DIETHYL ETHER ADSORPTION ON ACTIVATED CARBONS: AN IGC STUDY

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Introduction

Diethyl ether with the chemical formula $(C_2H_5)_2O$ is a polar molecule that can interact with the carbon surface via dispersive interactions of its hydrocarbon moiety, two ethyl groups. It can also be hydrogen bonded to oxygen containing surface functional groups such as carboxylic and phenolic compounds. In addition, ether is capable of donating a pair of electrons from the oxygen lone pairs and thus interacts with the electron pair receptors on the surface as a Lewis base [1]. The heat of diethyl ether adsorption on carbon black was reported to be about 36kJ/mol [2]. When adsorption of various ethers on amorphous nitrogenated carbons was studied the desorption energy of diethyl ether was found to be between 50 to 60 kJ/mol [1].

The objective of this paper is to study the adsorption of diethyl ether on two activated carbons of wood origin. The samples significantly differ in the porosity and surface chemistry due to their preparation by different activation methods [3]. These differences allow us to study the effects of oxygen containing surface groups and pore sizes, on the adsorption processes. The mechanism of adsorption is analysed based on the adsorption uptakes and the energetic of adsorption expressed as isosteric heats of adsorption.

Experimental

Two activated carbons of wood origin supplied by Westvaco were used for this study. The first carbon, WVA 1100 is referred to as WVA. It is obtained using phosphoric acid activation at 900 K [4]. The second carbon, designated as UMC, is a developmental adsorbent manufactured by KOH activation of WVA 1100 at 1300 K]. Both carbons were oxidized with ammonium persulfate [6, 7]. Prior to any analysis, the samples were washed in an Soxhlet apparatus to remove both water-soluble species and excess oxidizing agent (when oxidation was applied). Samples obtained after oxidation are referred to as WVA-O and UMC-O, respectively.

Methods

Boehm Titration.

Boehm titration method was used to assess oxygen-containing surface groups [8,9]. In method 1 gram of carbon is placed in 50.0 mL of the following 0.05 N solutions: sodium hydroxide, sodium carbonate, sodium bicarbonate, and hydrochloric acid. The vials are then sealed and shaken for 24 hours and the carbon suspension is filtered. 5 mL of each of filtrate is titrated with acid or base (HCl and NaOH). The number of acidic sites is calculated using the assumption that NaOH neutralizes carboxylic, phenolic and lactonic groups; Na_2CO_3 neutralizes carboxylic and lactonic; $NaHCO_3$ neutralizes only carboxylic groups. The number of basic sites is calculated from the amount of HCl that reacted with the carbon.

Sorption of Nitrogen.

Nitrogen isotherms were measured using an ASAP 2010 (Micromeritics) at 77 K. Before each experiment the samples were heated at 393 K and outgassed at this temperature under a vacuum of 10^{-5} Torr. The isotherms were then used to calculate specific surface area, micropore volume, V_{mic}, volume in pores smaller than 10 Å, $V_{<10Å}$, and pore size distribution. All these parameters were obtained using density functional theory, DFT [10].

Sorption of Diethyl Ether.

Inverse gas chromatography (IGC) at finite concentration was used to obtain adsorption isotherms for diethyl ether on the carbon samples. This method provides a useful way to determine isotherms of vapors, which are environmentally hazardous or may interfere with instruments of volumetric or gravimetric measurements [11, 12]. An important condition of measurement is the linearity of the detector's response. This condition is fulfilled by checking if several injections of different amounts of solute lead to chromatographic peaks whose tails superimpose [12]. According to this method, one single peak can be used to calculate the experimental isotherm [13-18].

In the characteristic point elution method [21-27] the total amount of solute adsorbed on the solid support is calculated from the following formula:

$$V = \frac{F_C}{m} k \int_0^h (t - t_0) dh \qquad (1)$$

where V is the amount adsorbed, F_c is the corrected flow of helium gas through the column [9], m is the weight of the adsorbent, and t and t_0 are the retention times of adsorbat and nonadsorbed species, methane, and k is a proportionality constant between the height of the peak h and the corresponding concentration at that particular height, c_i. Using this equation, one can divide the chromatographic peak into i slices that corresponds to i pressures and injected amounts [3, 19, 20] and thus:

$$C_i = \frac{q \bullet h_i}{F_C \bullet S_{peak}} \qquad (2)$$

where q is the injected amount, and S_{peak} is the area of the chromatographic peak. To transform concentration into pressure the following expression is used:

$$P_i = C_i \bullet R \bullet T \qquad (3)$$

where R is the ideal gas constant, and T is the temperature of the column in Kelvins. The amount adsorbed at different i's can be calculated from the following equation [12]:

$$V_i = \frac{q \bullet S_i}{m \bullet S_{peak}} \qquad (4)$$

where S_i indicates the adsorbat holdup contribution and is the area at h_i but it differs from S_{peak} in the respect that it includes the adorbat holdup time.

