Published in Langmuir 19, issue 3, pp. 9719–9723, 2003,
which should be used for any reference to this work

Adsorption of Phenol from Dilute and Concentrated Aqueous Solutions by Activated Carbons

Elena Fernandez,[†] Deirdre Hugi-Cleary,[†] M. Victoria López-Ramón,[‡] and Fritz Stoeckli*[,†]

Chemistry Department, University of Neuchâtel, Av. de Bellevaux 51, CH-2000 Neuchâtel, Switzerland, and Departamento de Química Inorgánica y Orgánica, Facultad de Ciencias Experimentales, Universidad de Jaén, 23071 Jaén, Spain

Combined calorimetric and adsorption techniques show that in the case of phenol adsorption from either dilute or concentrated aqueous solutions, water is always adsorbed preferentially by the oxygen-containing surface groups of the carbon. This reduces the surface and/or the micropore volume accessible to the phenol molecule and quantitatively explains the decrease in the limiting adsorption of phenol on a given carbon after oxidation. In the case of dilute solutions, as established earlier, the mechanism corresponds to the coating of the total surface (external surface and micropore walls) by a monolayer of phenol. On the other hand, for concentrated solutions (15−25% of water), one observes a process of micropore filling by phenol. Both mechanisms can be described in the framework of Dubinin's theory, which allows predictions based on simple physical and structural parameters.

Introduction

The adsorption of phenol from aqueous solutions onto carbons has received a great deal of attention, and an exhaustive review has been published recently by Radovic et al.[1] At the present time, the underlying mechanism and the prediction of adsorption equilibrium remain open questions, although a number of models have been proposed. It appears that the pH of the solution, the real surface area of the solid, and functional groups play a major role. A majority of authors describe the overall adsorption equilibrium in terms of Langmuir, Freundlich, or Redlich isotherms, and correlations have recently been suggested between the basic parameters of the isotherm and more fundamental properties such as the chemistry of the surface. Some authors have also attempted to correlate adsorption equilibrium with thermodynamic properties, by using calorimetry.[2−5] However, a major drawback of the classical models (Langmuir, Freundlich, etc.) is the difficulty in predicting adsorption equilibrium based on simple physicochemical parameters. As pointed out earlier and discussed in detail in a recent study by Stoeckli et al.,[2,3] it appears that an adaptation of Dubinin's theory to the solid−liquid equilibrium provides an interesting framework for the description of phenol adsorption from aqueous solutions. A major advantage of this approach is the fact that adsorption can be predicted over a temperature range of 20−30° around room temperature, on the basis of simple physicochemical parameters and structural characteristics.

It has been shown[3] that in the case of carbons with low oxygen contents, adsorption of phenol from dilute aqueous solutions corresponds essentially to the coating of the external surface and of the micropore walls by a monolayer. A good correlation was also obtained with the corresponding enthalpies of immersion at 293 K, based on a specific enthalpy near −0.110 J m^{-2}. On the other hand, a recent study by Stoeckli and Hugi-Cleary[2] on the adsorption of phenol from concentrated solutions (phenol liquefied with 15−25% water w/w) suggests that the mechanism corresponds to the filling of the micropore volume of activated carbons. This unambiguous result is provided by immersion calorimetry at 293 K, with benzene as a reference and combined with the adsorption of phenol from the vapor phase. Both types of experiment suggest an affinity coefficient β(phenol) close to unity.

It appears therefore that the adsorption of phenol, and possibly of its derivatives, follows two distinct mechanisms, and the next step, presented in this study, deals with the influence of the surface chemistry on these two mechanisms. We considered essentially the effect of surface oxygen [O], which can vary between less than 1 and 10 mmol g^{-1}. In view of their small concentrations (usually less than 1−1.5 mequiv g^{-1}), the basic surface groups, identified by HCl titration,[6,7] were not considered. As shown below, in both concentrated and dilute solutions, it appears that water is preferentially adsorbed by the oxygen-containing complexes. This leaves the remainder of the surface and/or the micropore volume to the phenol molecule. In the case of dilute solutions, this mechanism explains the decrease in the limiting amount of phenol adsorbed by the carbons with increasing oxidation. As before, immersion calorimetry plays an important role by providing complementary information to classical solution and adsorption work.

