Investigation of energetic heterogeneity of carbon black surfaces during adsorption of chromatographically low concentrations of *n*-pentane

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Energetic heterogeneity of different types of industrial carbons was studied by gas-adsorption chromatography in regions of low surface coverages. The main thermodynamic characteristics of *n*-pentane adsorption on the carbon black surfaces were experimentally determined under the conditions close to the zero coverage of the surface ("Henry region"). These characteristics include the Henry constants, differential molar heats of adsorption, changes in the entropy of adsorption, and differences in molar heat capacities of the adsorbate in the adsorbed state and its vapors at a constant pressure. The specific features of the geometric structure and ratio of surface regions different in the adsorption energy make it possible to establish the presence of the "Henry region" in the adsorption isotherm. The gas-chromatographic criteria, which can be used to estimate the degree of energetic heterogeneity of the adsorbent surface, were considered.

Key words: gas-adsorption chromatography, "Henry region," thermodynamic characteristics of adsorption, Henry constant, specific surface, carbon black, energetic heterogeneity of surface, graphitization, *n*-pentane.

One of the most important applications of gas-adsorption chromatography (GAC) is the study of the adsorption properties of the solid surfaces.[1—5] Presently, GAC was successful in analyzing the thermodynamics of adsorption in GAC [1—3] and its relation to the main parameters of chromatographic retention and specific features characterizing the structure of the variety of adsorbents different in the composition and surface properties (from graphitized carbons to zeolites).[1—9] In addition, GAC allows one to operate with the infinitely low concentrations of the adsorbate in the gas phase and to perform adsorption measurements in the regions close to the zero surface coverage. This is especially significant for the calculation of the adsorption equilibrium constant, *viz.*, Henry constant.[1,3,10—12] However, few works on the use of GAC in the investigation of the properties of energetically heterogeneous adsorbents have been published so far.[1,4,6,7,13] Many other adsorption methods allow only extrapolation of the experimental plots obtained (in particular, adsorption isotherms[1,3,4]) to the infinitely low (zero) coverage of the surface. Unlike these methods, inverse gas chromatography at infinite dilution (IGC-ID)[14] makes it possible to directly study the adsorption properties and characteristics of surface regions with the highest degree of heterogeneity. The fraction of these regions is low, as a rule, but their contribution to the adsorption properties of the total surface is very significant, especially at the infinitely low adsorbate concentrations. It is known[4,5,13,15] that the data on the adsorbent heterogeneity obtained, for example, by the GAC method at high adsorbate concentrations in the gas phase (IGC-FD) differ strongly from analogous characteristics determined at low surface coverages.[15] This makes difficult the estimation of the "true" surface heterogeneity by different variants of gas chromatography (IGC-ID or IGC-FD),[15] thus restricting the use of the dynamic adsorption methods in similar studies.

Different types of carbons, which are widely used in industry as packing of polymeric materials and dying pigments,[1,6,16—19] are interesting objects for studying the surface heterogeneity.

The purpose of this work is to study the energetic heterogeneity of the surface of different types of ungraphitized and graphitized carbons by analysis of the thermodynamic characteristics of adsorption (TCA) of *n*-pentane experimentally found at the adsorbate concentrations close to the zero surface coverage. In addition, it seemed of interest to find convenient gas-chromatographic criteria for the estimation of the energetic heterogeneity of carbons, which allow the use of the rapid and highly sensitive GAC method during routine adsorption measurements.

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Experimental

Measurements were carried out on a Vega 6000 gas chromatograph (Carlo Erba) with a flame-ionization detector using helium as the carrier gas. *n*-Pentane (Aldrich, for HPLC) was used as the adsorbate. Pentane was injected into the chromatographic column from the gas phase at room temperature using a microsyringe (sample volume 1 μL). Methane was the non-sorbing gas. The interval of operating temperatures of the thermostat in the chromatograph was varied depending on a specific carbon black sample. The temperature of the evaporator exceeded the corresponding value of the column thermostat by 20 °C. Carbons different in the morphological parameters from the set kindly presented by the Degussa Co. were used as adsorbents. Ungraphitized carbon black samples were subjected to preliminary extraction using various solvents (toluene, 36 h; MeOH—H_2O (1 : 1) mixture, 36 h). Solvent residues were removed in a tubular muffle furnace in a nitrogen flow at 200 °C. After this procedure, the carbon black samples were shaken for several hours until fairly stable ball-like aggregates were formed that were subsequently sieved were sifted out to obtain narrow (by particle size) adsorbent fractions. The temperature of glass columns packed with carbon black particles 0.4 mm in diameter was maintained before use in a carrier gas flow at 220—250 °C for 5—6 h. The main characteristics of the carbon blacks studied in the work are presented in Table 1.

