Effect of the Carbon Surface Layer Chemistry on Benzene Adsorption from the Vapor Phase and from Dilute Aqueous Solutions

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We present a complex study of benzene adsorption on chemically modified commercial activated carbons. The porosity of studied carbons is almost the same, whereas the chemical composition and the acid−base properties of surface layers differ drastically from amphoteric (initial de-ashed carbon D43/1, Carbo-Tech, Essen, Germany) and acidic (carbon modified with concentrated HNO_3 and fuming H_2SO_4) to strongly basic (carbon modified with gaseous NH_3). Benzene adsorption isotherms measured from aqueous solution at three temperatures (298, 313, and 323 K) and at the neutral pH level are reported. They are supported by studies of water and benzene adsorption from the gaseous phase (volumetric and calorimetric data) and the data of benzene temperature-programmed desorption (TPD). Moreover, the data of the enthalpy of immersion in water and benzene are also presented. Obtained data of benzene adsorption from the gaseous phase are approximated by applying the method of Nguyen and Do (ND) and the Dubinin−Astakhov (DA) equation. The data of adsorption from solution are described by the hybrid DA-Freundlich (DA-F) model. We show that there are similarities in the mechanisms of benzene adsorption from the gaseous phase and from aqueous solutions and that the pore-blocking effect is the main stage of the adsorption mechanism. This effect strongly depends on the polarity of the carbon surface. The larger the ratio of the enthalpy of carbon immersion in water to the enthalpy of immersion in benzene, the larger the reduction in adsorption from solution, compared to that in the gaseous phase, that is observed.

1. Introduction

Activated carbons are widely used in many industrial purification processes (e.g., gas separation, solvent recovery, and drinking water purification) mainly as an adsorbent to remove taste and other micropollutants.[1] It is assumed that the main driving force of the adsorption of organics from both dilute aqueous solutions and the gaseous phase is the interaction between the aromatic rings of adsorbed molecules and the carbon surface. Literature data show a number of examples describing these interactions. One of the most frequently studied adsorbents is benzene, and benzene adsorption experiments from the gaseous phase as well as from various solvents are carried out in many laboratories. It is worthwhile to point out that Dubinin[2] recommended benzene adsorption measurements as the standard test for the characterization of carbon porosity. However, benzene adsorption from aqueous solutions on carbons has been less frequently described, and the mechanism has not yet been cleared adequately. This is mainly caused by different experimental problems associated with low solubility in water and the high volatility of benzene.

It is well known that carbon surface chemical properties, particularly the content and the type of surface oxygen complexes, are the main factors influencing the adsorption

process from solutions.[1] This effect is frequently observed in the case of benzene adsorption from aqueous as well as nonaqueous solutions. For example, Gasser et al.[3] reported the data describing the adsorption by charcoal from mixtures of benzene and aliphatic alcohols. They postulated that the preferential adsorption of alcohols (in the studied concentration range) can be attributed to their specific adsorption in areas of concentrated oxygen on the surface by which they are more strongly held, possibly by the hydrogen bonds, than benzene is. Thus, they postulated that a highly polar surface preferentially adsorbs the more polar component of a mixture over the less polar component. Puri et al.[4] also studied the influence of oxygen complexes on adsorption from binary solutions on charcoal, and the adsorption of methyl and ethyl alcohols from benzene solutions was investigated. Benzene adsorption increased with the rise in temperature of the thermal treatment of carbon. Jankowska and co-workers suggested that benzene can also be adsorbed on the weakly acidic or nonacidic oxygen groups by the interaction of benzene ring π electrons with the positive charge of those groups.[5] In the past few years, an increasing number of papers reporting the adsorption of organics from dilute aqueous solutions have been published.[1] By knowing the mechanism of the interaction of the aromatic ring with carbon surface functionalities, the mechanism of benzene adsorption can be proposed. The influence of carbon surface chemistry on the adsorption of organic molecules from dilute aqueous solutions was recently reported by Moreno-

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Castilla.[6] The author emphasized that surface chemistry has an essential influence on both electrostatic and nonelectrostatic interactions. Beyond this, aromatic molecules are physisorbed on the carbon surface by dispersion interactions between the π electrons of the aromatic ring and graphene layers. The contribution of functionalities that can give rise to the creation of hydrogen bonds with water can lead to a decrease in adsorption for aromatic compounds. A more general mechanism of the adsorption of organics was proposed by Radovic et al.[1] They have suggested that the adsorption of aromatics is a more complex interplay of electrostatic and dispersive interactions. Recently, Terzyk published a comparative study on the effect of carbon surface chemistry on the adsorption of organics from dilute aqueous solutions.[7] He concluded that generally the mechanism of the adsorption of organics in carbon micropores is micropore filling, combined with adsorption on active sites. Applying the semiempirical calculations and the MOPAC package, he also showed that with the rise in temperature (due to the weakening of hydrogen bonds between specific carbon surface groups and adsorbed molecules) the opening of the pores occurs. Thus, with the rise in temperature the $\pi-\pi$ dispersion interactions appear to play a dominant role, whereas at lower temperatures the hydrogen bonding mechanism determines the adsorption properties of carbons via the pore-blocking effect.

Several papers published between 1950 and 2004 describe the adsorption of benzene from dilute aqueous solutions on well-defined carbons. However, there are practically no complex reports on the influence of carbon surface properties on benzene adsorption, and no mechanism of this process was given. The enthalpy of immersion in benzene and other solvents reveals the modification of the carbon structure during the heat treatment process.[8] Some authors described the data of adsorption of this compound from aqueous solutions by application of various equations and models. Koganovski et al.[9] analyzed the isotherms of adsorption of various organic compounds from aqueous solutions by applying the Dubinin–Radushkevich (DR) equation. They postulated that the theory of volume filling is applicable only for systems where the energy of interaction between adsorbed molecules is constant or small and for systems where the hydrogen bonds between an adsorbate and solvent (water) are negligibly small. They also proposed the modified affinity coefficient for the description of adsorption from solutions.[9] Mioduska et al.[10] presented a comparative analysis of adsorption data of benzene from the gaseous phase and from aqueous solutions. They concluded that the densities of benzene in carbon pores during adsorption from vapor and from aqueous phases are almost the same. A comparative study of benzene adsorption on activated carbon from the gas phase and aqueous solutions was also reported by Seidel et al.[11] They concluded that adsorption from solutions is much lower than that from the gas phase. Garbacz and co-workers formulated the solution analogue of the exponential equation of adsorption on microporous solids, describing experimental isotherms of adsorption from benzene–water solutions on active carbons.[12] The effect

of the relation of the number of molecules of water and the organic component of the solution in the adsorbed phase on the selectivity of adsorption from solution by activated carbon was recently investigated by Koganovski.[13] Eltekova et al.[14] studied the adsorption of benzene from aqueous solutions on activated carbon. They applied the DR and DS (Dubinin–Stoeckli) equation to describe the adsorption data; however, for the DS equation a considerably better fit was observed. They postulated that the adsorption of benzene takes place not only in micropores but also in mesopores. It was also shown that the presence of the solvent (water) leads to the adsorption of benzene on the hydrophobic parts of activated carbon. Recently, Hindarso and co-workers pointed out the lack of benzene adsorption results (determined over a wide range of temperature) from aqueous solutions on carbons.[15] The results of benzene adsorption measured in the range of temperature from 303–323 K on Calgon carbon were satisfactorily fitted by applying the Toth and Bradley (Sips) adsorption isotherm equations. Braida et al.[16] reported interesting results concerning the irreversibility of benzene adsorption from aqueous solutions on carbons. They concluded that this effect is caused by the swelling of charcoal particles. Similar results for adsorption from the gaseous phase were published by Gurianova et al.[17]

It is well known that porosity and the chemical composition of the carbon surface layer determine adsorption properties toward organics from aqueous solutions. To eliminate the differences in porosity between studied carbons (and to elaborate in this way only the influence of carbon surface composition on benzene adsorption), samples obtained from the same original carbon by carefully performed modifications are studied in this article. Studying adsorption at three temperatures, we discuss the influence of the carbon surface chemical composition on the adsorption of benzene from dilute aqueous solutions on four activated carbons. The comparison with the adsorption data from the gaseous phase, supported by TPD (temperature-programmed desorption), the enthalpy of adsorption, and some immersion results, leads to the general mechanism of benzene adsorption.