Theory

As discussed in detail in our previous study,[3] adsorption of phenol from dilute aqueous solutions can be described

* To whom correspondence should be addressed. E-mail: fritz.stoeckli@ich.unine.ch. Fax: +41 32 718 25 11.

[†] University of Neuchâtel.

[‡] Universidad de Jaén.

(1) Radovic, L. R.; Moreno-Castilla, C.; Rivera-Utrilla J. In *Chemistry and Physics of Carbons*; Thrower, P., Ed.; Marcel Dekker: New York, 2000; Vol. 27, pp 227−405.

(2) Stoeckli, F.; Hugi-Cleary, D. *Russ. Chem. Bull. Int. Ed.* **2001**, *50*, 2060−2063.

(3) Stoeckli, F.; López-Ramón, M. V.; Moreno-Castilla, C. *Langmuir* **2001**, *17*, 3301−3306.

(4) Barton, S. S.; Evans, M. J. B.; MacDonald, J. A. F. *Pol. J. Chem.* **1997**, *71*, 651−656.

(5) MacDonald, J. A. F.; Evans, M. J. B. *Carbon* **2002**, *40*, 703−707.

(6) Stoeckli, F. In *Porosity in Carbons*: *Characterization and Applications*; Patrick, J., Ed.; Arnold: London, 1995; pp 67−92.

(7) Dubinin, M. M. *Carbon* **1989**, *27*, 457−467.

by the following equation:

$$N_a = N_{am} \exp\{-[RT \ln(c^*/c_{eq})/E_s]^4\} \quad (1)$$

where N_a is the amount adsorbed by the carbon at temperature T and equilibrium concentration c_{eq}, c^* being the saturation concentration; N_{am} represents the monolayer capacity of the surface, and E_s is an energy characterizing the system under investigation (solid and adsorbate). These parameters are obtained from a logarithmic plot of eq 1. The fact that the adsorption of phenol from dilute solutions corresponds to the coating of the carbon surface, and not to the filling of the micropore volume, is suggested by the limiting amount N_{am} obtained from eq 1. As pointed out earlier,[3] this value corresponds to a volume that is systematically smaller than the actual micropore volume W_0 of the corresponding carbon.

Equation 1 itself is derived from Dubinin's theory,[6−8] originally developed for the adsorption of vapors by microporous carbons. (However, as discussed below, it was found later that a similar analytical form could be used to describe the adsorption of vapors on the surface of a number of nonporous solids.) Dubinin's theory rests on the thermodynamic potential $A = RT \ln(p_s/p) = -\Delta_{ads}G$, the reference state being the saturated vapor of the liquid at pressure p_s. The fundamental expression is the Dubinin−Astakhov (DA) equation,

$$N_a = N_{a0} \exp[-(A/E)^n] \quad (2)$$

where N_{a0} is the limiting amount filling the micropores at T and p_s. The micropore volume W_0 is equal to $N_{a0}V_m^a$, where V_m^a is the molar volume of the condensed adsorbate. The so-called characteristic energy E depends on the system under investigation. For adsorption of different adsorbates, $E = \beta E_0$, where β is a specific scaling factor relative to benzene, taken as the reference, and $\beta(C_6H_6) = 1$. For the majority of activated carbons, the exponent n is equal to 2, which corresponds to the classical Dubinin−Radushkevich (DR) equation used in this study.

It has also been shown[6,9,10] that E_0 is an inverse function of the average micropore width L_0 and its combination with the volume W_0 leads to a good assessment of the surface area of the micropore walls, S_{mi}. Recently,[11,12] independent confirmation has been provided by computer simulations based on CO_2 isotherms, assuming ideally slit-shaped micropores.

The external (nonmicroporous) surface area S_e can be assessed independently from a classical comparison plot,[13−15] and it is therefore possible to estimate the true surface area of a microporous carbon,[11,16] $S_{tot} = S_{mi} + S_e$.

If Dubinin's theory applies, parameters E and n must be temperature-invariant and eq 2 leads to an equation for the enthalpy of immersion of a microporous carbon into the corresponding liquid (e.g., benzene). As shown elsewhere,[6] in the case of the DR equation,

$$-\Delta_i H_{mi}\ (J\ g^{-1}) = \beta E_0 W_0 (1 + \alpha T)\sqrt{\pi}/2V_m \quad (3)$$

where α is the thermal expansion coefficient of the liquid.