The primary experimental chromatographic data were statistically processed and the main TCA were calculated according to known procedures.[21] The designations of TCA proposed in previously published works[10—12] were used. The error of the gas-chromatographic experiment did not exceed 5%. The Henry constant values ($K_{1,c}$/cm^3 m^{-2}), which at infinitely low surface coverages are equal to the specific retention volume of the studied compound per surface area unit of the adsorbent surface ($V_{A,1}$/cm^3 m^{-2}), were calculated using the expression

$$V_{A,1} = (t_R - t_M)jF_{P_i,T_a}P_iT_c/(m_AS_{N_2}P_aT_a), \qquad (1)$$

where t_R and t_M are the retention times of the adsorbate and non-sorbing substance (min), respectively; j is the James—Martin coefficient that takes into account the compressibility of the carrier gas; P_i is the pressure of the carrier gas at the inlet of the column (atm); P_a is the atmospheric pressure (atm); T_a is the room temperature (K); T_c is the column temperature (K); F_{P_i,T_a} is the flow rate of the carrier gas at the pressure P_i and temperature T_a (cm^3 min^{-1}); S_{N_2} is the specific surface of the adsorbent measured by the statistical volumetric method from the amount of nitrogen adsorbed at 77 K (m^2 g^{-1}); m_A is the weight of the adsorbent in the column (g). The values of the specific carbon black surface (S_{N_2}/m^2 g^{-1}) necessary for the calculation of the $K_{1,c}$ values were taken from the literature.[20]

Table 1. Initial characteristics of the carbon black samples studied

Carbon black	Sample	S_{N_2} /m^2 g^{-1}	d^a /nm	$D_S{}^b$
N115	**1**	143	11—19	2.61
	1_g^{c}	115		—
N326	**2**	78	26—30	2.55
	2_g^{c}	66		2.31
N660	**3**	37	49—60	2.58
	3_g^{c}	32		2.33
GTC	**4**	12	400—500	2.15^d

[a] Standard average diameter of carbon black particles.

[b] Roughness factor.

[c] Graphitized carbon black sample.

[d] The D_S value for GTC was accepted the same as that for graphite.[20]

Various approximations[1,3,10—12,22,23] based on the relations of the logarithm of the constant of adsorption equilibrium to the inverse temperature were used for the determination of the molar differential heats and changes in adsorption entropies. The temperature relations of $\bar{q}_{\mathrm{dif},1}$ and $\Delta(\bar{S}^{\circ}{}_{1,c})^s$ was neglected ($\Delta\bar{C}^s{}_{1,p} = 0$) in the first approximation, and the functional dependence $\ln V_{A,1} = f(T^{-1})$ was approximated by the straight line

$$\ln V_{A,1} = \frac{\Delta(\bar{S}^{\circ}_{1,c})^s + R}{R} + \frac{\bar{q}_{\mathrm{dif},1}}{RT} \approx A_1 + \frac{B_1}{T}. \qquad (2)$$

In the second approximation, the second derivative $K_{1,c}$ with respect to temperature was taken into account ($\Delta\bar{C}^s{}_{1,p} \neq 0$), and the corresponding temperature dependence was approximated by the modified expression

$$\begin{aligned}\ln V_{A,1} = {} & \frac{\Delta(\bar{S}^{\circ}_{1,c})^s - \Delta\bar{C}^s_{1,p}(\ln\hat{T} + 1) - R\ln\hat{T}}{R} + \\ & + \frac{\bar{q}_{\mathrm{dif},1} + R\hat{T} + \Delta\bar{C}^s_{1,p}\hat{T}}{RT} + \frac{\Delta\bar{C}^s_{1,p} + R}{R}\ln T \approx \\ & \approx A_2 + B_2/T + C\ln T, \end{aligned} \qquad (3)$$

where $\Delta\bar{C}^s{}_{1,p}$ is the difference between the differential thermal capacity of the substance in the adsorbed state ($\bar{C}_{\mathrm{ads}}$) and the molar heat capacity of the substance in the gas phase at p = const ($C_{\mathrm{gas},p}$); R is the universal gas constant equal to 8.315 J mol^{-1} K^{-1}; $\hat{T}$ is the temperature corresponding to the middle of the temperature interval studied (K). The initial values of the specific retention volumes for *n*-pentane on GTC were taken from the previously published work.[23] Based on these data, we calculated the TCA using formulas (2) and (3). The experimental error of determination of the $\bar{q}_{\mathrm{dif},1}$ and $\Delta(\bar{S}^{\circ}{}_{1,c})^s$ values was ±1 kJ mol^{-1} and ±4.5 J mol^{-1} K^{-1}, respectively.

The TCA values obtained in this work for the studied carbon black samples are presented in Tables 2 and 3.

Results and Discussion

From the earliest attempts to use GAC to investigate properties and structures of different adsorbents, a special interest was given to the measurements of specific retention volumes in the so-called "Henry region" to which Henry´s law applies

$$\Gamma \approx K_{1,c}c, \qquad (4)$$

where Γ is the amount of the Gibbs adsorption of a specific substance (μmol m^{-2}), c is the equilibrium concentration of adsorbate vapor in the gas phase (μmol cm^{-3}), and $K_{1,c}$ is the constant of adsorption equilibrium or the Henry constant (cm^3 m^{-2}).