2. Experimental Section

2.1. Adsorption Isotherms, Adsorption Enthalpy, and TPD Measurements. Benzene (pure for analysis, Polskie Odczynniki Chemiczne, Gliwice, Poland) and water (redistilled) adsorption isotherms were measured (at 298 and 310 K, respectively) using the volumetric apparatus with Baratron pressure transducers (MKS Instruments, Germany). The related enthalpy of adsorption and the enthalpy of immersion were measured using two isothermal Tian-Calvet microcalorimeters described previously.[18–21] The errors in the measurements are as follows: adsorption isotherms, $\pm1\%$; immersion calorimeter, ±1.5 J/g; and the Tian–Calvet adsorption calorimeter, $\pm1.5\%$.[18–21]

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Differential and integral molar entropies of adsorbed molecules were calculated following the well-known procedure[22] described previously.[18,23,24] Knowing the values of the adsorption (n_a) and the differential molar enthalpy of adsorption (q^{diff}) (both are, of course, measured experimentally, see above), it is possible to calculate the differential molar entropy of the adsorbed molecules (S^{diff}) from

$$S^{diff} = S_g - \left(\frac{q^{diff}}{T}\right) - R\ln\left(\frac{p}{p_0}\right) + R \qquad (1)$$

where S_g is the molar entropy of the gas at the measurement temperature, R is the gas constant, and p and p_0 are the equilibrium and standard-state pressures, respectively. The standard-state pressure is taken as $p_0 = 101\,325$ Pa. By knowing the differential molar entropy of adsorbed molecules, the integral molar entropy (S^{int}) can be calculated from

$$S^{int} = \frac{1}{n_a}\int_0^{n_a} S^{diff}\, dn_a \qquad (2)$$

where n_a is the number of adsorbed moles. On the basis of the definition of the differential enthalpy of adsorption, the integral molar enthalpy of adsorption (Q^{int}) can be calculated from

$$Q^{int} = \frac{1}{n_a}\int_0^{n_a} q^{diff}\, dn_a \qquad (3)$$

The TPD-QMS experiments were carried out in a flow reactor coupled to a quadrupole mass spectrometer (Dycor MA 200, Pittsburgh, PA). For TPD measurements, all carbon samples were powdered in an agate mortar. Each sample was flushed with liquid benzene (pure) and placed under a hood in an open container for 14 days. The volatile loss was replenished every day. Subsequently, the carbons were placed in the dryer and desorbed for 7 days at 308 K. The temperature and selected mass signals—14, 16, 17, 18, 28, 32, 44, 48, 64, 77, 78 amu—were monitored. The results from the analysis of all signals are similar to those obtained from 78 amu. Therefore, the discussion is reduced to only this peak.

2.2. Adsorption from Solution. Benzene was used for the preparation of the initial solutions. To determine a single adsorption isotherm, we prepared 20 bottles containing 0.125 dm³ of benzene solution with varying concentration (from 0.0007 up to 0.022 mol·dm⁻³) using a suitable amount of pure benzene and distilled water. Twenty carbon samples were prepared by means of an analytical balance and desorbed for 20 h at 383 K in a dryer. The bottles with benzene solutions were closed tightly after adding carbon (glass bottles with noncorrosive locks were applied), placed in a thermostat, and stirred mechanically for 4 days. The temperature was controlled to an accuracy of ±0.1 K. The concentrations of the obtained equilibrated solutions were determined using a UV−vis spectrophotometer (JASCO V-550, Japan). The maximum adsorption wavelength was determined to be 254 nm. Each adsorption measurement was repeated at least three times. Adsorption isotherms were measured at three temperatures (298, 313, and 323 K) and at pH 7.0.

The initial de-ashed carbon D43/1 (Carbo-Tech, Essen, Germany) was modified by adding concentrated HNO_3, fuming H_2SO_4, and gaseous NH_3. The procedures of carbon modification were assigned experimentally in such a way that the modification processes did not change the porosity of the carbon in a drastic way but drastically changed the composition of the carbon surface layer.[7] The chemical structures of carbon layers were studied by the following methods: FTIR, XPS, TPD, enthalpy of immersion, titration, electrochemical and resistance measurements, and

Scheme 1. Composition of Carbon Surface Layers, Values of the pH of the Point of Zero Charge (pH_{PZC}), and Enthalpy of Immersion in Water (Δh_{water})
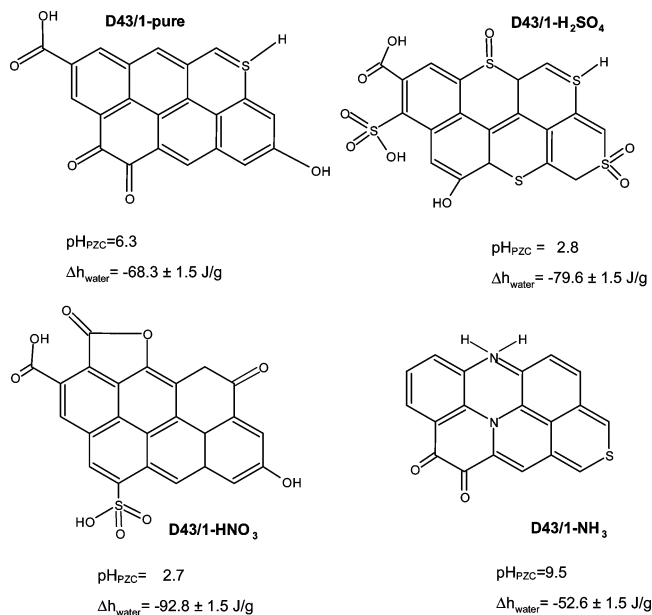

Table 1. Structural Properties of Investigated Carbons

carbon	$W_0{}^a$ cm³/g	$V_{water}{}^b$ cm³/g	$V_{benzene}{}^b$ cm³/g	$V_{poros}{}^c$ cm³/g	$S_{BET}{}^d$ m²/g	$x_{av}{}^e$ nm
D43/1- pure	0.384	0.970	0.986	0.543	991	0.86
D43/1-HNO₃	0.492	0.971	0.954	0.483	1100	0.90
D43/1-H₂SO₄	0.450	0.992	0.987	0.480	1113	0.89
D43/1-NH₃	0.487	0.983	1.004	0.523	1200	0.94

^{a} W_0, total micropore volume determined from low−temperature nitrogen adsorption data using the Dubinin−Atakhov equation. ^{b} V_{water}, $V_{benzene}$, total micropore volumes from Bachmann's method determined using water and/or benzene as an adsorbate. ^{c} V_{poros}, volume of pores with the diameter larger than 7.5 nm, determined from mercury porosimetry. ^{d} S_{BET}, total apparent surface area calculated from the BET method. ^{e} x_{av}, average micropore diameters determined on the basis of the relationship proposed by Terzyk et al.[18,24]

Table 2. Surface Properties of Investigated Carbons

carbon	$\Delta h_{water}{}^a$ J/g	$\Delta h_{water}/V_{water}{}^b$ J/cm³	$\Delta h_{water}/V_{benzene}{}^b$ J/cm³	$c_a{}^c$ mmol/g	$c_b{}^c$ mmol/g
D43/1-pure	−66.3	−68.3	−67.2	0.446	0.175
D43/1-HNO₃	−92.8	−95.6	−97.2	1.332	0.088
D43/1-H₂SO₄	−79.6	−80.2	−80.6	0.999	0.071
D43/1-NH₃	−52.6	−53.5	−53.3	0.100	0.564

^{a} Δh_{water}, enthalpy of immersion in water. ^{b} $\Delta h_{water}/V_{water}$ and $\Delta h_{water}/V_{benzene}$, "specific" enthalpy. ^{c} c_a and c_b, total concentration of acidic and basic surface groups, respectively.