The chromatographic experiments were carried out using a SRI 8610 gas chromatograph. Helium was used as a carrier gas. The flow rate was measured at the outlet of each column and was corrected for pressure drop across the column [19-21]. Before each experiment the column was conditioned by heating it to 473 K for 12 hours, under helium flow, to remove impurities form the carbon surface. The column used was a 1.0 meter long and 3 mm in diameter. The amount of diethyl ether injected ranged from 1 to 5 μl. Temperatures of the measurements were between 393 K and 433 K. The areas corresponding to the chosen pressure were calculated using the software package from SRI instrument

Results and Discussion

Carbons WVA and UMC have the same wood precursor, however, they are manufactured using different activation methods. As described in detail elsewhere [3], the samples significantly differ in their pore structure an surface chemistry. Here we summarized the basic parameters of carbons' surfaces in Tables 1 and 2. Figure 1 shows the pore size distributions calculated from nitrogen adsorption isotherms using density functional theory (DFT) [10]. From analysis of the data it is clearly seen that the surface area and micropore volumes of UMC are about 60% higher than those of sample WVA. Also volumes of pores smaller than 10 Å are more than twice larger in the case of UMC and UMC-O compared to WVA and it oxidized counterpart. It is worth to mention that the volume of small pores increased in the case of WVA-O, contrary to the expected decrease due to the destruction of pore walls [22, 23]. Figure 1 demonstrates that for sample UMC, most of the pores are smaller than 30 Å whereas in the case of WVA we have a large contribution of mesopores. Oxidation resulted in about 15 % reduction in the surface area and pore volume.

Table 1.
Structural parameters calculated from nitrogen adsorption isotherms measured at 77 K

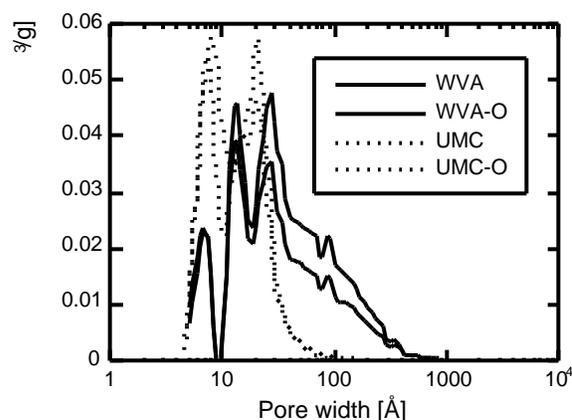| Sample	S [m²/g]	V_{mic} [cm³/g]	$V_{<10Å}$ [cm³/g]
WVA	1100	0.410	0.121
WVA-O	1010	0.385	0.134
UMC	1790	0.786	0.409
UMC-O	1570	0.682	0.353

Figure 1.
Pore size distributions (DFT) for the samples studied.

Summary of the results of Boehm titration (in molecules per square nanometer of the surface) is presented in Table 2. The details are described elsewhere [3]. Here only carboxylic acids and phenols are included. They can

contribute to diethyl ether adsorption providing sites for hydrogen bonding. When the initial samples are considered, WVA appears to be more acidic than UMC. After oxidation more groups are introduced on the surface of UMC-O carbon than on that of WVA-O carbon.

Table 2.
Surface chemistry of carbons (Boehm titration results [molecule/nm^2])

Sample	Carbox.	Phenolic	Carboxylic + Phenolic	All groups
WVA	0.137	0.219	0.356	0.739
WVA-O	0.738	0.373	1.111	1.350
UMC	0.042	0.223	0.256	0.488
UMC-O	0.532	0.254	0.786	0.940

