

Revisiting the Effect of Surface Chemistry on Adsorption of Water on Activated Carbons

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A sample of Westvaco carbon was oxidized with ammonium persulfate and both initial and oxidized samples were washed with methanol. The samples were characterized using sorption of nitrogen, Boehm titration, potentiometric titration, IGC, FTIR, TPD, and thermal analysis. Then water adsorption isotherms were measured at various temperatures close to ambient (relative pressure from 0.001 to 0.3). The isotherms were analyzed in terms of the thermodynamic consistency, presence of equilibrium, and water-activated carbon surface interactions. The results showed that washing with methanol significantly modifies the surface chemistry of carbons, creating phenols and new, very easily hydrolyzed esters. The latter, when in contact with water, is hydrolyzed, creating carboxylic acids and methanol. This may result in unjustified application of the Clausius–Clapeyron equation to calculate the isosteric heat of adsorption.

Introduction

Recently, growing interest has been observed in the study of the mechanism and kinetics of water sorption on activated carbons.^{1–12} This is due to the fact that very often activated carbons are used as adsorbents and separation media moisture is present. It was shown elsewhere that the presence of water in the gas phase significantly affects the breakthrough curves,¹³ increases sorption of methane,¹⁴ and contributes to the oxidation of hydrogen sulfide.¹⁵

However many papers have been published on water adsorption on activated carbons,^{1–12} the fundamentals of the process are still poorly understood. It is well-known that activated carbons are characterized by a certain degree of surface chemical heterogeneity, which is related to the presence of heteroatoms such as oxygen, nitrogen, hydrogen, and phosphorus. The content of these elements varies, depending upon the nature of an organic precursor and the method of activation.¹⁶ The presence of heteroatoms in various arrangements such as carboxyls, carbonyl, phenols, ketones, amines, and phosphates results in apparent acidity/basicity of the activated carbon surface.^{17,18} It follows that molecules that interact with carbon in a specific way will be adsorbed more strongly and in greater amounts when chemical groups are present.¹⁹ On the other hand, those groups may create obstacles for physical adsorption of nonspecifically interacting molecules, preventing them from occupying the most energetically favorable position on the surface.²⁰

The mechanism of water adsorption was proposed by Dubinin and Serpinsky (DS).²¹ Their interpretation of the shape of experimental isotherms is based on interactions of water molecules with either pure carbon or oxygen-containing surface species. According to the DS theory, water molecules are first adsorbed on primary adsorption centers, oxygen groups, and then adsorption on secondary centers, adsorbed water molecules, occurs. Thus, an increase in the water vapor pressure leads to

the formations of clusters of associated water molecules via hydrogen bonding.^{6,7,12} It was proposed that below $p/p_0 = 0.3$ surface chemistry governs the adsorption process while at higher relative pressure microporosity becomes an important factor.¹ Many experimental results along with their interpretation have been published based on the DS approach.^{1,23,24} In some cases, especially for carbons with a large number of chemical groups, the attempts to fit the experimental data to the proposed isotherm failed.^{2,24}

Recently, Carrasco-Marin and co-workers have presented an approach linking the enthalpies of immersion to the distributions of oxygen groups.³ The authors also demonstrated that water adsorption isotherm may be described as the sum of Dubinin–Astakhov isotherms of types I and V. In the study of the kinetics of water adsorption, Harding et al. observed cluster formation on the basis of changes in activation energy.²² The strong water–water interactions at very low relative pressure were reported by Salame and Bandosz in the discussion of the isosteric heats of water adsorption on carbon with different degrees of oxidation.^{9,10} Much weaker interactions were observed on “clean carbons” where, at very low surface coverage, the heats of water adsorption were much smaller than the heat of water condensation.⁵ A new approach that leads to an understanding of the phenomena of water adsorption on activated carbons employs Monte Carlo grand canonical computer simulations.^{4,8,12} Recent results obtained by Gubbins and co-workers showed a good agreement of molecular simulations with the experimental data.¹²

The objective of this paper is to show how certain chemical modifications of carbon surface may affect the results of adsorption thermodynamic analysis. As an example of such a case, we discuss effects of washing carbon with methanol on H₂O adsorption. It is well-known that carefully measured water isotherms at various temperatures allow one to thermodynamically evaluate the heat of water adsorption provided that the application of the Clausius–Clapeyron equation is justified. It means when the process is reversible, without other components present and when the pressure of only one component is measured. On the basis of the results obtained, we underline

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the possibility of chemical transformations that may take place during the water adsorption process. This is very often neglected in the interpretation of experimental data, and the discussions are limited only to the physical adsorption phenomena. Moreover, our objective is to increase the awareness of the researchers for the situation when they can or cannot use the isotherms to evaluate the energetics of the adsorption process.

Experimental Section

Materials. Activated carbon WVA 1100 (Westvaco, wood-based, H_3PO_4 activation) was chosen for this study. An amount of 10 g of the initial sample, referred to as W, was oxidized with 100 mL of saturated solution of ammonium persulfate ($\text{NH}_4\text{S}_2\text{O}_8$ in 1 M H_2SO_4 for 18 h. The oxidized carbon is designated as W-APS. Then both initial and oxidized samples were washed with methanol in a Soxhlet apparatus for 3 days. Carbons after washing with methanol are referred to as W/M and W-APS/M. The initial sample and the sample after oxidation with ammonium persulfate were extensively washed in Soxhlet to remove water-soluble species and an excess of oxidizing agent.