Table 2. Comparison of the thermodynamic characteristics of *n*-pentane adsorption on different carbons*

Carbon black	T	$\hat{T}$	$\ln V_{A,1}(\hat{T})$	$\ln V_{A,1} = A_1 + B_1/T$		$\ln V_{A,1} = A_2 + B_2/T + C\ln T$		
	K			$\bar{q}_{dif,1}$ /kJ mol^{-1}	$-\Delta(\bar{S}^\circ_{1,c})^s$ /J mol^{-1} K^{-1}	$\bar{q}_{dif,1}$ /kJ mol^{-1}	$-\Delta(\bar{S}^\circ_{1,c})^s$ J mol^{-1} K^{-1}	$\Delta\bar{C}^s_{1,p}$ J mol^{-1} K^{-1}
1	363—503	438	0.974	58.3	132.1	55.4	126.6	237
	363—503	438	0.657	45.4	105.8	43.4	102.0	160
$\mathbf{1_g}$	363—503	438	0.581	41.9	98.6	40.5	95.9	114
1**	363—503	438	0.448	38.0	91.0	35.6	85.8	107
2	363—483	423	0.488	47.3	115.1	46.1	115.0	201
	363—483	423	0.388	42.0	103.8	41.3	105.0	117
$\mathbf{2_g}$	363—483	423	0.281	38.4	96.2	37.8	95.3	95
2**	363—483	423	0.146	34.0	87.0	33.6	86.3	71
3	323—453	388	0.710	38.0	99.2	37.6	96.5	167
	323—453	388	0.608	33.9	90.1	33.9	92.8	98
$\mathbf{3_g}$	323—453	388	0.527	31.5	84.8	31.2	82.1	79
3**	323—463	388	0.294	27.9	77.4	27.8	79.1	62
4***	343—414	375	−0.140	32.9	97.2	32.8	97.1	37

* The values for region I are presented in the numerator, and those for region II are in the denominator.

** Non-extracted carbon black sample.

*** See Ref. 23.

The authors of several works[1,2,10,24] have established the chromatographic criteria of the existence of the "Henry region" based, first of all, on the symmetric character of chromatographic peaks and independence of the specific retention volume of the amount of the sample injected into the column. Assuming that under these conditions the adsorption equilibrium is established in the chromatographic column and the specific retention volumes are equal to the Henry constant $K_{1,c}$, the authors[1,3,10—12] developed the rigid thermodynamics of adsorption and proposed the theory of adsorption based on the molecular statistics,[1,24] which allows the simulation of complicated adsorption processes of molecules of many organic compounds on the energetically quasi-homogeneous surfaces of GTC and zeolites. At the same time, published data contain several evident contradictions related, first of all, to the procedure of gas-chromatographic measurements in the "Henry region" and the correct description of the obtained adsorption data in the framework of the adsorption model considered.

A decrease in the adsorbate concentration in the gas phase to infinite values should favor the achievement of the "Henry region" in the adsorption isotherm. However, as shown in several works for the graphitized carbon blacks with the sufficiently homogeneous surface, effects related to the residual heterogeneity of the surface are observed at very low surface coverages. This residual surface heterogeneity is characterized, as a rule, by an enhanced adsorption potential. In addition, each heterogeneous region is characterized by its adsorption equilibrium constant and, hence, its intrinsic "Henry region." [1,3,24,25] Strictly speaking, the very initial interval of the adsorption isotherm corresponding to adsorption in the surface regions with the highest adsorption energy should be considered as the "Henry region" and, therefore, this region does not reflect the properties of the whole surface.

Thus, a question arises concerning the principal possibility of the experimental determination of the Henry constant (as a physically substantiated, fundamental thermodynamic characteristic of the "Henry region") for heterogeneous surfaces. In several works,[19,26,27] the determination of $K_{1,c}$ for energetically heterogeneous adsorbents considered to be admissible although disputable.[26,28—31].

These problems are of interest for analysis of experimental data obtained by inverse GAC at infinitely low adsorbate concentrations in the gas phase (IGC-ID). Evidently, for low surface coverages the Henry constants are independent of the concentration of the adsorbate introduced into the column and, hence, they are reproducible in the series of independent chromatographic measurements. This very important condition often is not fulfilled, and some authors[14] question the possibility of using this GC variant for the correct estimation of the energetic heterogeneity of the surface. At the same time, it is the GAC in the "Henry region" and in the adjacent regions of the adsorption isotherm that provides the best technique for studying the adsorption properties and nature of the areas with the highest degree of heterogeneity. most heterogeneous surface regions. The contribution of these areas to the total adsorption energy at high coverages can be aligned noticeably and become comparable with the error of chromatographic measurements.

In the case of heterogeneous surfaces, the experimental determination of $K_{1,c}$ is very difficult, because the Γ

Table 3. The $\ln K_{1,c}$ and $\ln V_{A,1}$ values for *n*-pentane adsorption on different carbons in the temperature intervals studied