Good agreement has been found between $\Delta_i H_{mi}$ calculated from eq 3 and the experimental enthalpy of immersion, but the latter must be corrected for the wetting of the external surface h_i (J m^{-2}) S_e. Usually, this represents only a fraction of $\Delta_i H_{mi}$.

Dubinin's theory can be extended to the adsorption of vapors on certain nonporous surfaces such as graphitized carbons blacks[11,14] and manganese dioxide.[17] The DR equation takes the form of the so-called Dubinin−Radushkevich−Kaganer (DRK) equation:

$$N_a = N_{am}(\mathrm{DRK}) \exp[-(A/E_{DRK})^2] \quad (4)$$

The limiting amount N_{am}(DRK) represents the monolayer capacity of the surface. It is close to N_{am}(BET) (BET, Brunauer−Emmett−Teller), the monolayer capacity obtained from the same isotherm at higher relative pressures ($0.05 < p/p_s < 0.30-0.35$).

Equations 2 and 4 are valid for the adsorption of phenol vapors by microporous carbons[2] and onto carbon black[3] N234-G, respectively.

It can be seen that eq 1 is derived from the DRK eq 4 by replacing the thermodynamic potential $RT \ln(p_s/p)$ by the equivalent potential in solutions, $RT \ln(c^*/c_{eq})$, the reference being the saturated solution. As pointed out earlier,[3] it also appears that the exponent $n = 4$ leads to a better overall fit for the experimental data and it is known that the value $n = 2$, found in the classical DRK equation, is not necessarily valid for all adsorbate−adsorbent systems.[18] In fact, this exponent is directly related to the width of the adsorption energy distribution[9,19] and a high value denotes a relatively homogeneous distribution. It also appears that the energies E_s, E_{DRK}, and E are different.[3]

As discussed in detail elsewhere,[3,20−22] the interaction between water and carbons is characterized by a weak nonspecific interaction with the bulk of the solid and a relatively strong specific interaction with oxygen-containing groups, as well as basic centers. These studies, based on immersion enthalpies of carbons with various degrees of oxidation, suggest a specific interaction of −10 kJ per mol of oxygen and basic centers. Consequently, this relatively high specific interaction may confirm the preferential adsorption of water on the oxygen-containing centers and the exclusion of phenol, as suggested by different authors.[23−25]

Experimental Section

Solids. The study is based on a collection of well-characterized active carbons, the main structural properties of which are given in Table 1. These properties were obtained by the combination

(8) Bansal, R. C.; Donnet, J. B.; Stoeckli, H. F. *Active Carbon*; Marcel Dekker: New York, 1988.
(9) Stoeckli, F. *Russ. Chem. Bull.* **2001**, *12*, 1−8.
(10) Stoeckli, F.; López-Ramón, M. V.; Hugi-Cleary, D.; Guillot, A. *Carbon* **2001**, *39*, 1115−1116.
(11) Stoeckli, F.; Guillot, A.; Slasli, A.; Hugi-Cleary, D. *Carbon* **2002**, *40*, 211−215.
(12) Stoeckli, F.; Guillot, A.; Slasli, A.; Hugi-Cleary, D. *Carbon* **2002**, *40*, 383−388.
(13) Carrott, P. J. M.; Carrott-Ribeiro, M. M. L. *Carbon* **1996**, *37*, 647−656.
(14) Hugi-Cleary, D.; Stoeckli, F. *Carbon* **2000**, *38*, 1309−1313.
(15) Gregg, S. J.; Sing, K. S. W. In *Adsorption, Surface Area and Porosity*; Academic Press: London, 1982; p 238.
(16) Guillot, A.; Stoeckli, F. *Carbon* **2001**, *39*, 2059−2064.
(17) Stoeckli, F.; Hugi-Cleary, D.; Centeno, T. A. *J. Eur. Ceram. Soc.* **1998**, *18*, 1177−85.18
(18) Hugi-Cleary, D.; Wermeille, S.; Stoeckli, F. *Chimia* **2003**, in press.
(19) Rudzinski, W.; Everett, D. H. *Adsorption of Gases on Heterogeneous Surfaces*; Academic Press: London, 1992.
(20) Stoeckli, F. *Carbon* **2002**, *40*, 969−971.
(21) Stoeckli, F.; Lavanchy, A. *Carbon* **2000**, *38*, 475−477.
(22) Lopez-Ramon, M. V.; Stoeckli, F.; Moreno-Castilla, C.; Carrasco-Marin, F. *Carbon* **1999**, *37*, 1215−1221.
(23) Coughlin, R. W.; Ezra, F. S. *Environ. Sci. Technol.* **1968**, *2*, 291−297.
(24) Mahajan, O. P.; Moreno-Castilla, C.; Walker, P. J., Jr. *Sep. Sci. Technol.* **1980**, *15*, 1733−1752.
(25) Franz, M.; Arafat, H. A.; Pinto, N. G. *Carbon* **2000**, *38*, 1807−1819.