Boehm's method.[19,25−28] The application of all of these techniques makes it possible to elucidate the pH values of the point of zero charge (pH_{PZC}) as well as the chemical composition of carbon surface layers (i.e., the chemical structure of carbon surface groups[19,25−28]). The schematic representation of the proposed surface structures, the values of pH_{PZC}, and the values of the enthalpy of immersion in water are shown in Scheme 1.[27] The major characteristics of the studied samples are summarized in Tables 1−3.

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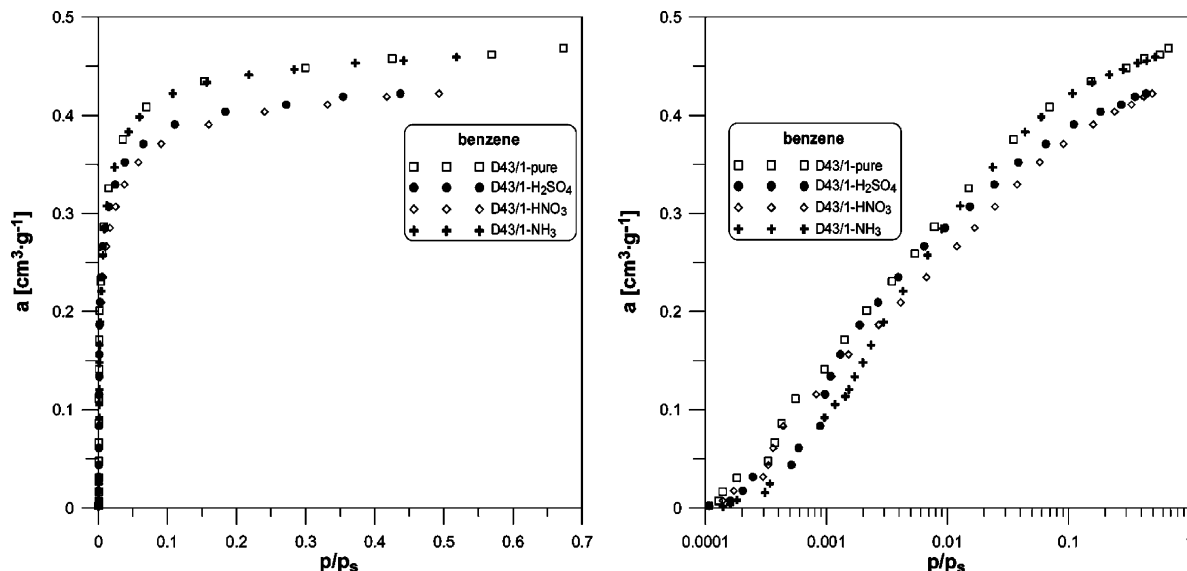(28) Terzyk, A. P.; Rychlicki, G. *Colloids Surf., A* **2000**, *163*, 135−150.

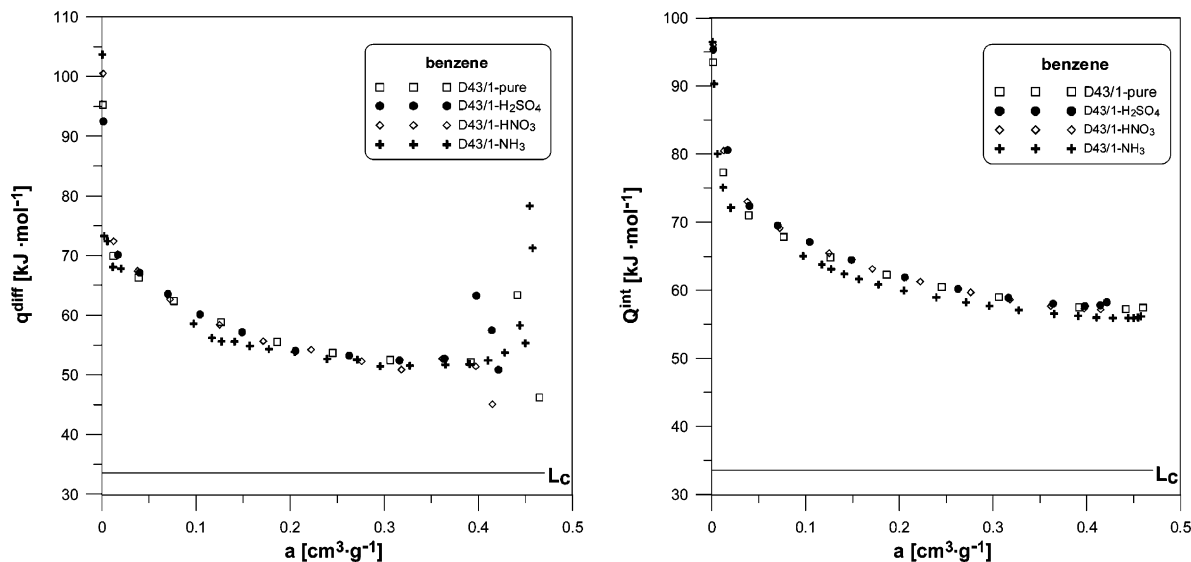**Figure 1.** Benzene adsorption isotherms ($T = 298$ K) on studied carbons.

Figure 2. Differential (q^{diff}) and integral (Q^{int}) molar enthalpies of adsorption of benzene ($T = 298$ K) on studied carbons. The horizontal solid line with L_c (i.e., $-L_c$) (the enthalpy of condensation) is equal to 33.54 kJ/mol.

Table 3. Enthalpy of Immersion of Studied Carbons in Benzene and Water

carbon	$\Delta h_{\text{benzene}}$ J/g	Δh_{water} J/g	$\Delta h_{\text{water}}/\Delta h_{\text{benzene}}$
D43/1-pure	-101.6	-66.3	0.6
D43/1-HNO$_3$	-106.3	-92.8	0.9
D43/1-H$_2$SO$_4$	-110.4	-79.6	0.7
D43/1-NH$_3$	-108.8	-52.6	0.5

3. Results and Discussion

3.1. Adsorption of Benzene Vapors. Figure 1 shows the isotherms of benzene adsorption ($T = 298$ K). It can be seen that the maximum measured adsorption (i.e., for relative pressure equal to 0.5) is almost the same as for adsorption on initial and basic carbon and decreases for adsorbents modified with acids. Figure 2 shows that the differences in the differential (q^{diff}) and integral (Q^{int}) molar enthalpies of the adsorption of benzene on various carbons are not large. At low coverage, the integral enthalpy is the largest for carbons having an acidic surface nature. Lower integral enthalpy is observed during adsorption on carbon modified with ammonia over the whole studied

adsorption range. The entropy of molecules (S^{diff} and/or S^{int}, respectively) adsorbed at small coverage (Figure 3) is lower that the entropy of solid benzene. At larger pore fillings, the entropy plot is located between that observed for solid and cooled liquid benzene. A similar effect was also reported by other authors.[24,30] Thus, it can be postulated that the differences in adsorption values reported in Figure 1 are caused by adsorbed benzene molecules blocking the entrances to some pores. To check this hypothesis (applying the adsorption data presented in Figure 1), we calculated the parameters of the Dubinin–Astakhov (DA) isotherm equation in the range of 0.0001 up to 0.1 p/p_s (the molar volume of liquid benzene equal to 89.40 cm^3 mol^{-1} was taken for the calculation of the micropore volumes). Figure 4 shows the correlation between the maximum adsorption in micropores (DA equation), N_{max}, and the concentration of carbon surface acidic groups (determined previously from Boehm's method[19]). It can be observed that the rise in total surface acidity (c_a/S_{BET}, where S_{BET} is the surface area determined

