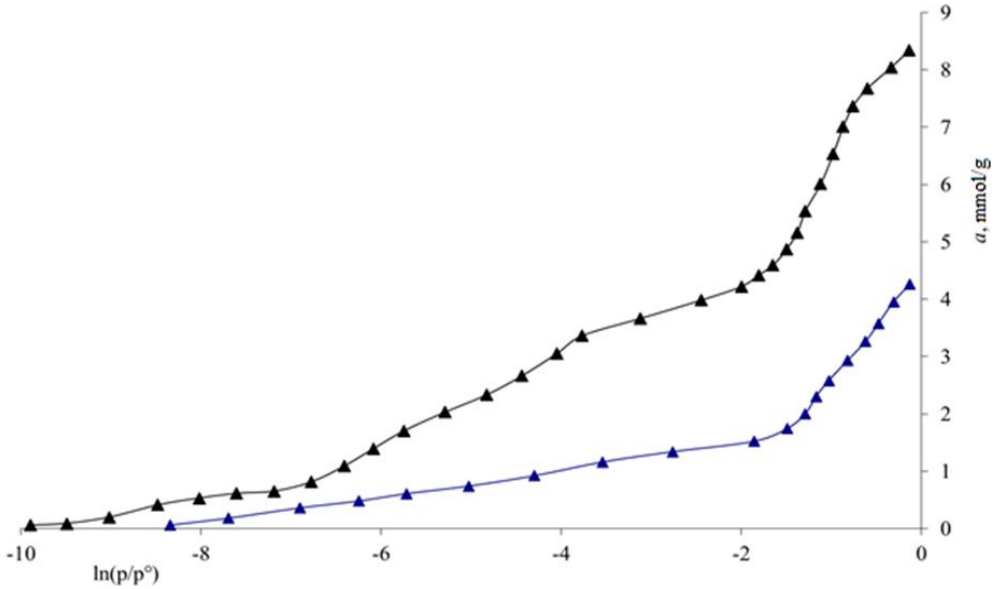

Figure 4. Adsorption values of benzene vapour adsorption in ▲ -modified carbon black and ▲ -unmodified carbon black samples at 303 K are given in ln (P/P0)

The isotherm of benzene adsorption in modified carbon black is explained by Dubin's theory by the three-membered equation of MHTN [9,10]:

$$a = 2,55exp\left[-\left(A/44,58\right)^{8}\right] + 5,25exp\left[-\left(A/19,2\right)^{6}\right] + 0,69exp\left[-\left(A/10,87\right)^{2}\right]$$

Where a is adsorption (mol/g), A = RTln (P/P) is the work done to bring 1 mole of gas (at pressure P) to the surface in equilibrium in the gas phase (pressure R). The adsorption isotherm of unmodified carbon black benzene is described by the three-dimensional equation of MHTN.

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

These values are: a01 = 1.8 mmol/g, E01 = 14.1 KJ/mol and n1 = 7; for the second member a02 = 2.1 mmol/g, E02 = 15.26 KJ/mol and n2 = 12; the third member values a03 = 0.28 mmol/g, E02 = 8.99 KJ/mol, and n3 = 3. It can be seen that adsorption in the microstructure is almost non-existent in the secondary structure.

The adsorption differential entropy was calculated using the Gibbs-Helmholtz equation using the isotherm and differential heat value. Figure 5 shows that in the initial cases, the unmodified carbon black adsorption values range from 0.043 mmol/g to 4.25 mmol/g, and the entropy values range from -12-19 J/mol ·K to -18-0 J/mol ·K.