T/K	$\ln K_{1,c}$ (I)*	$\ln V_{A,1}$ (II)*	$\ln K_{1,c}$**	$\ln K_{1,c}$***
		Carbon black N115 (**1**)		
363	4.70	3.55	3.21	2.75
373	4.00	3.00	2.72	2.29
383	3.4	2.55	2.32	1.99
393	2.91	2.12	1.91	1.68
403	2.39	1.74	1.59	1.35
413	1.96	1.39	1.26	1.08
423	1.54	1.08	1.00	0.81
433	1.17	0.81	0.73	0.56
443	0.81	0.55	0.47	0.31
453	0.52	0.33	0.25	0.13
463	0.23	0.08	0.03	−0.06
473	−0.11	−0.17	−0.21	−0.25
483	−0.33	−0.38	−0.40	−0.38
493	−0.54	−0.56	−0.58	−0.59
503	−0.69	−0.71	−0.72	−0.72
		Carbon black N326 (**2**)		
363	3.01	2.55	2.23	1.83
373	2.44	2.07	1.81	1.50
383	1.93	1.64	1.43	1.21
393	1.54	1.30	1.14	0.92
403	1.17	1.03	0.84	0.63
413	0.83	0.69	0.56	0.39
423	0.54	0.42	0.31	0.15
433	0.21	0.13	0.04	−0.09
443	−0.09	−0.16	−0.19	−0.30
453	−0.34	−0.35	−0.42	−0.48
463	−0.55	−0.57	−0.61	−0.63
473	−0.76	−0.78	−0.78	−0.79
483	−0.92	−0.93	−0.93	−0.94
		Carbon black N660 (**3**)		
333	3.00	2.51	2.24	1.79
343	2.35	2.10	1.89	1.52
353	1.91	1.67	1.50	1.19
363	1.54	1.34	1.19	0.94
373	1.14	1.05	0.89	0.63
383	0.89	0.73	0.67	0.41
393	0.58	0.44	0.39	0.19
403	0.33	0.25	0.16	−0.03
413	0.09	0.05	−0.03	−0.22
423	−0.15	−0.20	−0.25	−0.40
433	−0.39	−0.40	−0.44	−0.58
443	−0.60	−0.61	−0.62	−0.70
453	−0.76	−0.77	−0.78	−0.83

* For the extracted carbon black samples.

** For the graphitized carbon black samples.

*** For the non-extracted carbon black samples.

and *c* values formally obeying the Henry´s law lie in the very narrow concentration interval.

The chromatographic peaks obtained for the adsorption of low concentrations of *n*-pentane on the ungraphitized and graphitized carbon black samples N326 (samples **2** and $\mathbf{2_g}$, respectively) are presented in Fig. 1. The retention time remains constant and the shape of the chromatographic peaks retain its nearly symmetrical form (see Fig. 1, *a*) with an increase in the *n*-pentane concentration in the gas phase over sample $\mathbf{2_g}$. This indicates the achievement of the "Henry region" ($V_{A,1} \equiv K_{1,c}$). In the case of the ungraphitized sample (see Fig. 1, *b*), the retention time decreases monotonically and the chromatographic peaks become asymmetrical with increase in the adsorbate concentration in the gas phase.

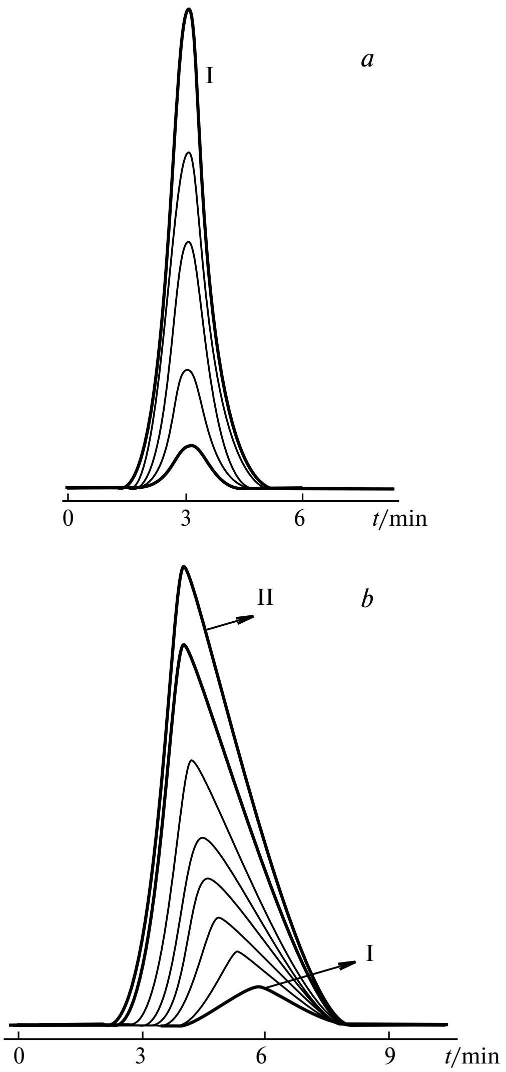

Fig. 1. Chromatograms of *n*-pentane obtained at different low concentrations of the adsorbate in the gas phase (sample volume 0.1—5.0 μL) on graphitized (*a*) and extracted ungraphitized carbon black N326 (*b*) at 413 K.