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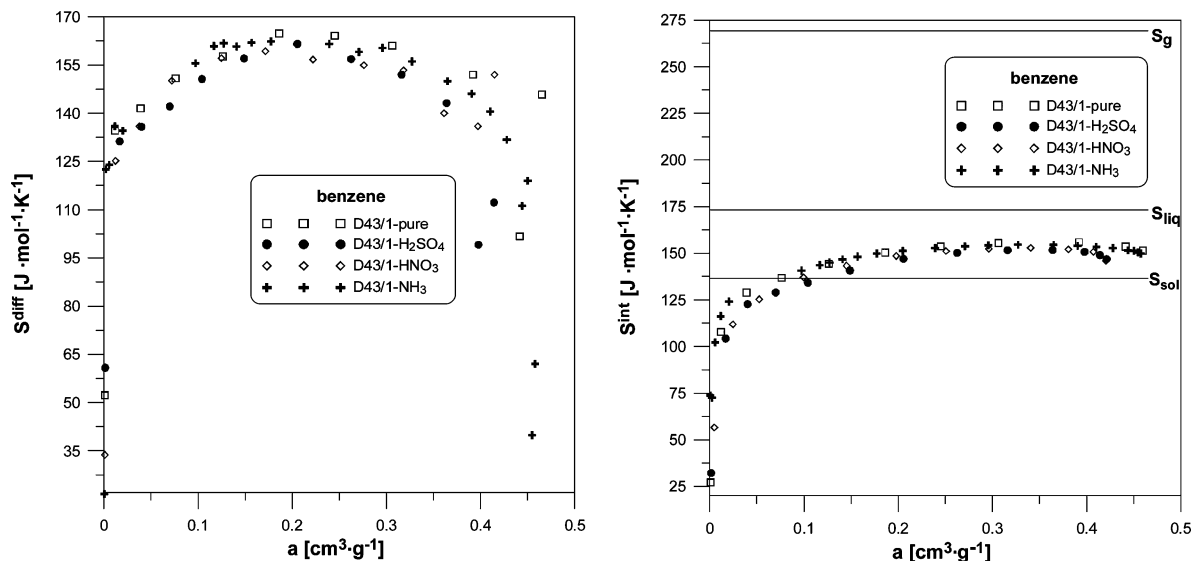
Figure 3. Differential (S^{diff}) and integral (S^{int}) molar entropies of benzene adsorbed on studied carbons. Solid horizontal lines denote the entropies of gaseous ($S_g = 269.2$ J/mol K), liquid ($S_{\text{liq}} = 173.2$ J/mol K), and solid ($S_{\text{sol}} = 136.5$ J/mol K) benzene at 298 K.
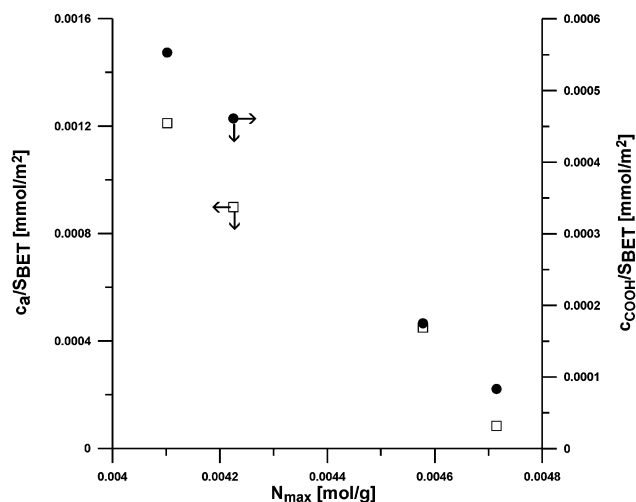

Figure 4. Correlation between the maximum benzene adsorption, N_{max} (calculated from adsorption isotherms shown in Figure 1 by applying the DA equation), and the concentration of carbon surface acidic (c_a) and carboxylic (c_{COOH}) groups determined for studied carbons by applying Boehm's method. S_{BET} is the surface area determined using the Brunauer–Emmett–Teller (BET) method.

using the Brunauer–Emmett–Teller (BET) method) of carbon leads to the decrease in calculated micropore volume. Also, very good correlation is observed if the most acidic surface groups (i.e., carboxylic, $c_{\text{COOH}}/S_{\text{BET}}$) are taken into consideration. This is due to the fact that carboxylic groups are the major acidic groups for the studied carbons; moreover, they are the most acidic (pK_a around 6.4).

This clearly confirms that the pore-blocking effect (also observed during adsorption from aqueous solutions, see below) influences the accessibility of benzene molecules to some pores.[31] However, during adsorption from gaseous phase this effect is not as spectacular as in the presence of polar solvent molecules (for example, water; see below). Figure 5 shows the pore size distributions (PSDs) determined from nitrogen ($T = 77$ K) and benzene

($T = 298$ K) adsorption data. Here we applied the most sophisticated, simplest, and fastest method of porosity calculation, namely, the method of Nguyen and Do (ND).[32] The PSDs were calculated by applying our constructed ASA algorithm,[33–35] with recently tabulated[24] parameters of the intermolecular interactions. The comparison of the PSDs calculated from nitrogen and from benzene adsorption data leads to the conclusion that the latter ones are shifted toward slightly larger widths. This is probably due to the larger kinetic diameter of the benzene molecule. Similar behavior was observed by us for other microporous adsorbents.[24] However, what is most important is that both groups of PSD curves show that there is no remarkable effect of carbon surface modification on pore diameter. Thus, it can be concluded that applied procedures of carbon surface modification do not change the porosity in a drastic way. However, the area under the PSD peaks is different for different carbons, and this is caused by the pore-blocking effect, as suggested above.

Figure 6 shows the TPD data of benzene (78 amu) desorbed from studied carbons. It is interesting that the peaks are shifted toward larger energies for acidic carbons, in accordance with the values of the integral enthalpy of benzene adsorption at small coverages (and according to the values of the enthalpy of adsorption of water; see Figure 8). We performed the deconvolution of the obtained peaks by applying the procedure proposed by Figuereido et al.[36] (Gaussian-shaped peaks were assumed). For D43/1-pure, three peaks are observed (433, 444, and 495 K, respectively). Because on the surface of this carbon a small number of functionalities are observed, it seems reasonable to postulate that only the high-energy peak is caused by benzene desorbed from pores partially blocked by molecules interacting with surface groups. In fact, for benzene desorbed from carbon modified with fuming sulfuric acid the peak at 433 K is still present, whereas two remaining peaks are shifted toward higher energies (i.e., 456 and

