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Heterogeneity of Adsorption Energy of Water, Methanol and Diethyl Ether on Activated Carbons

VLADIMIR GUN'KO*
Institute of Surface Chemistry, 17 General Naumov Street, 03164 Kiev, Ukraine
vlad-gun@in.ua

TERESA J. BANDOSZ
Department of Chemistry, The City College of New York, New York, NY 10031, USA

Abstract. Three samples of activated carbon of wood origin with various amounts of surface functional groups and different porous structure were used as adsorbents of water, methanol, and diethyl ether. Then the isotherms at three different temperatures were used to calculate distributions of adsorption potential, free energy of adsorption and adsorption energy. The results showed that the strength of interactions depends on both the porosity of the sample and its surface chemistry. The effect of surface chemistry is the most important in the case of water and the least important in the case of diethyl ether. The high-energy centers are related to adsorption in narrow pores containing functional groups. For molecules consisting of hydrocarbon moiety and oxygen containing groups (methanol and diethyl ether) the surface chemistry plays a role at low surface coverage.

Keywords: adsorption energy, activated carbon, surface heterogeneity

Introduction

Activated carbons due to the high sorption capacity are able to remove or separate traces of air and water contaminants. Such functions are linked to their high surface area, large pore volume, and the presence of pores diameter of few Angstroms. Those features play a significant role in the process of physical adsorption when only non-specific, dispersive interactions with the molecules to be adsorbed take place. For specific adsorption and chemisorption the surface chemistry of carbon becomes a crucial feature (Leon y Leon and Radovic, 1992). When the medium from which molecules to be removed are present is also able to interact in a specific way with a carbon surface competition for high energy sites exists and the feasibility of the removal process depends on the size of molecules, their chemical nature and the surface features of the adsorbent (Bagreev et al., 2002).

The objective of this paper to evaluate the energy of interactions of water, methanol and diethyl ether on oxidized activated carbons and the effects of carbon structure and chemistry on those interactions. Following the chemical nature of the molecules, the specific interactions via hydrogen bonding with surface functional groups should be the most pronounced in the case of water and the least pronounced in the case of diethyl ether (Salame and Bandosz, 2001). The sizes of pores should also play a role due to the various diameters of the molecules. Water molecule having $d \sim 2.9$ Å should be able to enter the narrowest pores of the adsorbents whereas some small pores would be excluded for diethyl ether molecule. The carbons chosen for this study were described in detail elsewhere (Salame and Bandosz, 2000). Here we only report parameters used for data interpretation.

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*To whom correspondence should be addressed.

Materials and Methods

Wood based activated carbons supplied by Westvaco were used for this study. They are WVA-1100 and developmental ultramicroporous carbon, UMC. The samples were oxidized using nitric acid, The details of oxidation are described elsewhere (Salame and Bandosz, 2000). Oxidized sample are referred to as WVA-O and UMC-O, respectively. The amounts of surface functional groups were evaluated using Boehm titration (Boehm, 1994). The structural parameters were calculated from nitrogen adsorption isotherms using either density functional theory (Lastoskie et al., 1993), or Dubinin-Astakhov approach (DA) (Dubinin, 1980). Water and methanol adsorption isotherms were measured at different temperatures close to ambient (283–303 K) using ASAP 2010 (Micromeritics) with a vapor sorption kit. Inverse gas chromatography (IGC) at finite concentration was used to obtain adsorption isotherms for diethyl ether on the carbon samples at 393–433 K (Salame and Bandosz, 2001).