There are some regions inside which the adsorbate concentration low enough to produce the most symmetrical peaks. Formally this is an indication that measurements are carried out directly in the "Henry region" of the heterogeneous surface. Such a region referred to as region I (see Fig. 1, *a*). Note that an increase in the concentration leads to a gradual decrease in the difference between the retention times of the peaks obtained on the ungraphitized samples and, as a result, it also can be accepted constant within the error of chromatographic measurements. The region of adsorbate concentrations corresponding to such chromatographic peaks is referred to as region II (see Fig. 1, *b*). The TCA values for the peaks in region II are fairly close to the TCA values for the corresponding graphitized carbon black sample. Analogous regularities were established for other carbons studied. The retention times of *n*-pentane corresponding to chromatographic peaks I and II were used for the further calculation of the main TCA by formulas (2) and (3) (see Tables 2 and 3).

For graphitized sample $\mathbf{2_g}$, unlike ungraphitized sample **2**, an increase in the adsorbate concentration in the gas phase does not distort the shape of the chromatographic peak, which allows one to equate the $V_{A,1}$ values, calculated from these elution characteristics, with the $K_{1,c}$ constant. On the contrary, for the ungraphitized carbon black sample, a decrease in the retention time is accompanied by diffusion of the initial region of the chromatographic peak with an increase in the adsorbate concentration in the gas phase. The latter confirms the above assumption on much more narrow concentration intervals of the "Henry region" on the heterogeneous surfaces.

Thus, to calculate $K_{1,c}$ for the ungraphitized carbon black samples, the t_R values corresponding to the smallest and accordingly most symmetrical chromatographic peaks should be used.

The plots of $\ln V_{A,1}$ *vs.* T^{-1} obtained at different low *n*-pentane concentrations in the gas phase are presented in Fig. 2, *a*. It is seen that at a given temperature the ungraphitized carbon black samples are characterized by a certain interval of $V_{A,1}$, and the maximum values of $V_{A,1}$ are the Henry constants $K_{1,c}$. The width of this interval of $V_{A,1}$, probably, reflects quantitatively the degree of energetic heterogeneity of the surface considered at a certain temperature, Thus, for case I, the $V_{A,1}$ values can be considered as the Henry constants ($V_{A,1} \equiv K_{1,c}$), and for case II they are the sum of different $K_{1,c}$ values, which depends, as a whole, on the adsorbate concentration in the gas phase (*i.e.*, surface coverage θ). Therefore, it is incorrect to designate the latter by symbol $K_{1,c}$.

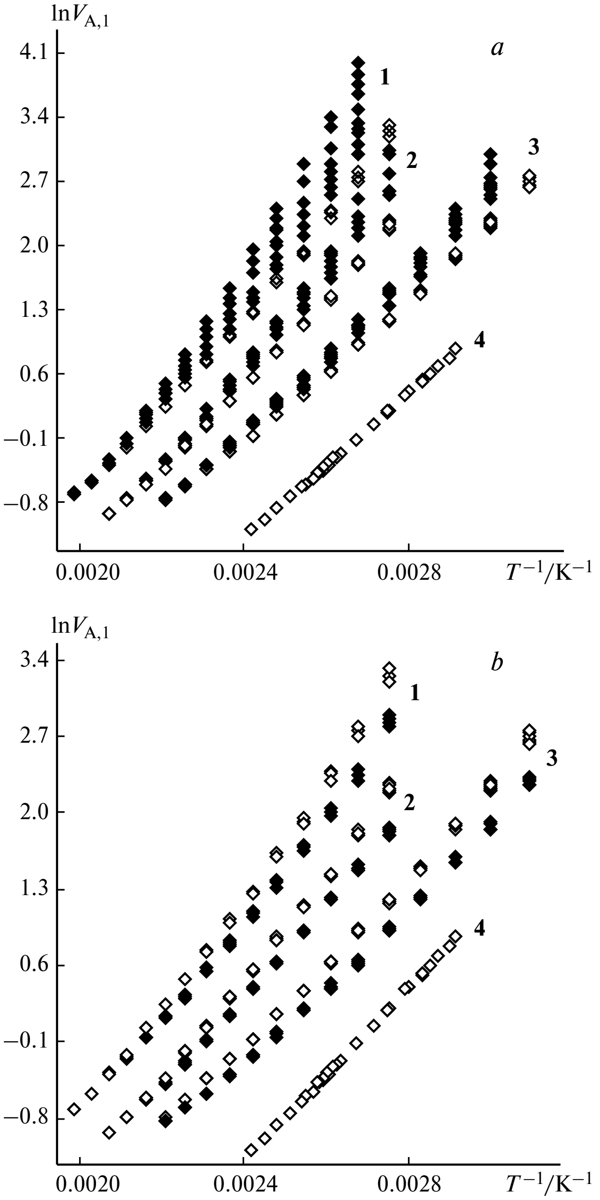

Fig. 2. Plots of $\ln V_{A,1}$ *vs.* T^{-1} for *n*-pentane on the studied carbon black samples N115 (**1**), N326 (**2**), N660 (**3**), and GTC (**4**): *a*, carbon black after extraction; *b*, untreated carbons (without extraction). Black points correspond to ungraphitized carbons, and light points indicate the corresponding graphitized carbon black samples.