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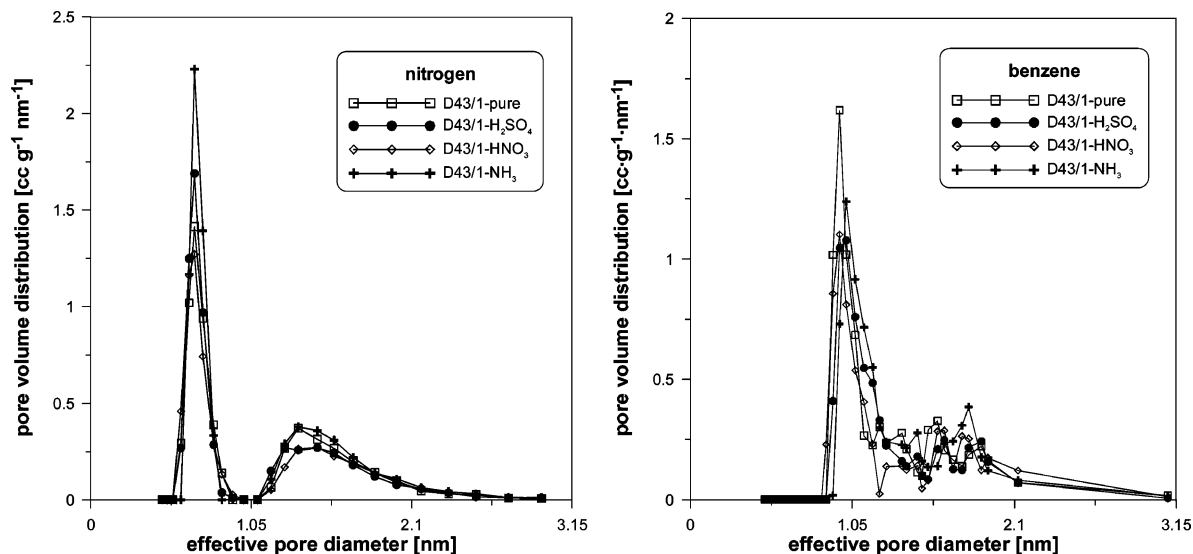
Figure 5. Pore size distributions obtained applying the method of Nguyen and Do (ND) to nitrogen and benzene adsorption data.
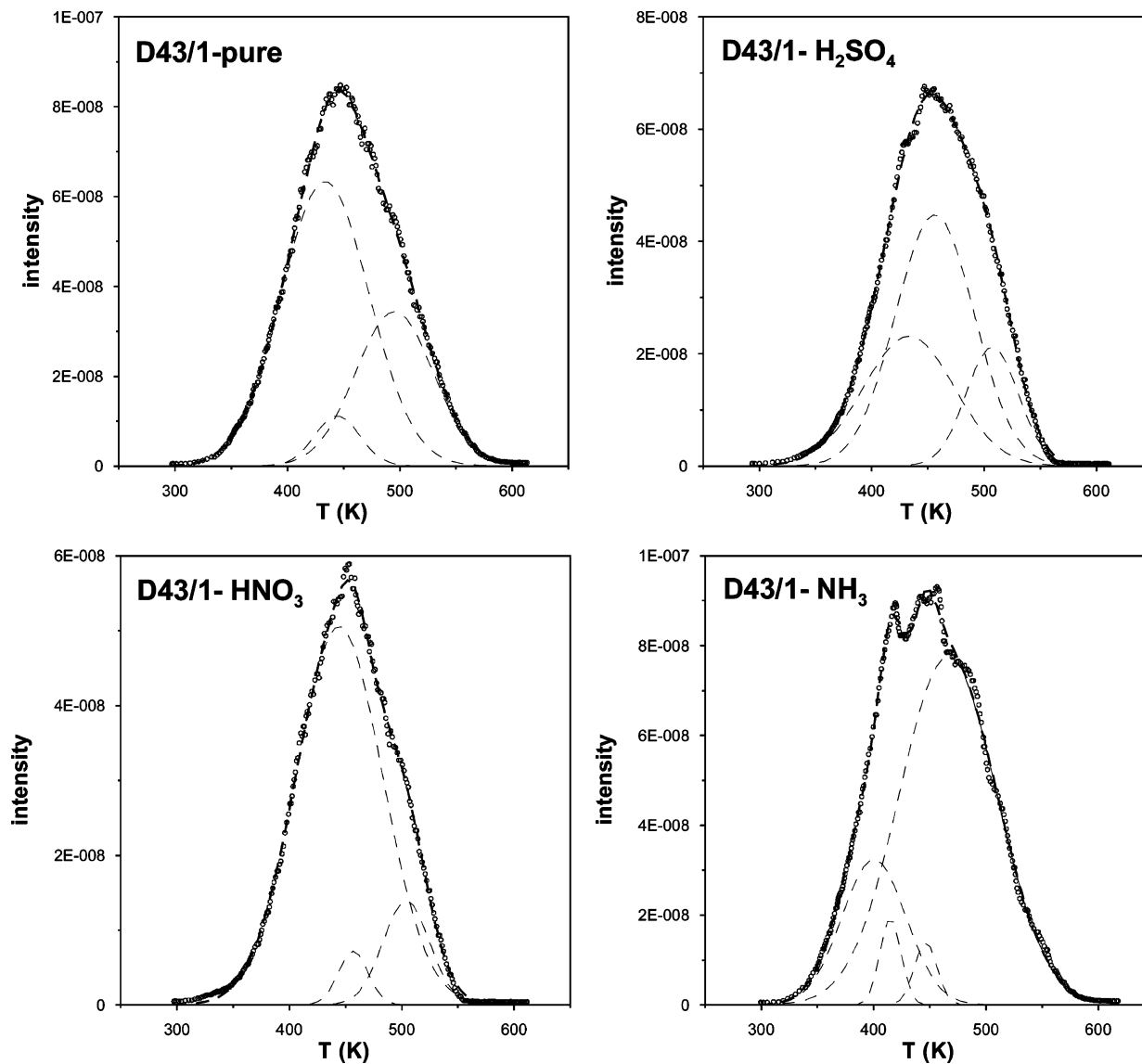

Figure 6. TPD spectra of benzene desorbed from the studied carbons (symbols), together with the theoretical results of the deconvolution procedure applying Gaussian peaks (dashed lines).

507 K, respectively). The modification with HNO_3 leads to the presence of the same high-energy peaks as for carbon

modified with H_2SO_4, and the low-energy peak (433 K) moves up to 444 K. Thus, the shifting of the peaks toward
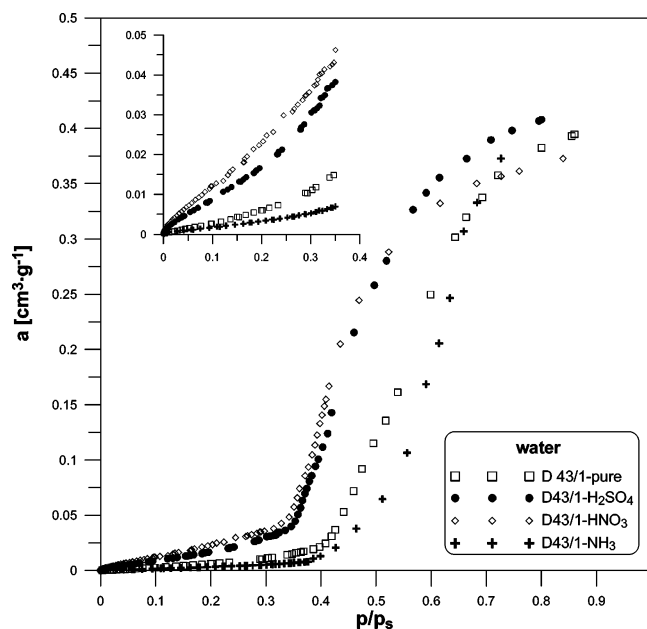
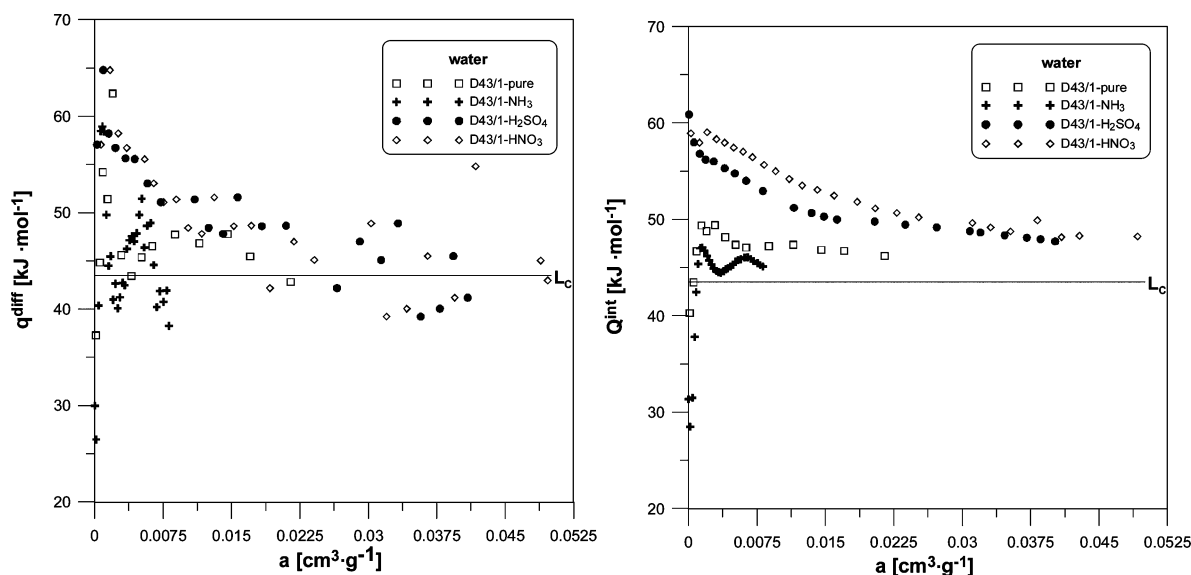**Figure 7.** Water adsorption isotherms ($T = 310$ K) on studied carbons.