Calculations

To characterize the adsorptive properties of carbons, the adsorption potential distributions ($f(A)$) were calculated as $f(A) = -d[spline(a(p/p_0))]/dA$, where a refers to the adsorbed; and $A = -\Delta G = R_g$ Tln (p_0/p) and represents the differential molar work equal to the negative change in the Gibbs free energy (Kruk et al., 1999). To calculate the free energy distributions ($f(\Delta G)$) of adsorption, the Langmuir equation (Adamson and Gast, 1997) was used as the kernel of the of Fredholm integral equation of the first kind. The Fowler-Guggenheim (FG) equation was used to describe localized monolayer adsorption with lateral interactions (Jaroniec and Madey, 1988). This equation was used as a local isotherm in the overall adsorption isotherm equation to calculate the distribution function $f(E)$ of the adsorption energy for different adsorbates. Calculations of changes in the Gibbs free energy on adsorption of water and methanol were performed using the Bender equation of the state of fluids and a simple equation $\Delta G = -$ RT ln $(x/(1-x))$, where $x = a_{\mathrm{ads}}/(\rho_{\mathrm{gas}}(\mathrm{V}_p - a_{\mathrm{ads}}/\rho_{\mathrm{liq}}) + a_{\mathrm{ads}})$, $\mathrm{a_{ads}}$ is the amount of adsorbate (liquid); V_{p} is the pore volume, $\rho_{\mathrm{gas}}(p, T)$ is the density of adsorbate vapor (calculated by using the Bender equation), $\rho_{\mathrm{liq}}(\mathrm{T})$ is the liquid density (Platzer and Maurer, 1989).

Results and Discussion

The structural parameters of the carbons studied are collected in Table 1. The adsorbents differ in porosity. UMC is highly microporous whereas in the porosity of WVA a significant contribution of mesopores exists. Although the total volumes of pores are similar, the micropore volume of UMC is twice of that for WVA. After oxidation the surface area and volume of pore slightly decrease either as a result of destruction of thin pore walls or blocking of pore accessibility by functional groups introduced to the surface.

Indeed, acid treatment changed the surface chemistry of carbons. Comparison of the initial samples indicates that WVA is more acidic than UMC. Oxidation significantly increased the acidity of UMC forming only acidic groups such as carboxylic, lactonic of phenolic. Overall, the susceptibility of both carbons for oxidation seems to be similar, which is likely caused by the same nature of organic precursor.

Changes in the nature of the adsorbent surfaces after oxidation should play more significant role in the adsorption of polar compounds such as water and methanol than nitrogen. Example of the comparison of water and methanol adsorption isotherms at 283 K is presented in Fig. 1.

Table 1. Structural parameters of carbons (S-surface area (BET or DFT), V_t-total pore volume, V_{mic}-micropore volume (DFT), V_{DA}-micropore volume from DA eq., x_{DA}-average size of micropores (DA equation) and Amounts of surface functional groups evaluated from Boehm titration

Sample	S_{BET} ($\mathrm{m^2/g}$)	S_{DFT} ($\mathrm{m^2/g}$)	S_{mes} ($\mathrm{m^2/g}$)	V_t ($\mathrm{cm^3/g}$)	V_{mic} ($\mathrm{cm^3/g}$)	V_{DA} ($\mathrm{cm^3/g}$)	X_{DA} (nm)	Acidic	Basic	All
WVA	1710	1100	729	1.33	0.41	0.49	0.92	0.38	0.08	0.47
WVA-O	1470	1010	527	1.07	0.38	0.47	0.84	0.88	0.04	0.92
UMC	2300	1790	273	1.23	0.78	0.94	0.70	0.25	0.12	0.37
UMC-O	1970	1570	228	1.07	0.68	0.82	0.70	0.74	0.00	0.74

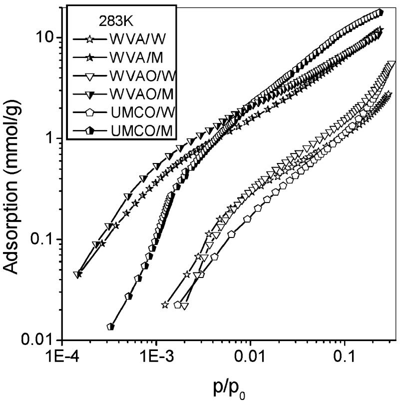

Figure 1. Water (W) and methanol (M) adsorption isotherms at 283 K.