It is known that the adsorption properties of carbons are significantly affected by the particle (crystallites) size of the adsorbent. Evidently, the relatively small particles are characterized by a high content of the edge fragments with an enhanced (compared to that of the basic face) adsorption potential.[1,4] The graphitization of carbons N326 (sample **2**) and N115 (sample **1**) in the 1500—2500 °C temperature region decreases, most likely, the phase heterogeneity of the surface (reduces the fraction of the amorphous component and enhances a relative ordering of crystallites). This leads also to the removal of chemical impurities from the surface but only insignificantly affects a decrease in the specific surface, which is determined, as a whole, by the crystallite size. The main distinction between the graphitized samples of the carbons under study is the difference between the geometrical sizes of the graphite crystallites formed that makes up the main portion of the surface of the graphitized carbon black This assumption is favored, in particular, by the high (compared to those of GTC) S_{N_2} values for carbons $\mathbf{1_g}$, $\mathbf{2_g}$, and $\mathbf{3_g}$ (see Table 1). The latter results in the situation when at a sufficiently high phase heterogeneity of the surface the TAC values, for example, for $\mathbf{1_g}$, are much higher than the TAC on the carbons, whose surface is formed of larger crystallites. Evidently, the mutual arrangement of the $\ln V_{A,1}$—T^{-1} curves can be explained similarly (see Fig. 2, *a*).

The intense growth of the crystallite size is known to be observed at higher temperatures (2500—3000 °C) and a prolonged graphitization time. It is seen from the data in Table 1 that the decrease in the S_{N2} value upon graphitization also depends on the particle size of the starting carbon black: the smaller the particle size of the starting carbon black, the stronger the decrease in the surface value upon graphitization. The energetic heterogeneity of the surface decreases in the same sequence.[6,20] It is likely that graphitization results in the removal of the highest-energy regions of the surface.

Let us compare the $K_{1,c}$ values for the starting and graphitized carbon black samples obtained at a fixed temperature (Table 4). The $\Delta\ln K_{1,c}$ value decreases monotonically on going from samples **1** and $\mathbf{1_g}$ to samples **3** and $\mathbf{3_g}$. The difference between the $\Delta\ln K_{1,c}$ values is strongly temperature-dependent and in the high-temperature region becomes comparable with the error of the GC experiment. Probably, when the temperature increases, the barriers, which should be surmounted by adsorbed molecules during migration along the surface, decrease, and the adsorption becomes delocalized, which is characteristic of energetically quasi-homogeneous surfaces. In fact, the temperature increase results in a decrease in the difference between the $V_{A,1}$ values in cases I and II for the ungraphitized surface, which indicates a decrease in the difference in the adsorption energies in different heterogeneous surface regions. In addition, as should be expected, the chromatographic peaks become more symmetrical and narrow with the temperature increase. As a result, the $\Delta\ln K_{1,c}$ value at a fixed temperature provides quantitative conclusions about the energetic heterogeneity of the surface in the series of adsorbents with a similar chemical nature. The diagram, which makes it possible to compare the $\Delta\ln K_{1,c}$ value for different types of carbons in a sufficiently broad interval of the studied temperatures, is presented in Fig. 3. Thus, the graphitized carbon black samples can serve as standards for comparison of adsorbents with different energetic heterogeneities but close average particle sizes.

The $\bar{q}_{\text{dif},1}$ and $\Delta(\bar{S}^{\circ}_{1,c})^{s}$ values calculated by Eqs. (2) and (3) are presented in Table 2. Comparison of the corresponding TCA values for different carbon black samples shows that in a sufficiently broad temperature interval expression (3) more reliably describes the plot of $\ln V_{A,1}$ *vs.* inverse temperature, because it allows the calculation of the $\Delta\bar{C}^{s}_{1,p}$ values, which directly indicate the differences in the energy states of the adsorbate molecules in the gas phase and on the adsorbent surface. These differences make it possible to better understand the molecular pattern and character of interactions of adsorbed molecules with the heterogeneous surface regions different in energy and to estimate thus the energetic heterogeneity of the surface under study. In addition, the deviations of the $\ln V_{A,1} = f(T^{-1})$ curves observed in Fig. 2 from linear

Table 4. The $\Delta\ln K_{1,c}\cdot 10^2$ values for *n*-pentane equal to the difference between the $\ln K_{1,c}$ values for the ungraphitized and corresponding graphitized carbon black samples **1—3** at different temperatures

T/K*	$\Delta\ln K_{1,c}\cdot 10^2$		
	N115 (**1**)	N326 (**2**)	N660 (**3**)
333	—	—	0.76
343	—	—	0.46
353	—	—	0.41
363	1.49	0.78	0.35
373	1.28	0.63	0.25
383	1.08	0.50	0.22
393	1.00	0.40	0.19
403	0.80	0.33	0.17
413	0.70	0.27	0.14
423	0.54	0.23	0.10
433	0.44	0.17	0.05
443	0.34	0.10	0.02
453	0.27	0.08	0.01
463	0.20	0.06	—
473	0.10	0.02	—
483	0.07	0.01	—
493	0.04	—	—
503	0.03	—	—

* The interval of working temperatures used for plotting the diagram in Fig. 3 is emphasized by bold.