Methods. Boehm Titration. The oxygenated surface groups were determined according to the method of Boehm.¹⁷ One gram of carbon sample was placed in 50 mL of the following 0.05 N solutions: sodium hydroxide, sodium carbonate, sodium bicarbonate, and hydrochloric acid. The vials were sealed and shaken for 24 h, and then 5 mL of each filtrate was pipetted and the excess of base and acid was titrated with HCl and NaOH, respectively. The number of acidic sites of various types was calculated under the assumption that NaOH neutralizes carboxyl, phenolic, and lactonic groups; Na_2CO_3 —carboxyl and lactonic; and NaHCO_3 —only carboxyl groups. The number of surface basic sites was calculated from the amount of hydrochloric acid that reacted with the carbon.

Potentiometric Titration. Potentiometric titration measurements were performed with a DMS Titrimo 716 automatic titrator (Metrohm). The instrument was set at the mode when the equilibrium pH was collected. Subsamples of the carbons of about 0.100 g in 50 mL of 0.01 M NaNO_3 were placed in a container thermostated at 298 K and equilibrated overnight with the electrolyte solution. To eliminate the influence of atmospheric CO_2 , the suspension was continuously saturated with N_2 . The carbon suspension was stirred throughout the measurements. A volumetric standard of NaOH (0.1 M) was used as titrant. The experiments were done in the pH range of 3–10.^{2,11,25,26}

FTIR. IR spectra were collected using a Nicolet Impact 410 FT-IR spectrometer equipped with a diffuse reflectance unit. The instrument resolution was set at 4 cm^{-1} . Carbon powder was placed in a microsample holder. Before each measurement, the instrument was run to collect the background, which was then automatically subtracted from the sample spectrum.

Thermal Analysis. Thermal analysis was carried out using a TA Instruments thermal analyzer. The instrument settings were the following: heating rate of 10 K/min and nitrogen atmosphere with 50 mL/min flow rate. TG/DTA and DTG curves were obtained and analyzed.

Temperature-Programmed Desorption. Temperature-programmed desorption experiments (TPD) were conducted on a Pulse Chemisorb 2705 (Micromeritics) using helium as a carrier gas. The dried carbon samples of about 0.2 g were placed in a U-shaped quartz reactor and heated at 393 K for 3 h under a helium flow (40 mL/min). Then the flow was changed to 18 mL/min, and after the baseline stabilization the temperature was

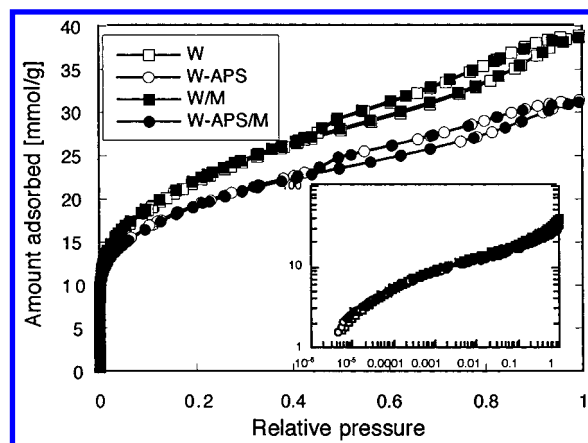


Figure 1. Nitrogen adsorption isotherms.

raised to 1273 K at a rate of 10 K/min. The decomposition products of surface-oxygen-containing groups (CO , CO_2 , and H_2O) were measured by a thermoconductivity detector. Three series of experiments were carried out for each carbon sample in order to separate the products of desorption. In the first step, the total amount of CO , CO_2 , and H_2O was detected. In the second step, the TPD curve for CO was measured using a cold trap with liquid nitrogen located before the detector. Then the curve representing CO and CO_2 was recorded using a cold trap with dry ice. The instrument was calibrated by injection of precise volumes of pure gases (CO and CO_2).

Inverse Gas Chromatography (IGC). The inverse gas chromatographic experiments were performed with an SRI 8610C gas chromatograph (SRI Instruments) equipped with a flame ionization detector. The stainless steel columns (25 cm long, 2.17 mm in diameter) were filled with carbon particles of size ranging from 0.2 to 0.4 mm. Helium was used as a carrier gas with a flow rate of about 108 mL/min. The samples were conditioned at 473 K in the chromatographic column under helium gas flow for 15 h prior to the measurement. The experiments were done at 413 K with methane as the nonadsorbing species. The W-APS/M sample was used for the study.

Sorption of Nitrogen. Nitrogen isotherms were measured using a ASAP 2010 (Micromeritics) at 77 K. Before the experiment the samples were heated at 393 K and then outgassed at this temperature under a vacuum of 10^{-6} Torr to constant pressure. The isotherms were used to calculate the specific surface area, micropore volume (DR method),²⁷ and pore size distributions (DFT).²⁸