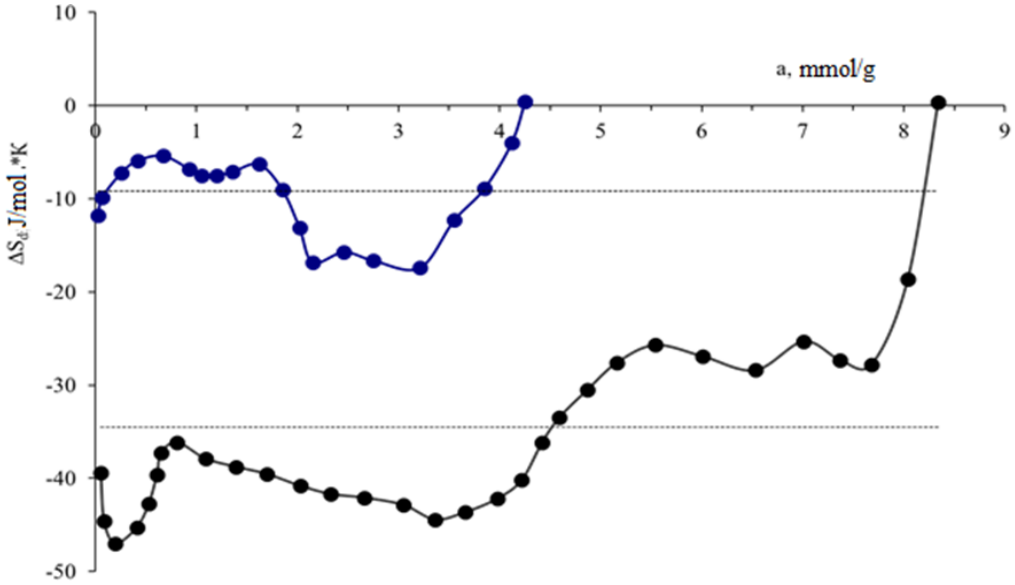

Figure 5. ● - modified at 303 K and ● - entropy of adsorption of benzene vapours on unmodified carbon black samples. Barcodes give an average integral entropy value

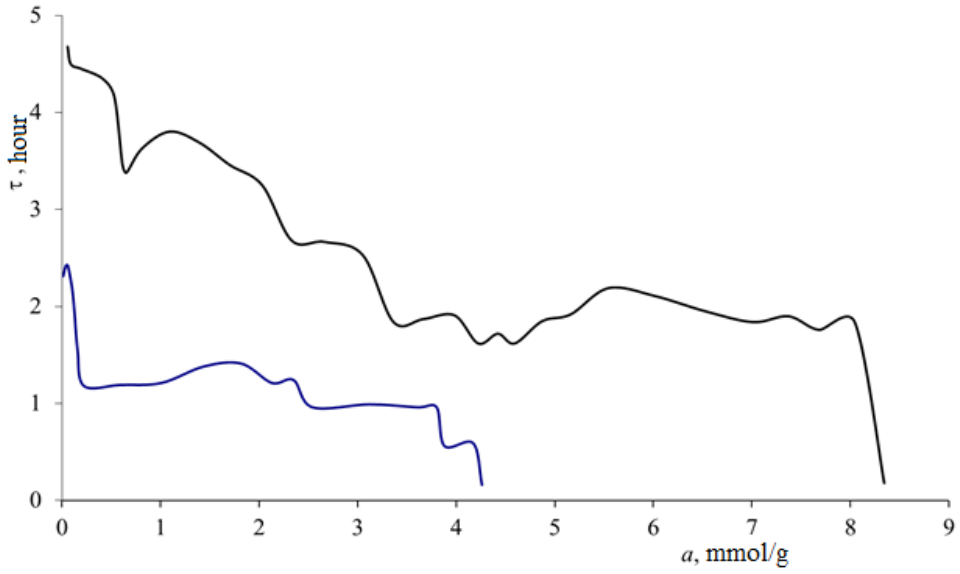

Figure 6. Kinetics of adsorption of benzene vapours in modified (-) and unmodified carbon black (-) samples at 303 K

In the modified carbon black, the adsorption values range from 0.29 mmol/g to 8.43 mmol/g, and the entropy values range from -38-47 J/mol ·K to -28-0 J/mol ·K. An increase in adsorption entropy indicates strong sorption of one benzene molecule into two robust functional groups at the intersection of pores. The molar differential entropy of benzene adsorption in carbon blacks has a wavy difference from liquid benzene entropy. At low saturation, differential entropy is formed as a result of the adsorbate-adsorbate interaction. The final minimum value on the differential entropy curve of benzene indicates the strong location of benzene molecules in the carbon black pores and their intersections. The time set to achieve adsorption equilibrium is in the form of a small wavy and stepped curve (Fig. 6). The equilibrium time of adsorption is initially large, gradually decreasing to equilibrium time, and is a few minutes at the end of the process.

In the initial cases, saturation lasts from 2.4-4.6 hours to 1-2 hours. In this case, the amount of adsorption is in the range of 0.04-0.3 mmol/g to 2.52-4.6 mmol/g. The high equilibrium time is explained by the formation of π-complexes that occur at high energies with groups of active centres of initially adsorbed benzene molecules. Adsorption equilibrium time continues after ~ 2-4 hours in the vertical and horizontal pores of carbon black [14].