Table 1. Structural Characteristics of the Activated Carbons Considered in This Study

carbon	W_0 (cm^3 g^{-1})	E_0 (kJ mol^{-1})	L (nm)	$S_{tot\ exp}$ (m^2 g^{-1})	[O] (mmol g^{-1})
1	0.06	22.4	0.98	250	0.45
2	0.45	20.0	1.26	819	0.68
3	0.74	15.5	2.63	1400	0.7
4	0.65	18.9	1.44	865	1.17
5	0.25	28.7	0.62	608	1.31
6	0.45	19.0	1.42	736	1.38
7	0.35	16.9	1.96	447	1.17
8	0.58	19.1	1.40	940	1.59
9	0.64	16.6	2.08	772	1.75
10	0.45	23.9	0.86	1097	1.8
11	0.54	21.2	1.10	1005	2.06
12	0.43	20.0	1.26	1005	2.21
13	0.54	21.2	1.10	968	2.29
14	0.42	19.8	1.29	763	3.26
15	0.74	15.0	3.0	1400	10
16	0.26	27.0	0.69	795	6.4
17	0.31	24.7	0.81	873	7

of vapor adsorption and immersion calorimetry.[6,8] The oxidized samples were obtained by a standard treatment with $(NH_4)_2S_2O_8$ in H_2SO_4 described in detail elsewhere,[22] and the oxygen content was determined by temperature-programmed desorption (TPD). In the present case, it appears that the basic groups (determined by immersion calorimetry into 2 N HCl solutions)[22] do not exceed 1 mequiv HCl per g of carbon. Nonporous graphitized carbon blacks N234-G, Hoechst, and Vulcan 3-G, with BET surface areas of 92, 54, and 71 m^2/g, were also considered for comparison purposes in immersion calorimetry. Immersion calorimetry into water[3,20,26,27] showed that these carbon blacks contain very little surface oxygen.

Adsorption from Solutions. The adsorption of phenol at 293 K was carried out as described previously.[3,28] No buffer was added to the solutions, to avoid the introduction of new electrolytes into the system.

Immersion Calorimetry. The enthalpies of immersion of the various carbons into dilute aqueous solutions of phenol (0.4 M) and concentrated solutions (15−25% of water w/w) were determined at 293 K with a Tian−Calvet calorimeter,[6,8] as described earlier.[2,26] In all cases, samples of 0.040−0.150 g were used. Outgassing at 10^{-5} Torr was limited to 383 K, to avoid the destruction of oxygen-containing surface groups, in particular carboxylic groups. The chemical state of the samples was checked by determining the enthalpy of immersion into water, which quantity is directly related to the amount of oxygen present on the surface.[6,20,21,23,26,29]

Results and Discussion

Phenol Adsorption from Dilute Solutions. In the case of the graphitized carbon blacks, the average enthalpy of immersion into 0.4 M aqueous solutions of phenol is h_i(phe/0.4M) = −0.105 ± 0.004 J m^{-2}, in good agreement with the earlier value of −0.109 ± 0.003 J m^{-2} obtained for N234-G only.[3] If one assumes that water is preferentially adsorbed on the primary sites [O] with an energy of −10 J mmol^{-1}, as shown earlier,[3,20,27,28,30] the experimental enthalpy of immersion of activated carbons is the sum of these interactions and of the coating of the remainder of the total surface by phenol in the form of a monolayer,

$$-\Delta_i H(\text{phe/0.4M})\ (\text{J g}^{-1}) = 0.105[S_{tot} - S_{sites}] + 10[\text{O}] \quad (5)$$