Since methanol can more effectively interact with hydrophobic surfaces of activated carbons, its adsorption is significantly greater than that of water. The amount adsorbed increases after oxidation, especially at low relative pressure range, as a result of formation additional centers for specific adsorption via hydrogen bonding (Fig. 1). Since oxidation decreases volume of micropores (Table 1), the isotherms for WVA and WVA-O cross over, at higher pressures, close to saturation.

Figure 2 presents the distributions of water and methanol adsorption potential. Significant differences in methanol adsorption between the carbons studied exist at high values of A, greater than 15 kJ/mol. These differences are likely related to the presence of functional groups being able to interact with methanol in a specific way (Salame and Bandosz, 1999). Indeed, closer look at that $f(A)$ indicates the following decreasing order of the potential: WVA-O, WVA, and UMC-O. For one carbon, WVA, this order is in the agreement with the density of the oxygen containing groups on the surface. As indicated elsewhere, in the case of energetics of adsorption comparison should be made within one category of material due to difficulties in clear separation of the contributions from pore sizes and surface chemistry (Salame and Bandosz, 1999b). For adsorption potential close to 15 kJ/mol the highest population of adsorption centers is found for UMC-O carbon. Those centers are likely micropores whose volume is much larger for UMC-O than for the WVA series. For adsorption potential smaller than 7 kJ/mol, $f(A)$ for WVA lies over that for WVA-O as a result of slightly higher volume of micropores for the former material. The plots of the water adsorption potential distribution shift towards lower A values in comparison with methanol (Fig. 2) due to weaker dispersive interactions of water molecules (than methanol) with the carbon surfaces.

It is well known that methanol interacts with different carbon structures stronger than water due to the availability of the hydrophobic surfaces. It is important to mention that $\Delta G_{s,\text{water}}$ for carbon clusters consisting pure carbon atoms is calculated to be positive (~3 kJ/mol) due to low wetting ability of water with respect to such hydrophobic surfaces. Nevertheless if a water cluster with six molecules is already in the hydrophobic narrow pore $\Delta G_{s,\text{water}}$ reaches negative values (−23 kJ/mol). In the case of oxygen functional groups at the edges $\Delta G_{s,\text{water}} < 0$ (as well as ΔG_s for solvation in methanol or diethyl ether) and close to $\Delta G_{s,\text{ether}}$. For the cluster consisting of only carbon atoms $-\Delta G_{s,\text{methanol}} < -\Delta G_{s,\text{ether}}$ but for the model with oxygen groups present at the edges, $-\Delta G_{s,\text{methanol}}$

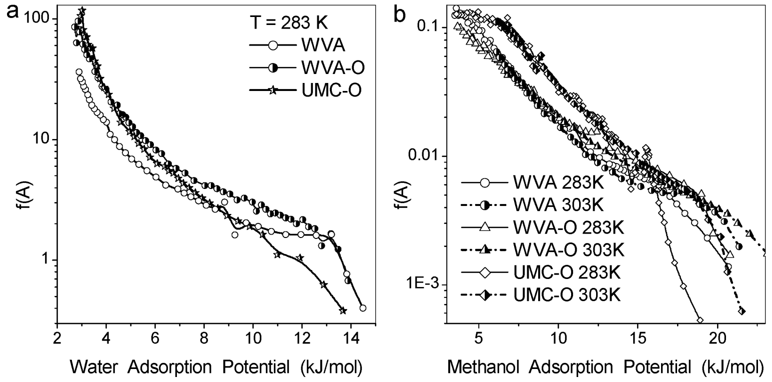

Figure 2. Water (a) and methanol (b) adsorption potential distributions.