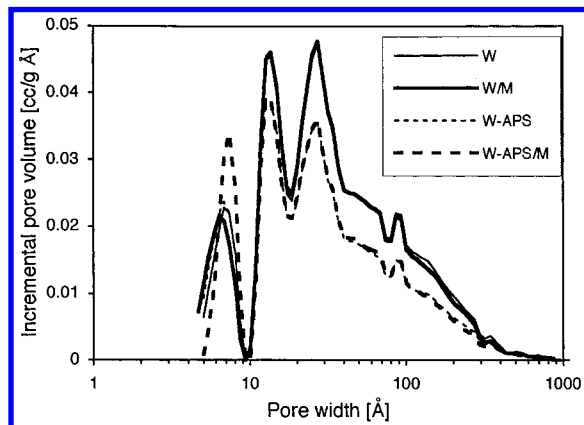
Sorption of Water. Water sorption experiments were carried out at different temperatures close to ambient (283–303 K) using a Micromeritics ASAP 2010 with vapor sorption kit. The instrument was equipped with a homemade thermostated system controlled by a Fisher Scientific Isotemp refrigerated circulator ($\Delta T < 0.1\text{ K}$). For each measurement a new sample was heated at 393 K and outgassed to 10^{-6} Torr. HPLC grade water used as an adsorbate was free of any dissolved gases. Using ASAP 2010, one is able to measure the water uptake starting from a very low relative pressure ($p/p_0 \approx 10^{-3}$). Each point of the isotherm was recorded after an equilibrium had been reached. The measurement of one isotherm to a relative pressure of about 0.3 takes few days because of the slow equilibrium process.

Results and Discussion

Nitrogen adsorption isotherms obtained for four carbons are presented in Figure 1. The calculated structural parameters and pore size distributions are collected in Table 1 and Figure 2,

TABLE 1: Structural Parameters Calculated from Sorption of Nitrogen

sample	S_{BET} [m ² /g]	V_{mic} [cm ³ /g]
W	1710	0.645
W-APS	1472	0.541
W/M	1730	0.561
W-APS/M	1460	0.474

**Figure 2.** Pore size distributions (DFT). (The thick lines (after methanol washing) overlap the thin lines representing samples before treatment.)**TABLE 2: Results of Boehm Titration [mmol/g]**

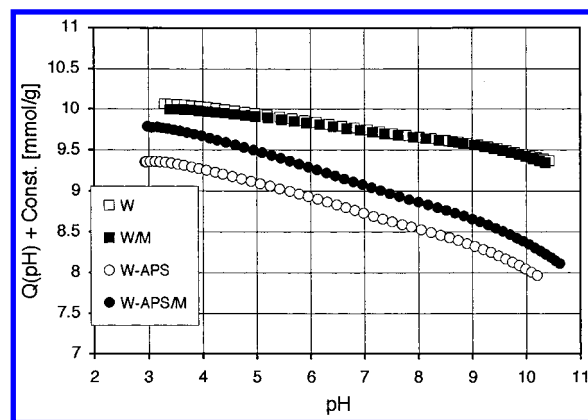
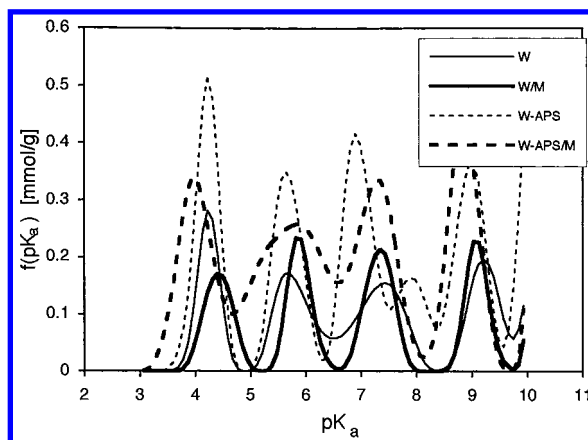
sample	carboxylic	lactonic	phenolic	basic	all acidic
W	0.250	0.250	0.325	0.225	0.825
W-APS	1.238	0.288	0.625	0.113	2.151
W/M	0.200	0.125	0.925	0.350	1.250
W-APS/M	0.980	0.050	1.275	0.050	2.305

respectively. After oxidation with ammonium persulfate, a decrease in the surface area and pore volume is observed as a result of the destruction of some thin pore walls and blocking of pore entrances by oxygen functional groups. As expected, washing with methanol did not cause any significant changes in the structure of carbon samples. A slight increase in the population of small pores can be due to replacement of water molecules with methanol and rearrangement of functional groups at the edges of crystallites.

The effect of oxidation on surface chemistry is much more pronounced. The type and quantity of surface groups were evaluated using the Boehm method.¹⁷ The results are summarized in Table 2. From the analysis of the data it is clearly seen that the oxidation caused a significant increase in the number of carboxylic groups and a small increase in phenols. On the other hand, the number of lactones and basic groups decreased. Overall, the number of acidic groups doubled, resulting in a decreasing pH of the carbon suspension in water.

Interesting results were obtained after washing with methanol; the number of phenols doubled along with a significant decrease in the number of lactones and a small decrease in the population of carboxylic groups. It is noteworthy that the total number of groups was not affected to a great extent by washing with methanol.

Changes in surface chemistry after washing with methanol are also observed from potentiometric titration data. The proton binding isotherms and distributions of acidity constants calculated using the SAIEUS (solution of the adsorption integral equation using splines) procedure employing the regularization method²⁹ are presented in Figures 3 and 4, respectively. The physical and mathematical treatments of the raw titration data were described elsewhere.^{11,25,26,30} Briefly, the proton binding

**Figure 3.** Proton binding isotherms.**Figure 4.** Distributions of acidity constants.**TABLE 3: Results of Potentiometric Titration: Peak Positions and the Number of Groups (in Parentheses; mmol/g)**

sample	pK_a 4-5	pK_a 5-6	pK_a 6-7	pK_a 7-8	pK_a 8-9	pK_a 9-11 ^a	all
W	4.23 (0.139)	5.80 (0.147)		7.31 (0.168)	9.23 (0.141)	10.30 (0.228)	0.823
W/M	4.41 (0.114)	5.91 (0.128)		7.33 (0.139)	9.09 (0.119)	10.35 (0.342)	0.842
W-APS	4.21 (0.272)	5.67 (0.229)	6.95 (0.279)	7.89 (0.109)	8.94 (0.260)	10.25 (0.607)	1.756
W-APS/M	4.06 (0.290)	5.69 (0.362)		7.21 (0.329)	8.85 (0.300)	10.25 (0.687)	1.968