S_{sites} is the area excluded from phenol adsorption, given by

$$S_{sites}\ (\text{m}^2\ \text{g}^{-1}) = s[\text{O}] \quad (6)$$

and s is the average area occupied by water attached to one mmol of oxygen. It follows that

$$-\Delta_i H(\text{phe/0.4M})\ (\text{Jg}^{-1}) = 0.105 S_{tot} + [\text{O}](10 - 0.105s) \quad (7)$$

As shown in Table 2 and in Figure 1, one obtains a good correlation (R^2 = 0.95) between the calculated and the experimental enthalpies for the 15 activated carbons, with s = 70 m^2 per mmol of surface oxygen. This excluded area is reasonable in view of the fact that 1 mmol of water corresponds to a monolayer of 64 m^2, based on a molecular area of 10.6×10^{-20} m^2. It also indicates that approximately

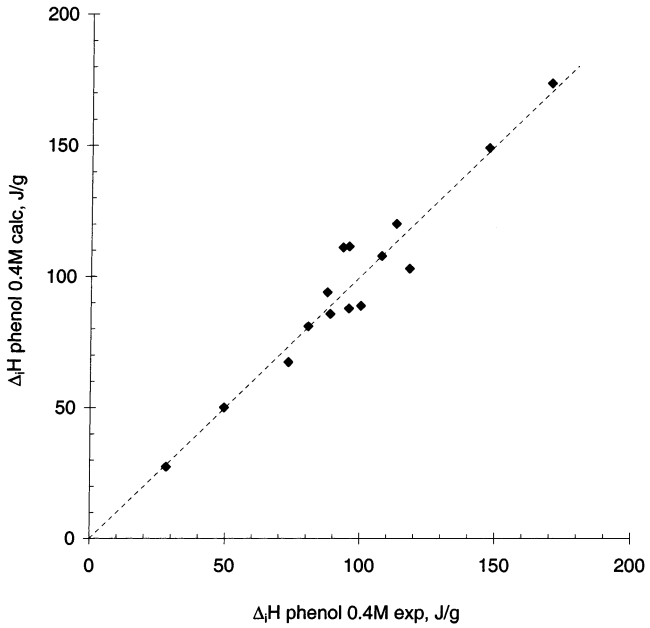

Figure 1. Correlation between the calculated, using eq 7, and the experimental enthalpies of immersion of the carbons at 293 K into aqueous solutions of phenol (0.4 M).

Table 2. Enthalpies of Immersion of Activated Carbons into Aqueous Solutions of Phenol (0.4 M) at 293 K

carbon	$-\Delta_i H$(phe/0.4M)$_{exp}$ (J g^{-1})	$-\Delta_i H$(phe/0.4M) from eq 7 (J g^{-1})	$-h_i$(phe/0.4M)$_{exp}$ (J m^{-2})
1	28.3	27.5	0.113
2	95.6	87.8	0.117
3	147.3	148.9	0.105
4	87.6	94.0	0.101
5	73.3	67.3	0.121
6	80.6	80.2	0.110
7	49.5	50.0	0.111
8	118.0	103.0	0.126
9	88.7	85.7	0.115
10	113.0	120.1	0.103
11	93.3	111.2	0.093
12	95.6	111.4	0.095
13	107.7	107.9	0.111
14	100.0	88.8	0.131
15	170.2	173.5	0.122

(26) Stoeckli, F.; Moreno-Castilla, C.; Carrasco-Marin, F.; López-Ramón, M. V. *Carbon* **2001**, *39*, 2235−2237.
(27) Lopez-Ramon, M. V.; Stoeckli, F.; Moreno-Castilla, C.; Carrasco-Marin, F. *Carbon* **2000**, *38*, 825−829.
(28) Moreno-Castilla, C.; Rivera-Utrilla, J.; Lopez-Ramon, M. V.; Carrasco-Marin, F. *Carbon* **1995**, *33*, 845−851.
(29) Lopez-Ramon, M. V.; Stoeckli, F.; Moreno-Castilla, C.; Carrasco-Marin, F. *Langmuir* **2000**, *16*, 5967−5972.
(30) Carrasco-Marin, F.; Mueden, A.; Centeno, T. A.; Stoeckli, F.; Moreno-Castilla, C. *J. Chem. Soc., Faraday Trans.* **1997**, *93*, 2211−1125.