$> -\Delta G_{s,\text{ether}}$ due to contribution of electrostatic interaction component to ΔG_s. These results are in agreement with calculations of the $f(\Delta G)$ and $f(E)$ distribution functions for water, methanol, and diethyl ether (Figs. 3–6).

The relationships between the porous structure of carbons and adsorption characteristics of water and methanol are seen in the plots of $f(\Delta G)$ (Fig. 3).Although for methanol (Fig. 3), small differences in the $f(\Delta G)$ plots calculated from measurements at various temperatures exit, the highest energy centers are found for WVA-O which has the highest density of surface groups. The peaks at free energy higher than 10 kJ/mol represent specific hydrogen bonding interactions in narrow pores (entrances into narrow micropores). Either for WVA-O or WVA the low-energy peaks linked to dispersive interactions are narrow and the highest energy end reaches 5 kJ/mol. On the other hand, for UMC-O the energy of dispersive interactions is higher than that for the WVA series. This happens due to the presence of smaller pores in the former carbon. Similar trends are seen on the energy distributions for methanol adsorption calculated using the Fowler-Guggenheim equation (Fig. 4).For WVA and UMC-O two peaks are revealed. As indicated above, they represent hydrogen bonding and cluster formation in small pores (the high-energy peak) and dispersive interactions in small pores, respectively. In the case of WVA-O an additional peak appears at low energy at about 20 kJ/mol.

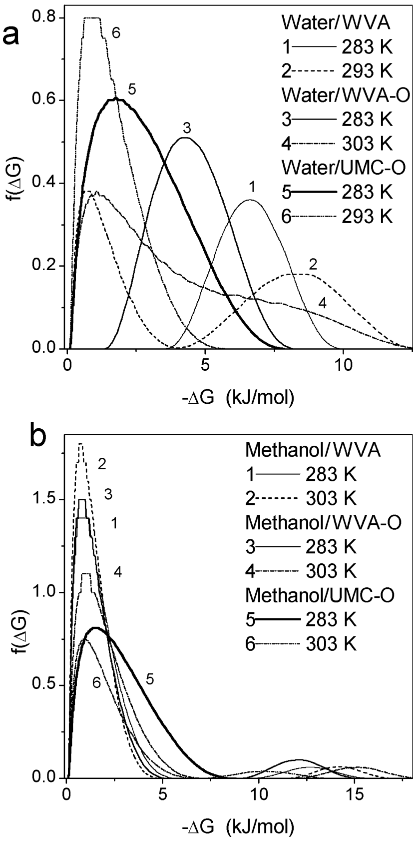

Figure 3. Distributions of changes in the Gibbs free energy of water and methanol adsorption.

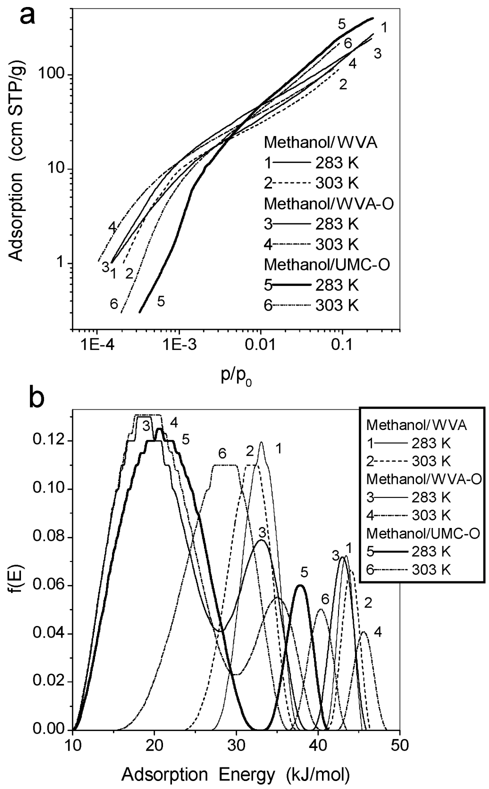

Figure 4. Methanol adsorption isotherms and corresponding distributions of adsorption energy.