Figure 8. Differential (q^{diff}) and integral (Q^{int}) molar enthalpies of adsorption of water at 310 K. The symbols are the same as those used in Figure 2.

larger energy is caused not only by the pore blocking but also by the interaction of the benzene ring with surface oxygen acidic groups. Recent TPD studies of benzene adsorbed on different zeolites performed by Sivasankar and Vasudevan[37] showed a similar effect (i.e., the high-energy maxima were caused by benzene molecules associated with the Brønsted acid sites of the zeolites). For carbon modified with ammonia, being the most hydro-phobic one (Tables 2 and 3), the peak around 444 K is also present, whereas the peaks around 430 and 495 K (observed for the initial carbon) are shifted toward lower energy (around 400 and 470 K). Thus, it can be seen that the location of carbon active surface functionalities (being located on the edges of entrances to pores[38]) is the crucial

factor determining the location of the peaks on the TPD spectra presented in Figure 6.

3.2. Adsorption of Water Vapor. Figure 7 shows adsorption isotherms of water on studied carbons. Figures 8 and 9 show the adsorption enthalpy and the entropy of water. Presented results confirm the well-known and often experimentally observed increase in water adsorption (and corresponding enthalpy) with the rise in carbon surface polarity. Also, similar shapes of water adsorption enthalpy curves were often reported. This enthalpy is larger than the enthalpy of condensation L_c for carbons modified with acids, whereas for initial adsorbents and those modified with ammonia (i.e., with the rise in carbon surface hydrophobicity) at low coverage it is below the enthalpy of water condensation. Consequently, the integral molar entropy of adsorbed molecules approaches the quasi-liquid state with the rise in carbon surface polarity (Figure 9). As will be shown below, adsorption properties of studied carbons toward benzene from aqueous solutions are mainly

(37) Sivasankar, N.; Vasudevan, S. *J. Phys. Chem. B* **2004**, *108*, 11585−11590.
(38) Bansal, R. C.; Donnet, J. B.; Stoeckli, F. *Active Carbon*; Marcel Dekker: New York, 1988.
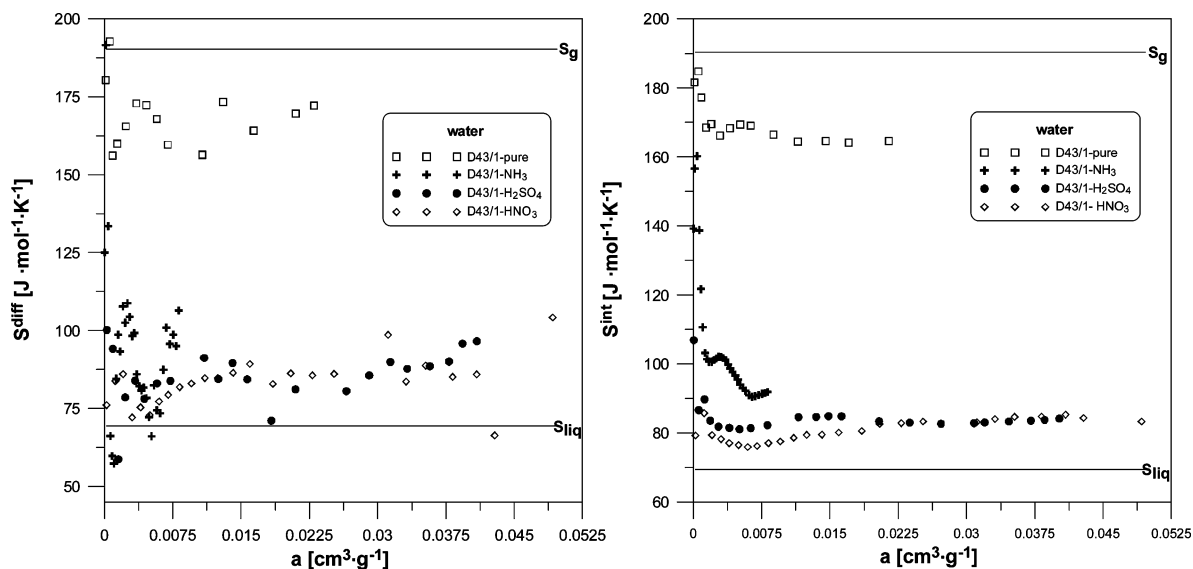
Figure 9. Differential (S^{diff}) and integral (S^{int}) molar entropies of water adsorbed on studied carbons. The symbols are the same as those used in Figure 3.
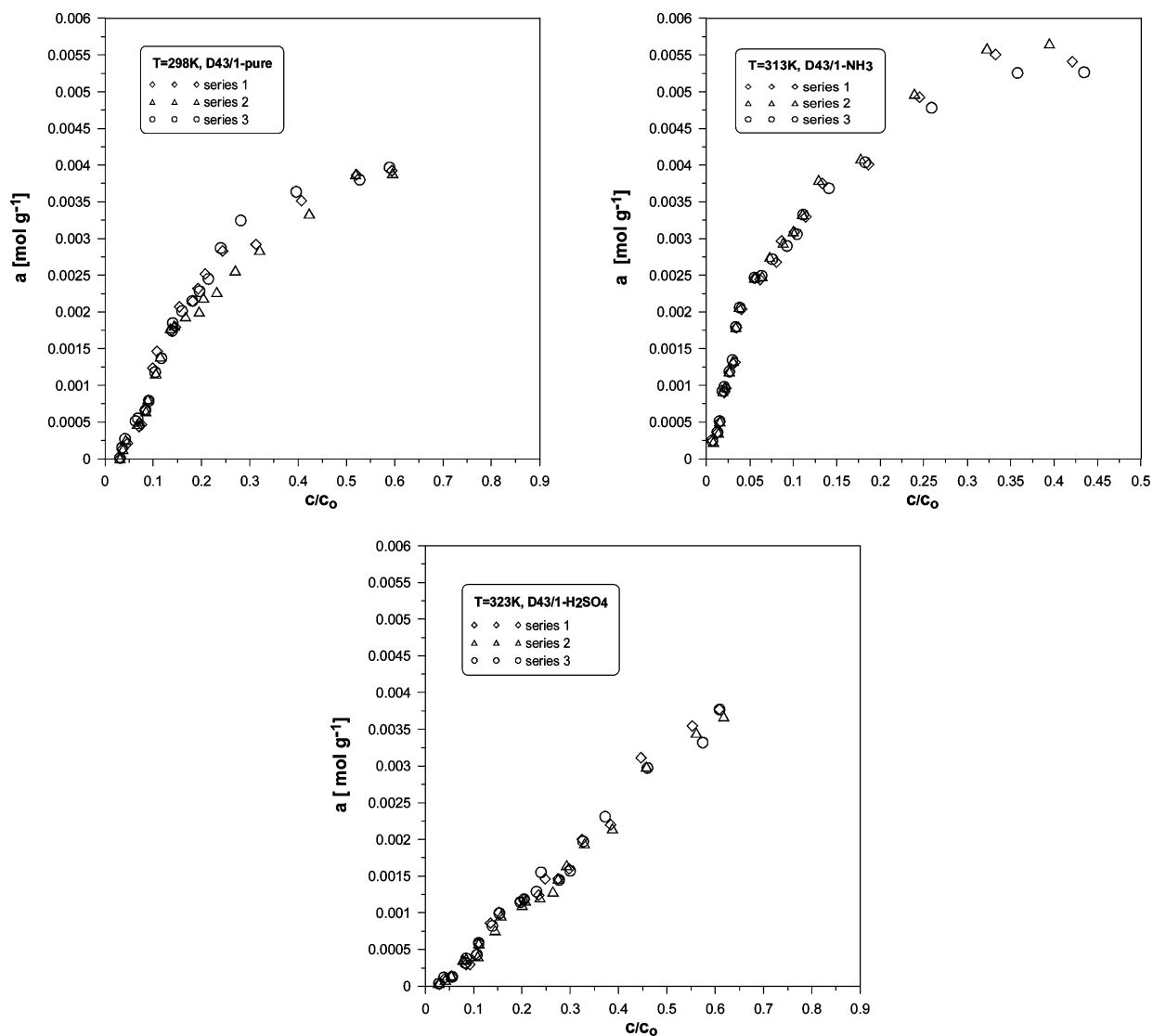

Figure 10. Reproducibility of the results of measurements of benzene adsorption from aqueous solution for arbitrarily chosen systems.

determined by the polarity of the carbon surface and the ability of carbon to adsorb water.