^a Uncertainty of the peak position due to the limit of the experimental window.

isotherms, $Q(\text{pH})$, are first calculated from the titration curves. It is assumed that the system under study consists of sites characterized by their acidity constant, K_a , whose population can be described by a continuous pK_a distribution. Then the integral equation representing the relationship between $Q(\text{pH})$ and $f(pK_a)$ is solved using the numerical SAIEUS procedure.²⁹

The peak positions and the number of groups are collected in Table 3. As expected, oxidation caused an increase in the categories of species detected (a new peak at pK_a about 8) and in the number of groups representing the initial pK_a s. As reported elsewhere, we classify species having $pK_a < 8$ as carboxylic acids and $pK_a > 8$ as phenols and quinones.^{25,26} After being washed with methanol, the total number of groups is not changed significantly; however, a small decrease in the population of strong carboxylic acids ($pK_a < 8$) is noted accompanied by an increase in phenols ($pK_a > 8$)^{32,33} (Table 3). This is in agreement with the results of Boehm titration. A small discrepancy in the number of groups detected is due to the fact that potentiometric

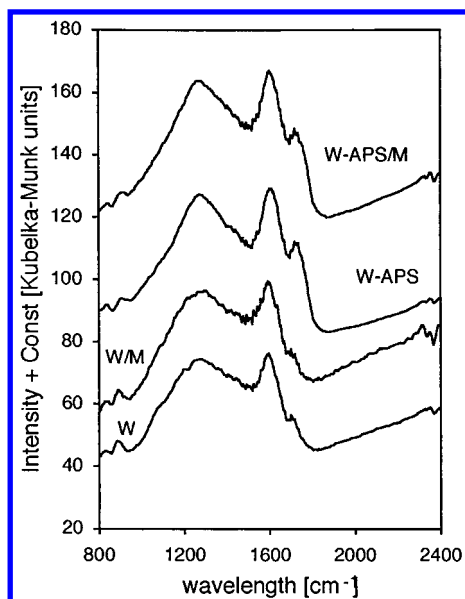


Figure 5. FTIR spectra.

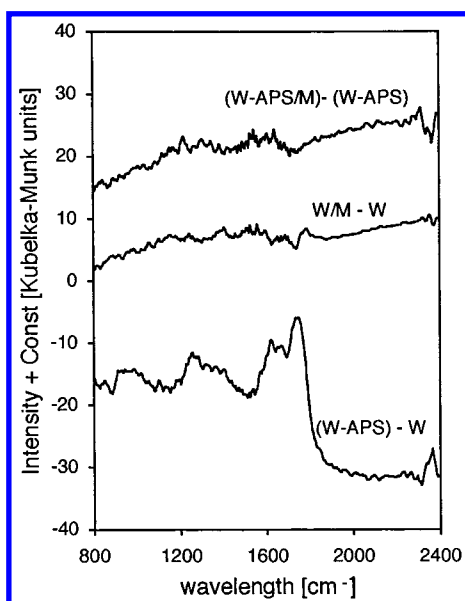


Figure 6. Differences in FTIR spectra for modified samples.

results are reported only in the experimental window between pK_a 3 and 10.

The method that can show us the surface chemistry of carbons in the "dry" form is infrared spectroscopy. The obtained spectra for our samples are presented in Figure 5. The band at around 1700 cm^{-1} is generally due to $\text{C}=\text{O}$ stretching vibrations in carboxyls, ketones, aldehydes, and esters. The presence of a peak at about 1300 cm^{-1} is a result of the $\text{C}-\text{O}$ stretching vibration and is usually the characteristic of alcohol, phenols, carboxylic acids, and esters. According to the approach proposed by Zawadzki³⁴ we link the bands at 1699, 1593, and 1288 cm^{-1} to vibrations of $\text{C}=\text{O}$, $\text{C}=\text{O}$, and $\text{C}-\text{O}$ bonds, respectively. They indicate the presence of various oxygen groups such as carboxyls, lactones, or phenols. To show the effect/lack of effect of modification, we subtracted the spectra of the initial samples from the modified ones³⁵ (Figure 6). The difference between W-APS and W clearly indicates that oxidation significantly increased the intensity of the bands at 1699, 1593, and 1288 cm^{-1} . It is noteworthy that after washing with methanol, the relative intensity of all of these bands is unchanged. This

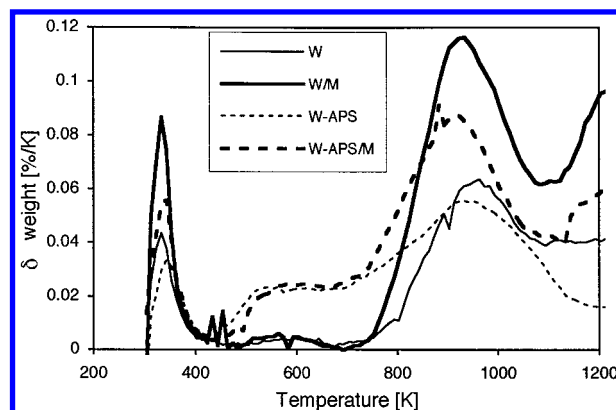


Figure 7. DTG curves.