The energy of the peak representing specific interactions (cluster formation) in small pores is the highest for WVA-O carbon following its highest density of oxygen containing groups. For UMC-O this peak covers the broadest energy range and starts the lowest energy. The appearance of the low energy peak on WVA-O carbon is likely the result of the presence of larger pores formed as a result of oxidation (Salame and Bandosz, 2000). The positions of those peak overlap with the dispersive interactions for UMC-O, which supports its

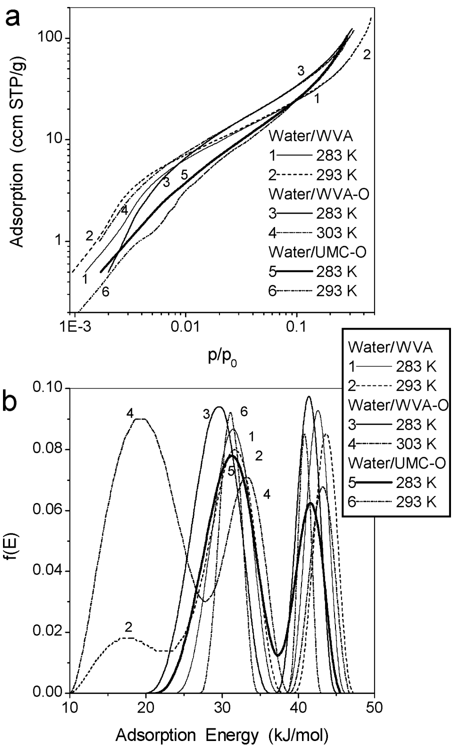

Figure 5. Water adsorption isotherms and corresponding adsorption energy distributions.

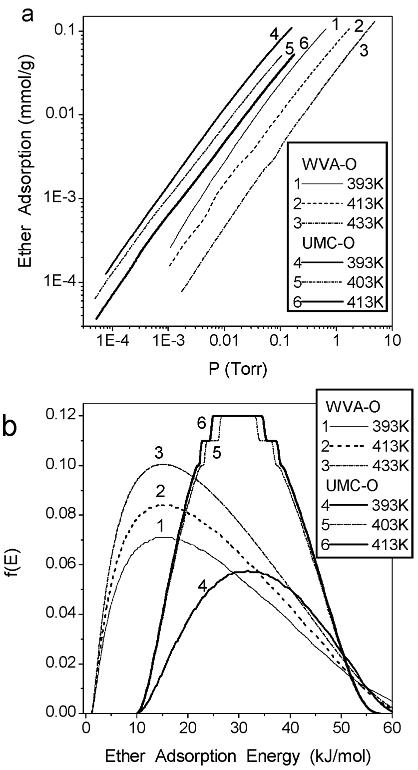

Figure 6. Diethyl ether adsorption isotherms and corresponding adsorption energy distributions.

origin in the oxidation and structural changes in the nature of wood based activated carbon. The values of adsorption energy are in the range of the heats of adsorption found for these carbons (Salame and Bandosz, 1999a).

The free energy for water adsorption once again has the lowest value for UMC-O. In the case of WVA series of carbons, for the highest adsorption temperature, the distribution of ΔG reveals higher degree of heterogeneity than that for UMC, which is expected based on the nitrogen adsorption and Boehm titration results. The centers with the highest energy are present for WVA-O (Fig. 3). It is important to mention that the Langmuir model does not seem to be appropriate for water adsorption and may lead to the erroneous results. When the energy distributions are calculated using Fowler–Guggenheim equation more differences in the energetic of adsorption are noticed (Fig. 5). For UMC-O two narrow peaks are found at 41 and 30 kJ/mol. They represent water condensation in small pores on oxygen containing groups and cluster formation in larger pores, relatively homogeneous in their size, respectively. For WVA, besides those two peaks at almost identical positions as for UMC-O, the low energy peak, centered at about 20 kJ/mol is found. Since dispersive interactions of water with the carbon surface are very weak, we link that peak to the adsorption of water on functional groups in larger pores where full condensation does not occur due to the big pore sizes. It is interesting to notice that the intensity of that peak increases significantly for WVA after oxidation as a result of formation of more oxygen containing groups. As in the case of methanol, the energy ranges are similar to those obtained for isosteric heats of adsorption (Salame and Bandosz, 1999b).