Examples of the isotherms of diethyl ether adsorption on the initial UMC samples are presented in Figures 2. The isotherms are calculated from chromatographic peaks according to the method described above [12]. Very small pressure values indicate that the surface coverage is low.
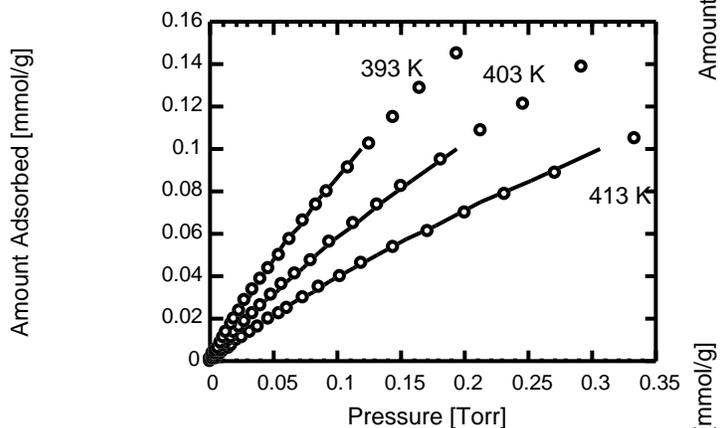

Figure 2
Diethyl ether adsorption isotherms on sample UMC. (Solid lines indicate the goodness of the fit to eq.5).

Figure 3 shows the comparison of the isotherms for four carbons studied obtained at common temperature, 393 K. In order to study the effect of surface chemistry and pore structure on the diethyl ether uptake the adsorption at arbitrary pressure, equal to 0.05 torr, was compared. Figure 4 shows the dependence of the amount adsorbed at 0.05 torr on micropore volume of carbons and volume of pores smaller than 10 Å. In both cases good correlation coefficients were obtained (R^2 = 0.90, and R^2 = 0.95 for V_{mic}, and $V_{<10Å}$, respectively). It is interesting that the amount adsorbed does not correlate well with the surface density of acidic groups, either specific carboxylic, or all acidic groups reported in Table 2 (correlation coefficients

equal to 0.36 and 0.62, respectvely). These results suggest that at the arbitrary chosen pressure the pore volume is a predominant factor governing the behavior of carbons as diethyl ether adsorbents. A closer look at the isotherms plotted in a logarithmic scale shows that at very small pressure, for the extremely low coverage, the adsorption uptake on WVA is higher than that on UMC, however, the trend in the pore volume is opposite (Table 1). This suggests that surface chemistry can be a driving force for adsorption phenomena only at the beginning of the process. Indeed, the density of surface acidic groups is twice higher for WVA compared to that for UMC carbon (Table 2).
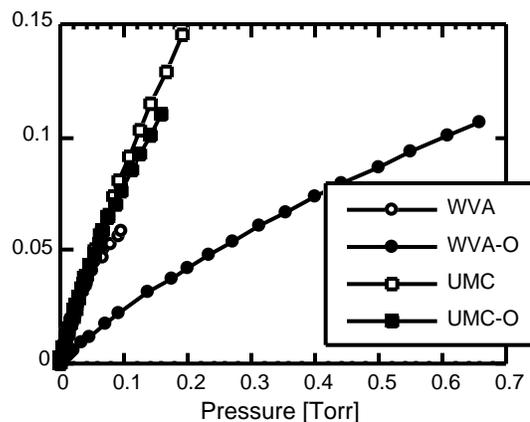

Figure 3.
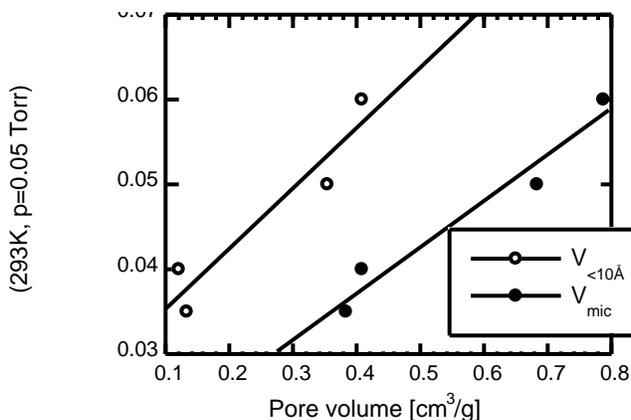Diethyl ether adsorption isotherms at 393 K on the samples studied

Figure 4.
Dependence of the amount adsorbed at 393K and p = 0.05 torr on the pore volumes of carbons