TABLE 4: Weight Loss at Various Temperatures [%]

sample	300–473 K	473–673 K	637–1073 K	1073–1300 K
W	2.35	0.29	13.20	7.32
W-APS	2.38	4.29	16.43	3.69
W/M	4.10	0.69	24.44	14.32
W-APSM	3.11	4.10	22.88	9.46

suggests that the total balance of the groups remains more or less the same after methanol treatment. Indeed, the introduction of methanol, even though resulting in a decrease in the number of carboxylic groups and lactones accompanied by an increase in phenols, should not create more oxygen–carbon bonds. What is changed is the rearrangement of those bonds in different functional groups, as shown from titration results. Moreover, for carboxylic acids and esters the same bands should be present owing to the fact that both of them possess the same types of $\text{C}=\text{O}$, $\text{C}-\text{O}$, and $\text{C}=\text{O}$ bonds. It follows that one cannot clearly distinguish among those groups using the FTIR technique.

Changes in the amount of oxygen groups can be also evaluated using thermal analysis. It is assumed that during heating at elevated temperatures in an inert atmosphere, the oxygen groups present on the carbon surface decompose to CO and CO_2 . At the temperature range between 475 and 875 K, CO_2 is released from the decomposition of carboxyls and lactones, whereas the decomposition of phenols, quinones, and esters at the temperature range between 875 and 1300 K results in the release of CO.³⁶ Those changes are seen as a weight loss on TG curves and as peaks on DTG and DTA curves. DTG curves obtained for our carbons are collected in Figure 7. Table 4 summarizes the weight loss at various ranges of temperatures. From a comparison of the DTG curves, it is seen that oxidation caused an increase in the weight loss due to the increased number of the decomposed oxygen species. The significant difference in weight loss between W and W-APS is between 475 and 875 K when carboxylic and lactonic groups decompose (Table 4). This is in agreement with the results of Boehm and potentiometric titrations presented above. It is interesting to note that for the samples washed with methanol, thermal analysis does not reveal significant changes in the number of groups decomposing at low temperature; however, the weight loss at temperatures between 775 and 1075 K is significant (Table 4). This weight loss cannot be linked precisely to the presence of specific groups because of the instability of the Westvaco carbon at temperatures higher than 900 K; 900 K is the temperature of its activation. Nevertheless, taking into account that all samples have the same precursor and on the basis of the results of the "wet" titration, this weight loss may be due to an increase in phenols and esters (not detected in "wet" titration), which is supported by further weight loss for the methanol-treated samples between 1075 and 1300 K.

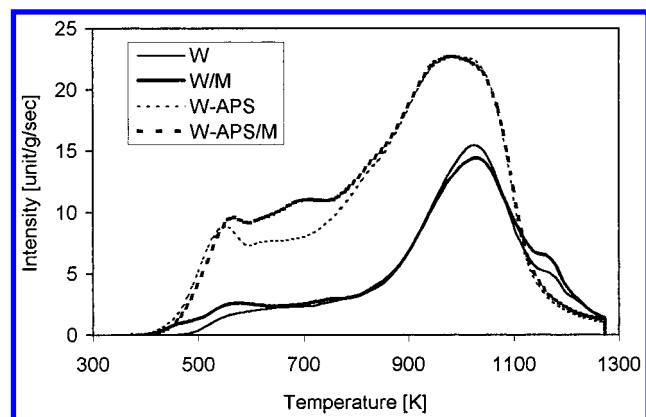


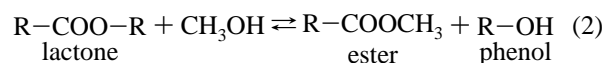
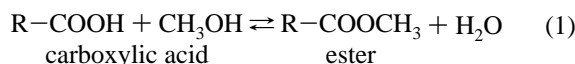
Figure 8. TPD curves.

TABLE 5: Results of TPD Analysis

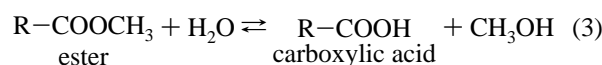
sample	amount of thermodesorbed species [mmol/g]			
	CO	CO ₂	H ₂ O	total
W	2.58	0.41	0.92	3.91
W/M	2.45	0.34	1.04	3.83
W-APS	4.47	1.68	1.25	7.40
A-APS/M	4.70	1.73	1.4	7.83

Information about the effects of oxidation can be also derived from the analysis of TPD curves presented in Figure 8. They represent the total amounts of the decomposed species (CO₂ from carboxyl and lactones at a temperature range between 450 and 900 K; CO and CO₂ from the decomposition of phenols, carbonyls, and pyrenes between 800 and 1300 K; H₂O).³⁶ The amounts of a particular species are collected in Table 5. As expected, oxidation resulted in an increase in the amount of thermodesorbed gases with a significant contribution of decomposed carboxylic acids. After treatment with methanol only slight changes in the spectra are observed at the low temperature range (small increase in intensity). Since titration methods along with FTIR did not indicate an alteration in the overall acidity, this increase in the amount of desorbed species is likely the result of the decomposition of species (not acidic) created as a result of the methanol washing.