Since interactions of diethyl ether with carbons were studied at relatively high temperature, the adsorption energy distributions are broad (Fig. 6) and independent of the regularization parameter value.

Figure 7 shows that the dependence of ΔG on p/p_0 (p and p_0 denote the equilibrium and saturation pressures of the vapor) is non-linear. This non-linearity may be connected to interaction not only of adsorbate-adsorbent but also adsorbate-adsorbate molecules. For instance, a decrease in ΔG for adsorbed water at $p/p_0 > 0.1$ can be caused by formation of the hydrogen

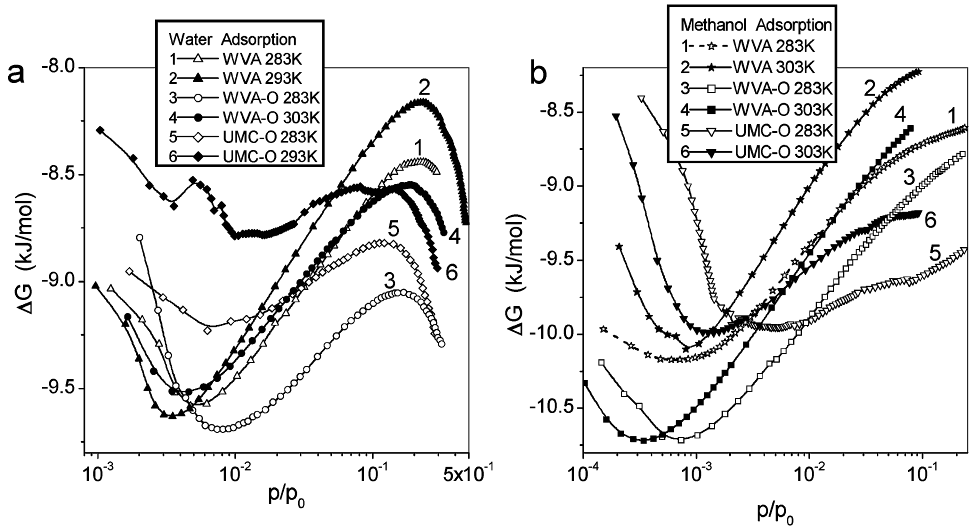

Figure 7. Changes in Gibbs free energy upon relative pressure for adsorption of water (a) and methanol (b).

bonds between water molecules at coverage higher than that of a monolayer. The difference in the behavior of $\Delta G(p/p_0)$ for water and methanol shows slightly stronger interaction of methanol with oxidized carbon WVA-O.

Conclusions

The results presented in this paper show the significance of the specific interactions to the process of physical adsorption of polar compounds. When the dispersive interactions of the molecule with the carbon surface are weak (water) or comparable to dispersive interactions of hydrocarbon moiety (methanol) the high-energy centers for adsorption are located in narrow pores where functional groups are present (e.g. at the entrances to the pores). In the case of diethyl ether for which dispersive interactions of hydrocarbon moiety are much stronger than hydrogen bonding, the broad, one-peak energy distribution is revealed, suggesting adsorption on one, heterogeneous group of adsorption centers. This can be the result relatively high adsorption temperature. For small polar molecules the heterogeneous (multi center) distributions are obtained indicating sensitivity of the physical adsorption process on the size of the molecule, its chemistry and sizes of carbon pores along with chemical heterogeneity of the surface.

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