4. Conclusions

As a result of acid treatment of carbon black, its quality has improved, and the level of sol has been reduced. The effect of hydrochloric acid concentration on the sol of level was determined and the process conditions were optimized. When treated in a 30% solution of hydrochloric acid for 4-5 hours, the sol of the carbon black was reduced from 15.8% to 1.88%.

The adsorption heat stepwise and adsorption properties of the systems studied with low saturation were determined. Molecular mechanisms of adsorption of benzene on carbon black, and interrelationships between adsorption-energy characteristics were determined. Adsorption of benzene molecules to the active centres of carbon black has been shown to proceed with the formation of p-complexes. Adsorbed benzene molecules are in a stationary state, i.e., in the solid state entropy. A correlation was observed between the thermodynamic characteristics of the studied systems.

Based on the calculated and experimental data, it can be said that the adsorption of benzene in carbon black consists of the localization of benzene molecules with a sandwich-like character in the active centre, in the pores and around it.

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REFERENCES

[1] Kholkina, T.V., Nikiforov, I.A., Chirkova, E.M. and Sevostyanov, V.P., 2011. A new method for the synthesis of nanosized carbon black. Bulletin of the Saratov State Technical University, 4(1 (59)), pp.126-129.

[2] Zuev V.P., Mikhailov V.V. 1970. Carbon black production. Moscow. Chemistry, pp.120-124.

[3] Rodríguez-Reinoso, F. 1998. The role of carbon materials in heterogeneous catalysis. Carbon. 36(3). pp. 159-175.

[4] Grishchenko, L., Bezugla, T., Zaderko, A., Vakaliuk, A., Mischanchuk, O., Novychenko, N., Cheremenko, A. and Diyuk, V., 2019. Catalysts of acid-base process on the basis of the modified carbon fiber. Ukrainian Chemistry Journal, 85(7), pp.38-48. doi: 10.33609/0041-6045.85.7.2019.38-48.

[5] Khokhlova, T.D. and Thi, H.L., 2007. Adsorption of dyes on active carbons and graphitized thermal soot T.D. Moscow University Bulletin. Series 2. Chemistry, 48(3), pp.157-161.

[6] Timoshchuk, I.V., Golubeva, N.S., Krasnova, T.A. and Tumanova, T.A., 2010. The study of the state of the surface of active carbons after the adsorption of phenol and formaldehyde. Ecology and industry of Russia, (10), pp.58-59.

[7] Leboda, R., Łodyga, A. and Gierak, A., 1997. Carbon adsorbents as materials for chromatography I. Gas chromatography. Materials chemistry and physics, *51*(3), pp.216-232. doi:10.1016/S0254-0584(97)80310-0.

[8] Kudryashov, S.Yu., Pavlov, M.Yu., Kopytin, K.A. and Onuchak, L.A., 2010. Adsorption of organic compounds on graphitized carbon blacks modified with monolayers of polar anisometric molecules. Liquid crystals and their practical use, (1), pp.68-78.

[9] Kopytin, K.A., Bykov, E.S., Onuchak, L.A., Kudryashov, S.Yu., Kuvshinova, S.A. and Burmistrov, V.A., 2015. Thermodynamics of the adsorption of organic compounds from the gas phase on a monolayer of a liquid crystal formed on the surface of a carbon adsorbent. Journal of Physical Chemistry, 89(4), pp.688-693.

[10] Yakubov Y. Yu. 2021. Energetics of adsorption of molecules with different structures on synthetic zeolites. Izv. Disser. Ph.D., pp. 15-46.

[11] Kurbanov, S.D., 2010. Energy adsorption of water and aromatic molecules and defective and non-defective zeolitax

type ZSM-5: Dis... kand. chem. nauk (Doctoral dissertation, --T., IONX An RUz). pp. 10-35.

[12] Khudoinazarov F., Nurmonov S. 2021. Physicochemical analysis of acetylene compound. Scientific journal of the National University of Uzbekistan named after Mirzo Ulugbek. 3/1/1. Tashkent, pp. 336-38.

[13] Khudoynazarov. F.S., Nurmonov. S.E., Mirkhamitova. D.Kh. 2021. Improving the quality of natural gas pyrolysis products. Journal of Oil and Gas of Uzbekistan. No. 4. pp. 33-39.

[14] Khudoynazarov, F.S.U., Nurmonov, S.E. and Yakubov, Y.Yu., 2022. Composition and thermodynamic properties of pyrolysis soot. Universum: Chemistry and Biology, (6-3(96)), pp.24-27. doi: 10.32743/UniChem.2022.96.6.13846.