Table 3. Adsorption of Phenol at 293 K from Aqueous Solutions (0.4 M)[a]

carbon	[O] (mmol g^{-1})	N_{am} (mmol g^{-1})	S_{am} (m^2 g^{-1})	$S_{tot\ exp}$ (m^2 g^{-1})	S_{tot} from eq 9 (m^2 g^{-1})
1	0.45	0.437	118	250	150
4	1.17	3.37	913	865	995
10	1.8	3.75	1016	1097	1142
14	3.26	2.14	580	763	808
15	10.0	1.75	474	1400	1174
16	6.4	1.41	382	795	830

[a] The limiting amounts N_{am} are obtained from eq 1.

one molecule of water is attached to a surface oxygen atom and the corresponding surface area is no longer available to phenol. Due to a compensating effect, the enthalpy of immersion of a given carbon into aqueous solutions of phenol changes moderately with the amount of oxygen. For example, in the limiting case of carbons 3 and 15 this enthalpy increases from −147.3 to −170.2 J g^{-1}as [O] increases from 0.7 to 10 mmol g^{-1}. As confirmed by adsorption and immersion experiments based on benzene,[29] the microporous structure and, furthermore, the total surface area S_{tot} of carbons are practically not modified by $(NH_4)_2S_2O_8$ oxidation. In the present case, one obtains specific enthalpies h_i(phe/0.4M) = $\Delta_i H$(phe/0.4M)/S_{tot} of −0.105 and − 0.122 J m^{-2}, respectively. A numerical analysis of the modified eq 7,

$$h_i(\text{phe/0.4M}) = -\Delta_i H(\text{phe/0.4M})/S_{tot} = 0.105 + [\text{O}](10 - 0.105s)/S_{tot} \quad (8)$$

confirms the relatively limited variation of this ratio as the oxygen content increases, as shown in Table 2.

This result justifies the use of an average value of −0.115 J m^{-2} to estimate, within 5−10%, the total surface areas of typical activated carbons from their enthalpies of immersion into aqueous solutions of phenol. As pointed out above, these areas are in good agreement with independent assessments of S_{tot}, such as computer modeling based on CO_2 adsorption.[11,12]

The blocking of the oxygen-containing groups by water leads to an effective decrease in the maximum phenol uptake at saturation, N_{am}, given by eq 1 (see Table 3). Assuming a molecular surface area of 45 × 10^{-20} m^2 for phenol[3], 1 mmol occupies an area of 271 m^2. On the other hand, the excluded area of s = 70 m^2 per mmol of surface oxygen due to water, suggested by eq 7, corresponds to a reduction of 0.258 mmol of phenol adsorption on the given surface, per mmol of oxygen present on the surface.

If this assumption is correct, the total surface area of the carbon should be related to the limiting amount adsorbed from solution, N_{am}, and the surface oxygen [O] by

$$S_{tot}\ (\text{m}^2\ \text{g}^{-1}) = N_{am} \times 271\ (\text{m}^2\ \text{mmol}^{-1}) + [\text{O}] \times 70(\text{m}^2\ \text{mmol}^{-1}) \quad (9)$$

The data for microporous carbons (see Table 2) with oxygen contents [O] between 1.17 and 10 mmol g^{-1} lead to fair correlation between the calculated and the experimental values of S_{tot}, without any additional parameter fitting (see Table 3 and Figure 2).

This result quantitatively explains the change in the total amount adsorbed N_{am} with oxidation. At this stage, it should be pointed out that this change is well-known.[1,23,31] However, the exact correlation suggested by eq 9 was not obvious, due to the fact that most oxidation processes (e.g., HNO_3) modify simultaneously the structure of the carbons and their total surface areas.[1,4,5] This means that two parameters have to be taken into account and no clear correlation could be established. Moreover, the nitrogen BET surface area, often used as a reference, is not necessarily a reliable measure of the real surface area, as suggested by other studies.[6,11,12]