3.3. Adsorption of Benzene from Aqueous Solution. Figure 10 presents the reproducibility of the results,
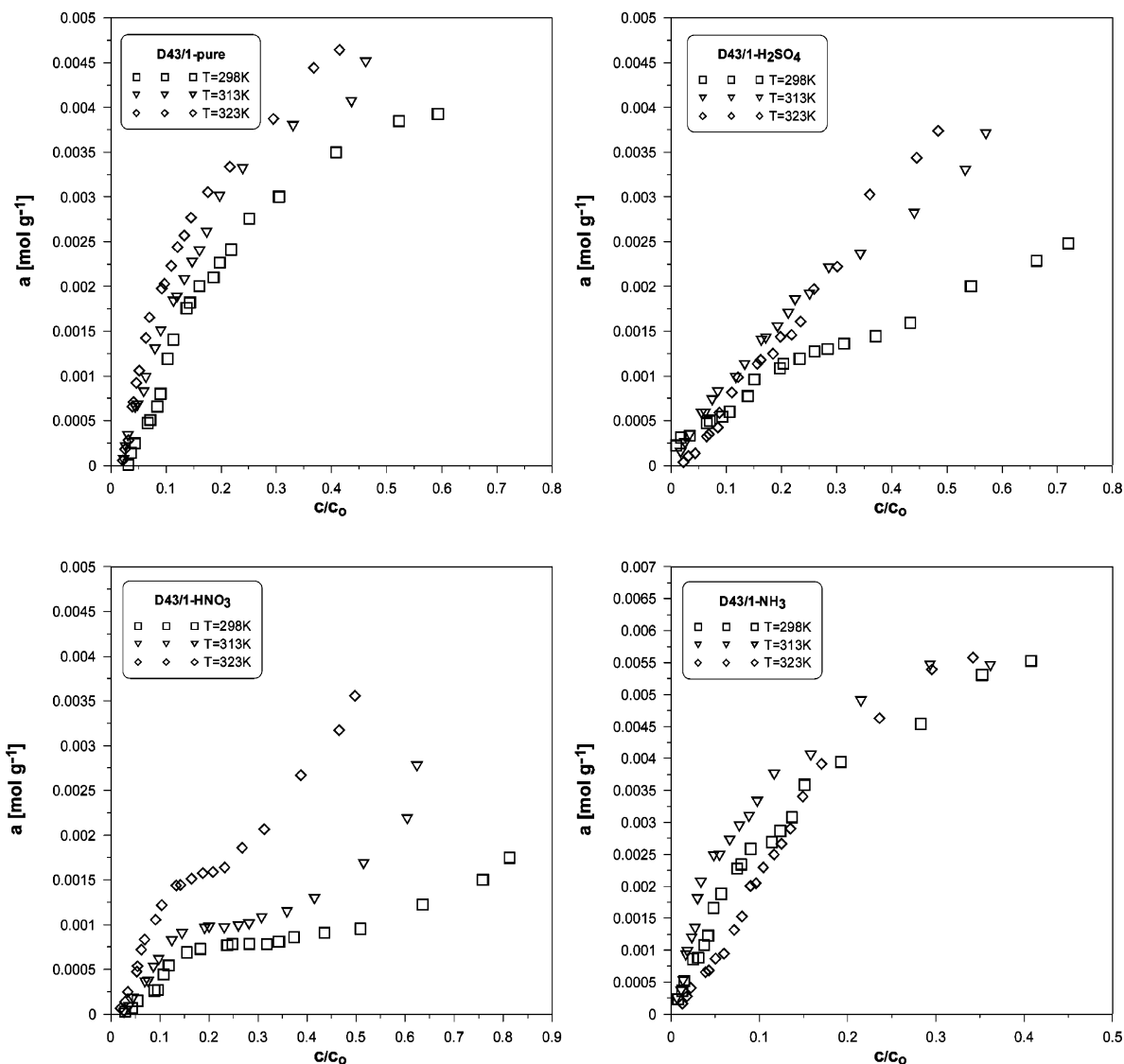
Figure 11. Influence of temperature on benzene adsorption on studied carbons. (Averaged results of three measurements are shown.)

where we show the systems with the best (D43/1 - H$_2$SO$_4$) and the worst (D43/1 - pure) reproducibility of data. It can be noticed that, despite the above-mentioned experimental obstacles, the error is not larger than ±0.000025 mol/g and very good reproducibility is observed. Figure 11 shows the effect of temperature on benzene adsorption. (Averaged results from three measurements are presented.) The most important is that the shape of the adsorption isotherms depends on the type of studied carbons (i.e., on the content of oxygen surface complexes). Thus, for the most polar carbon (D43/1-HNO$_3$) type L3, following the classification of Giles et al.,[39] is observed. The same type occurs for the second most acidic carbon (D43/1-H$_2$SO$_4$) but only at the lowest studied temperature. For other cases, intermediate types L1/2 are observed. The increase in adsorption with the rise in temperature is attributed to the opening of the pore structure of carbons due to a decrease in the energy of hydrogen bonds between water and benzene molecules adsorbed on surface active groups located at the entrances to micropores. A similar effect was observed for the adsorption of other solutes on studied carbons.[7]

Figure 12 shows the effect of the carbon surface chemical composition on benzene adsorption on studied carbons. It

can be seen that at each temperature benzene adsorption increases with the rise in hydrophobicity of the carbon surface (Tables 2 and 3). The largest adsorption is observed on carbon D43/1-NH$_3$, and the smallest, on D43/1-HNO$_3$. With the rise in the temperature, the isotherms approach one another because of the (above-mentioned) decrease in the pore-blocking effect.

To show some general quantitative correlations between benzene adsorption and the parameters determining the chemical composition of carbon surface layers, obtained data of benzene adsorption from solution were described by applying the hybrid of the DA and Freundlich (DA-F) equations in the form

$$N_a = N_{am} \exp\left\{\left[\frac{RT \ln(c/c_0)}{E}\right]^4\right\} + K_F(c/c_0)^{n_F} \quad (4)$$

where N_a and N_{am} are the adsorption and the maximum adsorption in micropores, respectively, R and T are the gas constant and the temperature, c and c_0 are the equilibrium benzene concentration and the saturation concentration at temperature T, K_F and n_F are the Freundlich equation constants, and E is the DA equation constant related to the characteristic energy of adsorption. The power of the DA equation is taken to be equal to 4.