In the discussion of the mechanism of diethyl ether adsorption on activated carbons it is important to

emphasize the balance of the adsorption forces which play a role in this process. Those forces are very strong dispersive interactions of the hydrocarbon moiety with carbon pore walls, which were found to be equal to 36 kJ/mol on a flat carbon surface [8], and hydrogen bonding of diethyl ether oxygen with surface functional groups, such as carboxyls or phenols. The later interactions are weak compared to the former ones (less than 12 kJ/mol [2]). It follows that even though the dispersive interactions and hydrogen bonding can coexist the overall effect can give the energy value where it maybe impossible to distinguish between the two phenomena.
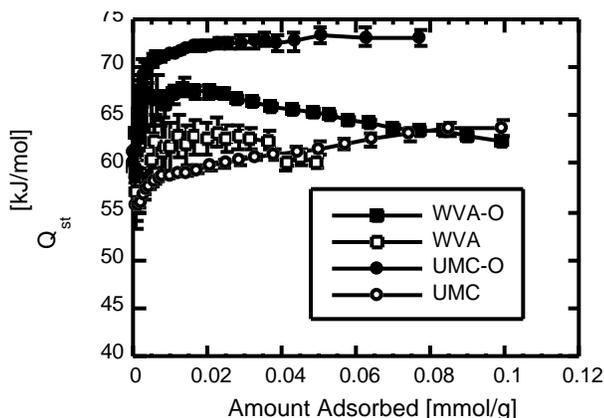

Figure 5.
Isosteric heats of diethyl ether adsorption on the samples studied.

Based on the analysis of the shapes of isotherms and a crossover observed at a very low surface coverage we can conclude that the mechanism of adsorption is somehow different at low pressure. As a result of this the small contribution of hydrogen bonding is visible. Information about the mechanism of the adsorption process can be obtained from analysis of isosteric heats of adsorption, Q_{st}. They were calculated from the isotherms using a virial type equation [24]. This equation has been successfully applied to systems where equilibrium is reached and the adsorption process can be reversible [6, 7, 24-27]. The virial equation has the following form:

$$\ln p = \ln v + \frac{1}{T} \sum_{i=1}^{m} a_i v^{i-1} + \sum_{i=1}^{n} b_i v^{i-1} \tag{5}$$

where v, p, and T are the amount adsorbed, pressure, and temperature, respectively. a_i and b_i are empirical parameters. The above equation was derived under the assumption that over a limited range of temperatures, the

isosteric heats of adsorption is temperature invariant and the adsorption isotherm obeys Henry's law in the limit of zero pressure. Fitting the virial type equation simultaneously to adsorption isotherms obtained at several temperatures gives a set of temperature independent-parameters a_i which leads to the direct calculation of Q_{st}

$$Q_{st} = -R \frac{\partial \ln p}{\partial \frac{1}{T}}\bigg|_v = -R \sum_{i=1}^{m} a_i v^{i-1} \tag{6}$$

where R is the universal gas constant. To calculate Q_{st} from isotherms with inflection points, a procedure which is discussed somewhere else was applied [26]. Briefly, the virial type equation is fitted into subsets of data points rather than the entire isotherm. Each subset contains a certain number of data points selected consecutively with respect to v. By considering a sequence of overlapping subsets, one can cover the whole range of data.

Based on the result published in the literature we would expect the heat of diethyl ether adsorption to be smaller than 72 kJ /mol and close to the heat of butane adsorption which was reported to be in the range of 50 kJ/mol [285] (the same number of carbon atoms, however, different size of molecule). Indeed, the calculated heats are in the expected range. The dependence of the isosteric heats of adsorption on the amount adsorbed in molecules per square nanometer of surface is presented in Figure5. Trends in the heats show some similarities and differences. Surprisingly, for all samples a small increase in the heat of adsorption at the beginning of the process (from 5 to 10 kJ) occur. Then, for the WVA series a monotonic decrease is found, as expected for heterogeneous surfaces. On the other hand, in the case of the UMC carbons after an initial increase the heats reach some kind of plateau in their values close to 70 kJ/mol. It is noteworthy that for all carbons the heats of diethyl ether adsorption are between 60 and 70 kJ/mol which is close to twice the value of the heat measured on carbon black and reported by Avgul and Kiselev (36 kJ/mol) [2]. This indicates that the adsorption occurs in very narrow pores, similar to the sizes of diethyl ether molecule which is in fact expected so low surface coverages as those reached in our experiments.

An increase in heats of adsorption with surface coverage was also found for adsorption of water and methanol [6, 7, 27]. In the case of those system an increase was possible due to the weak interactions of sorbates with carbon surface and strong contribution of hydrogen bonding. The initial heats of adsorption in those cases were smaller than the heat of condensation. In the case of diethyl ether adsorption the initial heat is much higher than heat of condensation (26 kJ/mol). This can be explained by the strong interactions of hydrocarbon moiety with narrow