An increase in the number of phenols accompanied by a decrease in lactones and carboxyls detected consistently using various methods suggests that during washing with methanol esterification occurs. If the necessary energy is supplied (the system is kept at high temperature around the boiling point of methanol), the following pathways of reactions are expected:³⁷



Then, when exposed to water in “wet” titration methods, hydrolysis occurs:



Reaction 3 needs an acidic environment, which is easily provided by the acidic nature of the carbon surface.³⁸ The proposed pathways of reactions can explain changes in the number of acidic groups detected by “wet” titration methods and changes observed using “dry” approaches. Significant changes in the nature of carbons studied seen from Boehm titration are (1) an increase in phenols and (2) a decrease in

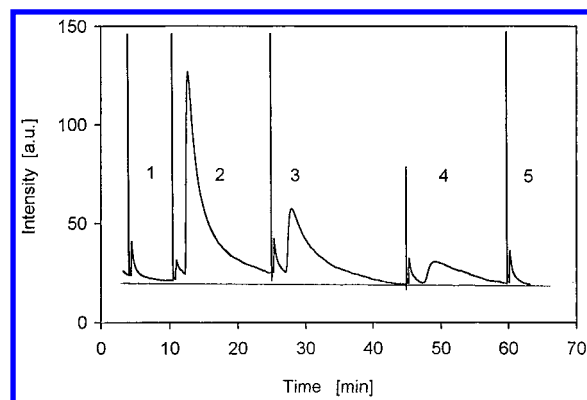


Figure 9. Results of IGC experiments (injection of water and methanol to heat-treated W-APS/M sample).

lactones. This is exactly what we see in reaction 2. The number of carboxyls is not significantly altered, since they are produced from hydrolysis of esters coming from reactions 1 and 2. It is difficult to make mass balance of all the species taking part in these reactions. It is likely that there are species on the carbon surface that are not detected using acid/base titration that may contribute to the above reactions with methanol. Nevertheless, it is worth noting that despite only a slight change in the total number of groups obtained using both “wet” titration methods, their distributions are different. Also, changes in surface chemistry detected by thermal analysis can find their origin in the reaction of esterification; reactions 1 and 2 account for significant peaks on DTG curves between 775 and 1075 K and the offset of a big peak from the decomposition of phenols or/and esters between 1075 and 1300 K.

To check the susceptibility of our carbon for esterification, we performed the inverse gas chromatography experiments^{39,40} (Figure 9). Since the column filled with W-APS/M was conditioned at 473 K, its surface chemistry was changed and it is likely that esters, if present, partially decomposed. In the first step 0.3 mL of water vapor was injected and two peaks were obtained on the chromatogram (1). The first one represents CH₄, and the second one is likely the result of the presence of the impurities. Then 0.3 mL of CH₃OH vapor was added, resulting in a significant nonsymmetrical peak with a maximum at $t_N = 2.8$ min (2). Assuming the esterification was imposed, we subsequently injected 0.3 mL of water vapor (3–5). As a result of this the peak representing methanol reappeared with decreasing intensity (3 and 4). It is noteworthy that it vanished after the last injection (5). These results indicate the hydrolysis of esters created when methanol was injected.

If the above-mentioned hydrolysis occurs, the indication of it should be revealed on the water adsorption isotherms. The examples of isotherms measured for W and W/M at three temperatures are presented in Figures 10 and 11. Although the temperature dependence of the amount adsorbed looks apparently correct for both samples, the subtle but significant discrepancies are seen in a logarithmic scale at a very low pressure range. In the cases of the W and W-APS samples the isotherms show an increase in the amount adsorbed with lowering of the temperature. It is also important that for these two carbons a good reproducibility was obtained. On the other hand, in the case of samples after methanol treatment, the low-pressure ranges of the isotherms sometimes cross each other and it is hard or almost impossible to get good reproducibility (Figure 11). This behavior indicates a lack of equilibrium, which is likely caused by a chemical process (hydrolysis) occurring in the system. When water molecules are adsorbed on the carbon surface decorated with esters, hydrolysis takes place resulting

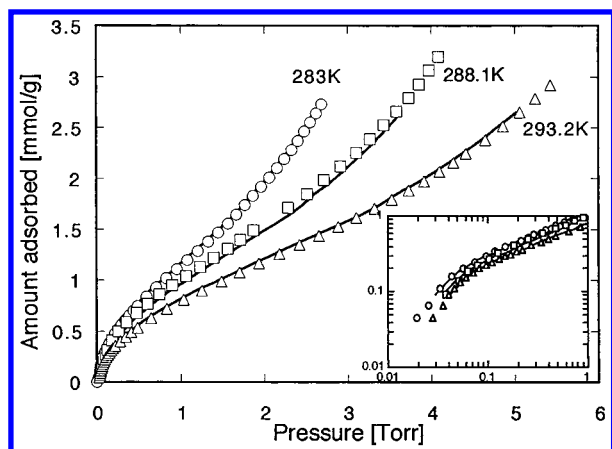


Figure 10. Water adsorption isotherms on the W sample. Solid lines indicate the goodness of the fit to virial equation.