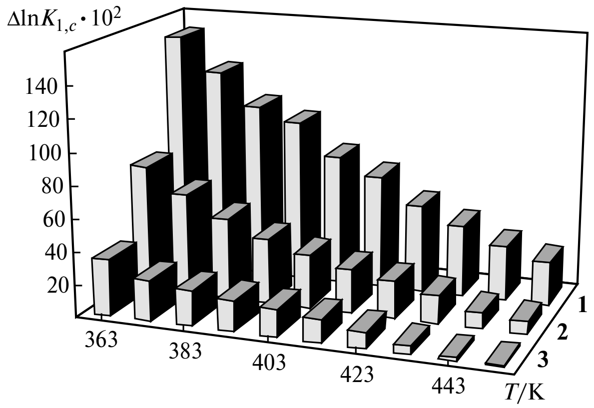

Fig. 3. Comparison of the $\Delta\ln K_{1,c}\cdot 10^2$ values calculated from the difference between the $\ln K_{1,c}$ values for the ungraphitized and graphitized carbon black samples N115 (**1**), N326 (**2**), and N660 (**3**).

dependence (2) also indicate the higher reliability of the TCA calculated by Eq. (3). The use of Eq. (3) provides the approximation of the experimental $\ln V_{A,1}$ values with a higher accuracy, because the $\Delta\bar{C}^{s}{}_{1,p}$ differences reflecting the deviation from a straight line are very high. The TCA values calculated by formula (2) are noticeably higher (especially for samples with small-size particles) than the corresponding values based on the temperature plots of $\bar{q}_{\mathrm{dif},1}$ and $\Delta(\bar{S}^{\circ}{}_{1,c})^{s}$. The TCA values, usually obtained by the GAC method for the estimation of the energetic heterogeneity of the surface in sufficiently broad temperature intervals, are approximated by a linear dependence,[17] which is not likely always reasonable. The TCA values determined in this work for ungraphitized carbon black samples **2** and **3** are close to the data for the carbons with the similar surface morphology.[17] It is seen from the data in Table 2 that carbon black **1** is characterized by the highest TCA values, and the $\bar{q}_{\mathrm{dif},1}$ and $\Delta(\bar{S}^{\circ}{}_{1,c})^{s}$ values approach the analogous parameters for GTC as the particle size increases. The difference in the $\bar{q}_{\mathrm{dif},1}$ values, which characterize regions I and II, also indicates the energetic heterogeneity of the surface of the starting carbons. As can be seen from the comparison of the corresponding values, the $\bar{q}_{\mathrm{dif},1}$ value obtained at the ultimately low adsorbate concentrations in the gas phase (region I) is much higher than $\bar{q}_{\mathrm{dif},1}$ for concentration region II. This agrees with the fact that the $\bar{q}_{\mathrm{dif},1}$ value on the heterogeneous surfaces usually decreases monotonically with an increase in the θ coverage, gradually approaching the heat of condensation, which corresponds to the gradual transition from coverage of the surface regions with higher adsorption energies to the regions with the lower surface energy. The decrease in the heat of adsorption with the coverage indicates the heterogeneous character of the surface of the adsorbent studied, because on the homogeneous surfaces the $\bar{q}_{\mathrm{dif},1}$ values increase with an increase in θ.[1,4] The $\bar{q}_{\mathrm{dif},1}$ values for *n*-pentane change from 31.2 kJ mol^{-1} (for sample $\mathbf{3_g}$) to 55.4 kJ mol^{-1} (sample **1**). This substantial difference suggests that $\bar{q}_{\mathrm{dif},1}$ is highly sensitive to the energetic heterogeneity of the surface. The difference in the $\bar{q}_{\mathrm{dif},1}$ values for the ungraphitized and graphitized samples decreases with an increase in the particle size of the adsorbent, indicating a lower energetic heterogeneity of carbons with larger crystallites.

Similar regularities are observed in the series of $\Delta(\bar{S}^{\circ}{}_{1,c})^{s}$ values. On comparing the changes in the differential molar entropy of adsorption $\Delta(\bar{S}^{\circ}{}_{1,c})^{s}$ for the same adsorbate, which were obtained in the approximately equal temperature intervals on different adsorbents, a qualitative conclusion about the relative mobility of adsorbed molecules can be drawn.[10] The lower the $\Delta(\bar{S}^{\circ}{}_{1,c})^{s}$ value, the lower the mobility of the molecules on this adsorbent. It follows from our data that the ungraphitized carbon black samples are always characterized by lower $\Delta(\bar{S}^{\circ}{}_{1,c})^{s}$ compared to those of the graphitized samples. It is most likely that the energetic heterogeneity of the ungraphitized samples imparts the more localized character to adsorption. It can be assumed that the increase in $\Delta(\bar{S}^{\circ}{}_{1,c})^{s}$ on the heterogeneous surfaces is related, in the general case, to the change in translational motions by rotational or vibrational motions relatively to the surface. The $\Delta(\bar{S}^{\circ}{}_{1,c})^{s}$ value is significantly affected by the surface roughness (D_S), whose values decrease noticeably upon the graphitization of the starting carbon black sample (see Table 1). Thus, the $\bar{q}_{\mathrm{dif},1}$ and $\Delta(\bar{S}^{\circ}{}_{1,c})^{s}$ values, as well as $K_{1,c}$, allow the estimation of the energetic heterogeneity of the surface.