pores of activated carbons. To interpret the initial increase in the heat is a challenge. If dispersive interactions of hydrocarbon moiety are the predominant forces of adsorption the heat should have a decreasing trend. In our view, this small increase at very low coverages can be explained only by an affinity of ether to bond to surface groups present in small pores. Those pores are similar in size to diethyl ether molecule (x, y, z = 4.027Å, 8.822 Å, 4.556 Å, respectively, [29], = 4.76 Å (calculated from van der Waals equation) but big enough to accommodate functional groups. In this case the dispersive interactions are enhanced by the presence of hydrogen bonding. After this stage, which in fact may be only temporary, diethyl ether tends to occupy pores closest to its size, with no groups present, and the maximum in the heat of adsorption is reached.
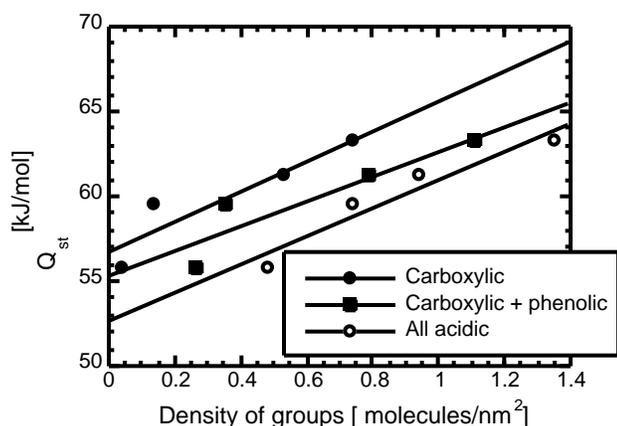

Figure 6.
Dependence of the initial heat of adsorption the density of acidic groups.

Supporting to the above mentioned hypothesis is the fact that the initial heats increased after oxidation. The initial rise is also steeper after oxidation than that for the initial samples. The dependence of the initial heat of adsorption on the density of surface groups (all and carboxylic and phenolic) is presented in Figure 6. Good correlation coefficients ($R^2 =0.86$, $R^2 =0.84$, $R^2 = 0.93$ for carboxylic, phenolic and all acidic groups on the surface, respectively) indicate that hydrogen bonding has a contribution to the adsorption in narrow pores. No correlation with the pore volume was found, since the pore sizes, not the volumes, are important for the energetics of the process. It is important to mention here that the amount adsorbed is very small, around 10 times smaller than the average density of surface groups. This suggests that only narrow pores take part in the adsorption. After the first stage of the process, it is likely that adsorption becomes more stable and

interactions of hydrocarbon moiety are predominant, and the effect of hydrogen bonding can not be distinguished due to its low energy.

The differences in the observed trends in the heats of adsorption between WVA and UMC carbons can be explained by the differences in their pore structure. As shown from Figure 1 the sizes of narrow pores are similar in both groups of carbons, however, in the case of UMC and its oxidized counterpart the volume is much larger (more than three times according to the data in Table 1). Since the coverage is less than 0.1 molecule/nm^2 adsorption likely occurs in the range of very narrow pores, as mentioned above, close in size to diethyl ether molecule. Differences in the volumes of these pore cause that in the case of WVA we observe a monotonic decrease in the heat whereas for UMC the heats are at the constant, maximum level. The latter can be explained by the fact that pores are very similar in sizes and when smaller pores are filled adsorption occurs in slightly larger ones with the contribution of hydrogen bonding (around 10 k/mol [2]) which enhances the adsorption energy. In the case of WVA and WVA-O the pore structure is more heterogeneous than for the UMC samples (Figure 1) and at the same coverage the larger pores have to be filled which results in a slight decrease in the heat of adsorption. This decrease occurs since the contribution of hydrogen bonding is small compared to the interaction of hydrocarbon moiety the carbon surface (36 kJ/mol for carbon blacks [2]).

Conclusions

The results described in this paper demonstrate that carbons structural heterogeneity, the sizes and the volumes of pores, is the predominant factor, which governs diethyl ether adsorption on activated carbons. Hydrogen bonding in this case is weak compared to the interactions of hydrocarbon moiety with pore walls. Surprisingly, at very low surface coverage and low pressure diethyl molecules tend to adsorb in very narrow pores but wide enough to accommodate an oxygen-containing group. Then the adsorption in pores similar in size to diethyl molecule occurs. This results in an increase in the heat of adsorption. With increasing surface coverage diethyl ether molecules adsorb in larger pores, where functional groups contribute to the heat of adsorption, however, its contribution is not distinguishably marked due to the low energy of the process compared to dispersive interactions. The high value of heat of adsorption on very microporous carbon (exactly twice of that obtained on carbon black) indicates that only pores similar in size to ether molecule take part in the process at our experimental conditions. When process proceeds further the heat of adsorption is expected to

decrease as observed for the carbon with more heterogeneous pore structure.

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