(39) Giles, C. H.; MacEwan, C. H.; Nakhwa, S. N.; Smith, D. *J. Chem. Soc.* **1960**, 3973−3993.
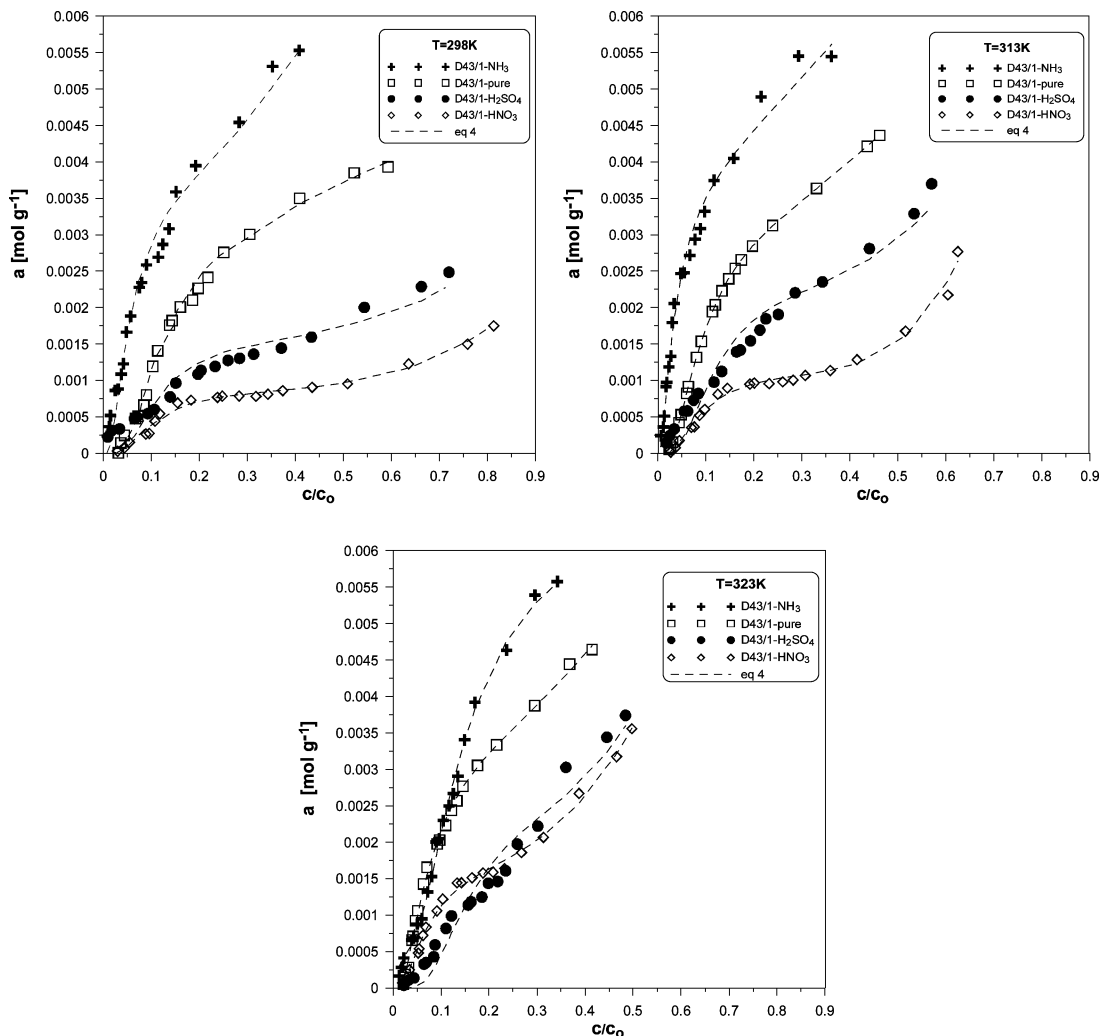
Figure 12. Influence of the carbon surface composition on benzene adsorption on studied carbons. (Averaged results of three measurements are shown.) Points, experimental data; dashed lines, the data fitted by applying eq 4.
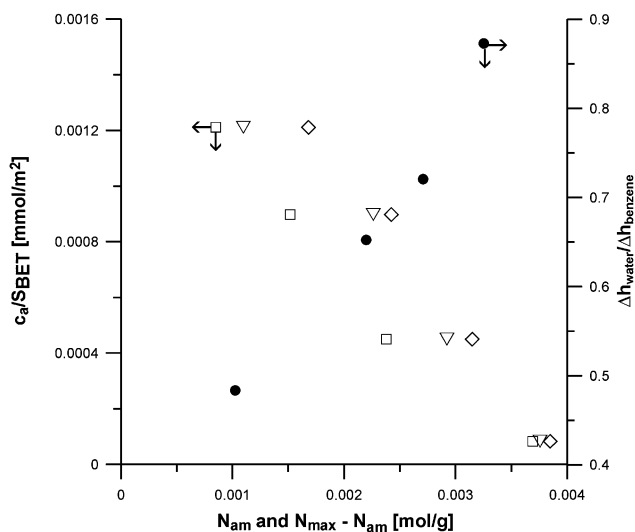

Figure 13. Left y axis − correlations between N_{am} (eq 4) and the concentration of surface acidic groups, c_a/S_{BET} (300 K, squares; 310 K, triangles; 320 K, diamonds). Right y axis − dependence of the reduction of maximum adsorption from the gaseous phase compared to that determined from aqueous solution ($N_{max} − N_{am}$) plotted as a function of the ratio of the enthalpy of immersion of studied carbons in water to the enthalpy of immersion in benzene, $\Delta h_{water}/\Delta h_{benzene}$ (Table 3). S_{BET} − surface area was determined using the Brunauer−Emmett−Teller (BET) method.

This is in accordance with the observation of Stoeckli and co-workers[40,41] showing that regardless of the thermodynamic inconsistency[42] the DA equation (with $n = 4$)

describes phenol adsorption data on the series of carbons in the relatively wide range of temperatures. The results of our recent adsorption studies of phenol, paracetamol,

aniline, and acetanilide on the same carbons confirmed that the DA equation ($n = 4$) and Freundlich equations adequately describe the obtained experimentally isotherms.[7] However, as was shown by Cerofolini and others[43,44] and pointed out by Rudziński and Everett,[45] the overall adsorption isotherm for heterogeneous solids should be a hybrid of the Freundlich and DA equations. In our opinion, this remark justifies the applicability of the adsorption isotherm equation (eq 4). The fit of theoretical and experimental data is also shown in Figure 12. It can be seen that excellent agreement between theoretical and experimental data is observed. Obtained N_{am} values (for all studied temperatures) are correlated with the contents of surface acidic groups determined from Boehm's method (Figure 13). As in the case of benzene vapor adsorption (Figure 4) also during adsorption from solution, N_{am} decreases with the rise in carbon surface acidity. This Figure also shows that the difference between the adsorption of benzene from the gaseous and the liquid phase ($N_{max} - N_{am}$) is a function of the ratio of the enthalpy of immersion of studied carbons in water and benzene.

4. Conclusions

Benzene adsorption data measured from the gaseous phase can be applied to the determination of the pore size distribution; however, calculated pore volumes are insignificantly affected by the presence of surface acidic groups. The enthalpy of adsorption of benzene for acidic carbons is increased by the energy of interaction between

benzene molecules and surface acidic groups, and this effect is also visible on the TPD spectra of desorbed benzene. Here the rise in acidity of the carbon surface leads to the shifting of the peaks toward larger energies. Benzene in pores of the investigated adsorbents is in a state similar to quasi-solid.

The major factor influencing the behavior of studied carbons toward benzene in aqueous solutions is the ability of carbon to adsorb water. As during adsorption from the gaseous phase and also during adsorption from solution, the pore-blocking effect is the major one, and it determines the adsorption mechanism. It should also be mentioned that pore blocking was observed by other authors. The adsorption of water on surface active groups located at the entrances to micropores (i.e., pore-blocking effect) is the dominating factor responsible for the observed irregularities and leads to the rise in adsorption with the rise in the temperature. Thus, the mechanism of adsorption is mixed between micropore filling (benzene) and adsorption on surface active sites (water). This mechanism is analogous to that proposed previously for adsorption of the series of different molecules on the studied carbons.

The data of adsorption from solution are described by the hybrid DA-Freundlich (DA-F) model. This equation satisfactorily describes the obtained data. Moreover, obtained N_{am} values are correlated with the contents of surface acidic groups determined from Boehm's method.

We show that there are similarities in the mechanisms of benzene adsorption from the gaseous phase and from aqueous solutions. The proposed mechanism of benzene adsorption is supported by the correlations between the values of maximum adsorption of benzene from aqueous solution, the reduction of adsorption compared to that observed from the gaseous phase, and the content of surface acidic groups (and/or surface hydrophobicity).

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(44) Ozawa, S.; Kusumi, S.; Ogino, Y. *J. Colloid Interface Sci*. **1976**, *56*, 83−91.

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