Let us consider $\Delta\bar{C}^{s}{}_{1,p}$ (see Table 2) calculated from the approximated plots of $\ln V_{A,1}$ *vs.* T^{-1} by Eq. (3). For all carbon black samples studied, the $\Delta\bar{C}^{s}{}_{1,p}$ values are several times larger than $\Delta\bar{C}^{s}{}_{1,p}$ for GTC with the specific surface equal to 11.7 m^2 g^{-1}. Since the molar thermal capacity of *n*-pentane in the gas phase ($C_{\mathrm{gas},p}$) is constant for our adsorbents, the increase in $\Delta\bar{C}^{s}{}_{1,p}$ on going from GTC (sample **4**) to carbon black **1** (see Table 2) is directly related to an increase in the differential heat capacity of the adsorbed substance ($\bar{C}_{\mathrm{ads}}$). Although the temperature dependence of $\bar{C}_{\mathrm{ads}}$ was ignored in this work, we can compare the $\Delta\bar{C}^{s}{}_{1,p}$ values in the series of adsorbents of the same type.[21,32]

A decrease in the particle size for both graphitized and ungraphitized carbon black samples sharply increases $\Delta\bar{C}^{s}{}_{1,p}$ (see Table 2). This regularity can likely be explained by the noticeable increase in the energetic heterogeneity on going from GTC (sample **4**) to sample **1**. This increase is probably related to the presence of edges on the surface, growth steps, different dislocations in the crystallite structure, a set of allotropic modifications (amorphous carbon, fullerene structures), *etc.*[32] In addition, small carbon black particles contain many developed edges of graphite crystallites, which determines the enhanced adsorption potential of carbons $\mathbf{1_g}$ and $\mathbf{2_g}$ compared to those of sample $\mathbf{3_g}$ and GTC. It can be assumed that the $\bar{C}_{\mathrm{ads}}$ values for *n*-pentane noticeably exceed the $C_{\mathrm{liq},1}$ values for *n*-pentane in the liquid state at the corresponding temperature. This agrees well with analogous data for a great number of aliphatic and aromatic hydrocarbons adsorbed on Silochrom C-120 with the homogeneous surface.[33] It is commonly accepted[33] that the enhanced heat capacity of the substance in the adsorption state is associated with the presence of more complicated lateral intermolecular interactions of the adsorbate molecules with the surface. As a whole, an increase in the energetic heterogeneity of the surface and, hence, in its adsorption potential, results, most likely, in an increase in the $\bar{C}_{\mathrm{ads}}$ values, which depends, to a great extent, on the adsorbent nature and specific features of the molecular structure of the adsorbate. Therefore, it is better to calculate energetically heterogeneous adsorbents by Eq. (3), because the approximation equation (2) ignores the contribution related to $\Delta\bar{C}^{s}{}_{1,p}$, whose values are sufficiently high for the adsorption systems under study. Thus, the $\Delta\bar{C}^{s}_{1,p}$ values in the series of adsorbents considered in this work adequately reflect the influence of the energetic heterogeneity of the surface on the adsorption characteristics of the adsorbates and can be used for the quantitative estimation of the surface heterogeneity.

Our analysis of the TCA of the ungraphitized carbons concerns samples of the adsorbents, which were preliminary extracted with various solvents. The adsorption properties of the non-extracted samples were also studied (see Tables 2 and 3). As should be expected, the surface of the non-extracted carbons is close in the energetic characteristics to the corresponding graphitized carbons. It is established that the TCA of the non-extracted samples are lowest for all adsorbents considered in the work. This phenomenon is observed in GAC when the modified GTC surface is used. In these cases, the adsorption properties of the surface are determined by the nature and specificity of intermolecular interactions of the modifier. The surface admixtures on the industrial carbon black samples are shown[5—7,17] to be based on polyaromatic hydrocarbons and different oxygen-containing compounds (as a rule, polysaccharides). As known,[34,35] polysaccharides decrease considerably the adsorption potential of GTC with respect to dispersion interactions. This decrease is observed by comparison of the TCA of *n*-pentane for the corresponding graphitized and ungraphitized carbons, which were not subjected to extraction. Similar results were obtained for the pre-oxidized surfaces of different carbons.[36,37] The plot of $\ln V_{A,1}$ *vs.* T^{-1} shows (see Fig. 2, *b*) that the curves corresponding to the non-extracted samples lie lower than the curves for the analogous samples of the graphitized carbons.

Thus, the following conclusions can be drawn from the results of the study:

— TCA in the regions close to the zero surface coverage can serve as quantitative characteristics in the estimation of the energetic heterogeneity of carbons and can be used for the development of theoretical models of adsorption on heterogeneous surfaces;

— energetic heterogeneity of carbons decreases with an increase in the average particle size and almost completely determines the adsorption potential of the surface in the region of low coverages;

— experimental $\bar{q}_{\mathrm{dif},1}$ values can serve as the initial data for the calculation of the function of the energy distribution of interaction in the adsorbateљ—heterogeneous surface system;

— concentration boundaries of the chromatographically accessible "Henry region" for the adsorbents considered cannot be determined exactly by standard chromatographic analysis; however, these boundaries become considerably more narrow with an increase in the energetic heterogeneity of the surface.

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