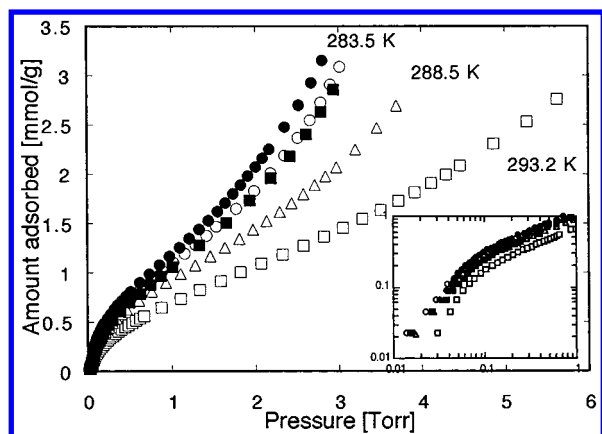


Figure 11. Water adsorption isotherms on the W/M sample.

in the production of carboxylic surface groups and methanol molecules. The presence of methanol contributes to the vapor phase pressure and may block some centers for water adsorption. The apparent result of this is the measured isotherm, which represents sorption of the water–methanol mixture. The shape of the isotherm depends on the partial pressure of both components and the amount of esters able to break into methanol. The latter is directly dependent on the amount of the carbon sample taken for measurement (if we consider replicate samples). Besides the above-described irreproducibility of the measured isotherms and an inconsistency in their temperature dependence, another indication for the occurrence of the hydrolysis and the presence of methanol as a byproduct is a consistent decrease in the amount of water adsorbed for W/M and W-APS/M compared to the samples without methanol treatment (Figure 12). This happens despite their slight increase in the number of acidic groups (Tables 2 and 3). The isotherms were repeated at least three times, and the estimated average standard deviations for three pressure ranges are 0.02 ($p < 0.01$), 0.053 ($0.01 < p < 1$), and 0.11 ($1 < p < 3$).

The correct measurement of isotherms at two temperatures (at least) is necessary to calculate isosteric heats of adsorption, Q_{st} , provided that the process is reversible and equilibrium is reached. A convenient way to calculate the isosteric heat of adsorption from isotherms measured at different temperatures is by using a virial-like equation:⁴¹

$$\ln p = \ln v + \frac{1}{T} \sum_{i=1}^m a_i v^{i-1} + \sum_{j=1}^n b_j v^{j-1} \quad (4)$$

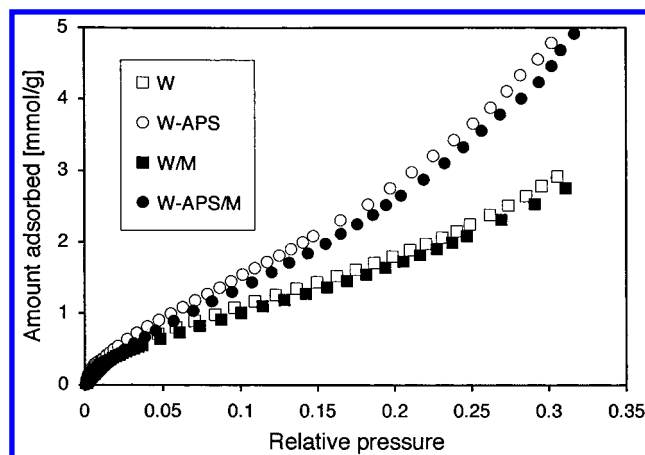


Figure 12. Comparison of the water adsorption isotherms at 293.2 K on carbons before and after washing with methanol.

where v , p , and T are the amount adsorbed, pressure, and temperature, respectively, and a_i and b_i are empirical parameters. This equation was derived under the assumption that in the limited range of temperatures the isosteric heat of adsorption, Q_{st} , is temperature-invariant and that the adsorption isotherms obey Henry's law in the limit of zero pressure. Fitting eq 4 simultaneously to adsorption isotherms obtained at different temperatures gives a set of temperature-independent parameters a_i , which lead to direct evaluation of Q_{st} :

$$Q_{st} = -R \left(\frac{\partial \ln p}{\partial (1/T)} \right)_v = -R \sum_{i=0}^m a_i v^{i-1} \quad (5)$$

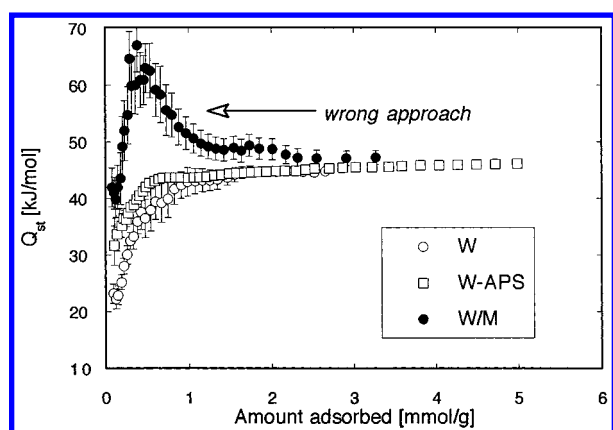
where R is the universal gas constant. Equation 4 was successfully applied to several adsorption systems over a broad range of pressures using relatively low values of m and n .^{20,41,42}

To calculate Q_{st} from isotherms showing the inflection points (Figures 10 and 11), the procedure discussed elsewhere is applied.⁴³ Briefly, eq 4 is fitted to subsets of data points rather than to all experimental data. Each subset comprise N_s data points selected consecutively with respect to v . By considering a sequence of overlapping subsets, one can scan the whole range of data. As an example, the fitting parameters for the W, W-APS, and W/M samples (every fifth subset) are collected in Table 6. From the data of each subset one value of $Q_{st}(v_s)$ is calculated using eq 5. For the value v_s at which Q_{st} is calculated, the average of the minimum and maximum values of v in the subset is chosen. The error range is evaluated according to the approach described elsewhere.^{9,43}