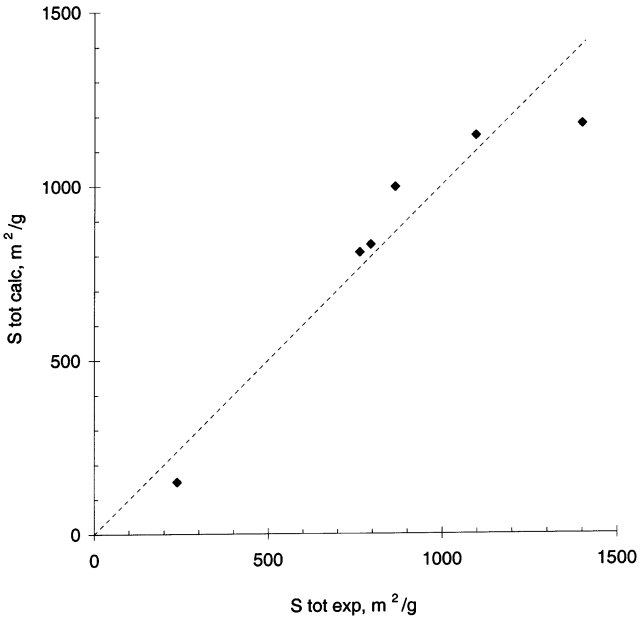

Figure 2. Correlation between the calculated, using eq 9, and the experimental surface areas, S_{tot}, of carbons with variable amounts of surface oxygen.

The fact that the enthalpy of immersion into aqueous solutions, given by eq 8, shows a relatively smaller variation with the degree of oxidation than with N_{am} has been discussed above, and it appears that calorimetry and adsorption from solution are not in contradiction.

The present treatment neglects the basic sites on the surface, but two arguments may be brought forward. First, these sites always represent a mere fraction of the oxygen-containing sites.[22,30] Second, it appears that a large proportion of the basic sites do not contain oxygen[22] and correspond to π-electron-rich regions found on the basal planes.[23] Therefore, it is not excluded that these centers show some affinity for phenol.

Phenol Adsorption from Concentrated Solutions. As shown earlier,[2] the comparison of enthalpies of immersion of carbons with low oxygen contents into concentrated solutions (phenol fluidized with 15−25% water w/w) with the values obtained for benzene shows that the process corresponds to the filling of the micropores. In the present study, the procedure was repeated with the 11 carbons listed in Table 4, some of which contain relatively large amounts of surface oxygen. If water, still present in phenol, is adsorbed preferentially by the oxygen-containing surface groups, one must observe two separate processes, namely, (i) the specific interaction with the sites, involving one to two water molecules per site, and (ii) the filling of the remainder of the micropore volume, W_0 − W(water), as well as the coating of the external surface S_e by phenol.

As suggested by experiments with carbon blacks N234-G, Hoechst, and Vulcan 3-G, the specific enthalpy of immersion h_i(phe/concn) = −0.131 ± 0.005 J m^{-2}. This value is larger than that observed for dilute solutions (−0.105 ± 0.004 J m^{-2}) and probably reflects differences

(31) Barton, S. S.; Evans, M. J. B.; MacDonald, J. A. F. *Pads. Sci. Technol.* **1993**, *10*, 75−84.

Table 4. Enthalpies of Immersion of Activated Carbons into Concentrated Aqueous Solutions of Phenol (15−25% Water w/w) at 293 K

carbon	$-\Delta_i H$(phe/concn)$_{exp}$ (J g^{-1})	$-\Delta_i H$(phe/concn)$_{calc}$ from eq 10 (J g^{-1})
1	39.0	35.6
2	143.4	149.8
3	171.7	188.0
4	177.6	198.2
5	112.2	106.7
8	196.5	172.1
9	171.4	184.3
10	196.5	166.0
15	193.7	207.3
16	125.0	93.3
17	84.3	115.4

in the transfer of phenol from the two types of solutions onto the surface. On the basis of a molecular surface area of 45×10^{-20} m^2 (see above), these values correspond to molecular heats of transfer of −35.5 and −28.5 kJ/mol phenol from concentrated and dilute solution, respectively. The latter is in good agreement with earlier estimates.[2,5]

If the model outlined here is correct, the enthalpy of immersion of the carbons into the concentrated solutions (15−25% water w/w) should be given by

$$-\Delta_i H(\text{phe/concn})\ (\text{J g}^{-1}) = c_1 E_0\{W_0 - c_2(18\ \text{cm}^3\ \text{mol}^{-1})[\text{O}]\} + 10[\text{O}] + 0.131 S_e \quad (10)$$