As mentioned above, calculation of the isosteric heats of adsorption requires the reversibility of the process and equilibrium conditions. Analysis of the isotherms of water adsorption obtained for W and W-APS and the fact that they were extensively washed before sorption experiments indicate the esterification reaction does not occur in these two cases. This allows one to calculate Q_{st} , which will represent the meaningful quantity. The results are presented in Figure 13. The obtained heats of water adsorption show common features in their shape: an initial increase reaching the plateau at a value of Q_{st} close to 45 kJ/mol. It was reported elsewhere that 17 kJ/mol is an initial value of the water adsorption heat on the pure carbon surface without water–surface group interactions.^{5,19} In the case of our carbons, the initial rise is due to the interactions of the water molecule with primary adsorption centers, surface groups. When these centers are occupied, horizontal and vertical interactions of water–water take place, raising the heats of

TABLE 6: Virial Parameters (Every Fifth Subset) Obtained for the W (a), W-APS (b), and W/M (c) Samples

subset	a_0	a_1	a_2	b_0
Part a				
1	-2595.93	-2959.82	8835.83	8.77
5	-3213.48	-1808.45	4922.43	10.65
10	-4882.06	1130.89	-653.79	15.06
15	-5147.08	595.59	-173.73	16.49
20	-5699.50	689.91	-220.88	18.20
25	-6064.65	798.29	-226.47	18.95
30	-5561.24	172.13	-41.84	19.04
34	-5495.92	106.46	-25.43	19.03
Part b				
1	-3569.71	-3443.86	10710.39	12.53
5	-4218.89	-1399.68	2922.97	14.33
10	-4801.38	-216.60	631.69	15.81
15	-5407.41	500.82	-207.12	17.35
20	-5537.97	443.67	-145.20	17.84
25	-5580.93	337.31	-93.41	18.17
30	-5548.67	170.63	-36.85	18.48
35	-5435.98	18.95	-1.55	18.65
40	-5432.15	-15.80	0.60	18.89
45	-5440.73	-18.02	-0.27	18.97
49	-5495.66	2.98	-2.67	19.00
Part c				
1	-4813.69	-3957.77	12914.37	16.81
5	-5099.46	-1340.21	3257.60	17.23
10	-7131.74	-977.97	2445.92	24.18
15	-7863.32	580.87	45.00	25.82
20	-7336.85	1578.78	-785.20	22.83
25	-6256.12	457.61	-142.00	20.78
30	-6065.85	138.71	-37.70	20.98
35	-5627.68	-8.65	-2.73	20.01

**Figure 13.** Isosteric heats of adsorption with the calculated error bars.

adsorption to its limiting value, 45 kJ/mol, which represents the heat of water condensation.⁴⁴ It is interesting to note that the water–water interactions become predominant at the very low surface coverage. It follows that the energetics of the process becomes insensitive to the structural and chemical features of the carbon surface. For the oxidized sample, the rise at the beginning is very steep because of the high density of acidic groups.^{9,10} This rise is less steep for the initial carbon, W, where adsorption on oxygen groups gradually takes place, reaching the limiting value at the higher surface coverage. This can be explained by the distribution of groups with relatively large distances between them, which unables the direct interactions of water–water at a very low surface coverage.

To underline the proper conditions for calculation of the isosteric heat of adsorption, a deliberate attempt was made to calculate the heat from the isotherms obtained for the W/M sample (Figure 13). The quantity obtained starts from a much

higher value than for other samples (~ 40 kJ/mol), reaches its maximum at about 70 kJ/mol, and decreases to about 45 kJ/mol. On the basis of the discussion presented above, this Q_{st} does not represent the isosteric heat of water adsorption, and we mark it in Figure 13 as a wrong approach. Moreover, the calculated error is high.

The presence of esters or other groups that can react with water may result from other surface treatments or carbon production methods. Recently, high values for the heat of water adsorption on activated carbons, initial and oxidized, have been reported by some researchers.⁴⁵ Those high heats, ~ 100 kJ/mol, are obtained when the calorimetric technique is used. In this approach the cumulative heat effect of the process is measured. Such high values may indicate the heat of the chemical reaction of water with carbon surface functional groups, which is beyond the physical adsorption process. The discussion presented in this paper indicates that the surface functionality of activated carbon used for an experiment strongly depends on the pretreatment procedure and the history of the samples. In our case we pointed out the hydrolysis. However, the heat effect of this reaction is not high;³⁸ we evaluated it to be a maximum value of 12 kJ/mol for esters involved in aromatic rings. The probability for the hydrolysis of esters during water sorption seems to be high when carbons are unwashed (as received) and oxidized using “dry” methods such as heating in air. In some cases, especially when the surface is very complex from a chemical point of view and susceptible for reaction with water, it is practically impossible to be aware of all reactions occurring in the system. In such a situation adsorption of byproducts such as methanol occurs, which may contribute to the measured heat effect. The hydrolysis of esters presented here is just an example for consideration.

Conclusions

The results presented in this paper show significant changes in surface chemistry due to washing with methanol. These changes are due to esterification, leading to an increase in the number of phenols and esters. The esters, when in contact with water, are hydrolyzed, giving carboxylic acids and methanol as products. When the probability of such a reaction exists, one cannot use the isotherms to calculate the isosteric heats of adsorption owing to irreversibility, nonequilibrium conditions, and the presence and adsorption of another component, methanol. That the Clausius–Clapeyron equation can give accurate results in the case of water adsorption can be made on the basis of the history of samples, their surface chemical inventory, reproducibility of isotherms, and the analysis of their thermodynamic dependence. In the case when only physical adsorption is considered, the calculated isosteric heats of adsorption represent meaningful quantities.

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