As shown previously,[2] c_1 corresponds to $\beta(1 + \alpha T)\sqrt{\pi}/2V_m$ found in eq 3. Parameter c_2 reflects either the actual number of water molecules retained by the oxygen atom or the correction for the molar volume of water, assumed to be that of the free liquid. However, the latter is less likely. The last two terms in eq 10 represent the average specific interaction between water and the sites and the coating of the external surface by phenol. As shown in Table 4 and Figure 3, one obtains a good correlation for the 11 activated carbons. The best fit leads to $c_1 = 0.0151$ and $c_2 = 1.80$, with a regression coefficient $R = 0.84$. Using a molar volume of 89 cm^3 and an expansion coefficient $\alpha = 8.3 \times 10^{-4}$ K^{-1}, both extrapolated from the data for liquid phenol between 45 and 70 °C, parameter c_1 leads to a formal affinity coefficient β(phenol) ≈ 1. It is in reasonable agreement with the values of 0.8−0.9 obtained from the adsorption isotherms of phenol vapors on carbon and 1.06 from the ratio of the parachors of phenol and benzene, as reported recently.[2]

The value of $c_2 = 1.80$ implies that the interaction with each oxygen atom involves between one and two water molecules, in agreement with an earlier estimate by Carrasco-Marin et al.[30]

Conclusions

The present study shows that the combined use of techniques based on adsorption from solution and on immersion calorimetry leads to a coherent picture for the adsorption of phenol by carbons. In all cases, water is adsorbed preferentially on oxygen-containing surface complexes with an energy of −10 J per mmol [O]. In the case of dilute solutions, phenol is adsorbed as a monolayer on the remaining surface, with a specific enthalpy of -0.105 ± 0.004 J m^{-2}. The preferential blocking of the surface oxygen atoms by water explains the reduction, with increasing oxidation, of the adsorption capacity N_{am} for phenol from aqueous solutions.

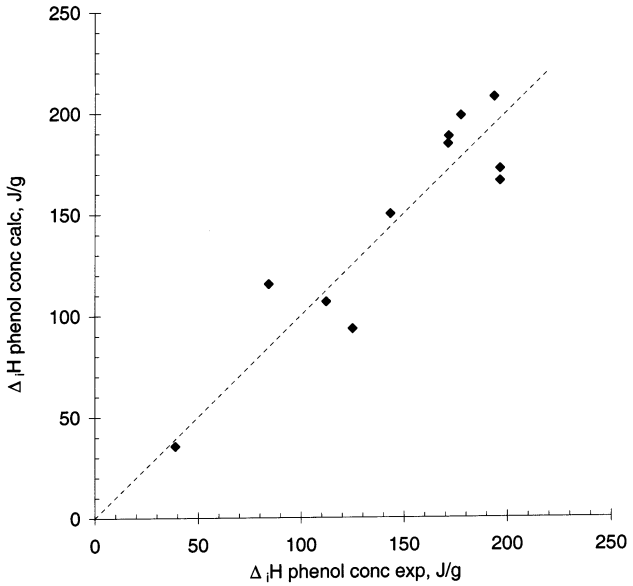

Figure 3. Correlation between the calculated, using eq 10, and the experimental enthalpies of immersion at 293 K of carbons with various amounts of oxygen into concentrated solutions of phenol.

In the case of concentrated solutions (15−25% w/w of water to fluidize phenol), water is still adsorbed preferentially by the oxygen-containing groups, but phenol fills the fraction of the micropore volume not occupied by water. This process of micropore filling is in agreement with the adsorption of pure phenol from the vapor phase, as opposed to the coating of the surface in the case of removal from dilute aqueous solutions. It is likely that this general pattern also applies to other phenolic compounds with limited solubilities into water.

Finally, the present study confirms that the technique based on immersion calorimetry of carbons into dilute solutions of phenol, with a specific enthalpy of approximately −0.105 J m^{-2}, provides a reasonable assessment of the real surface of porous and nonporous carbons with variable degrees of surface oxidation. However, in the case of microporous carbons this approach does not take into account very fine pores or the internal surface of pores with "gate" effects,[32] which exclude the phenol molecule.

Acknowledgment. The authors thank Professor C. Moreno-Castilla (University of Granada, Spain) for useful discussions and comments.

LA030137D

(32) Stoeckli, F.; Slasli, A.; Hugi-Cleary, D.; Guillot, A. *Microporous Mesoporous Mater.* **2002**, *51*, 197−202.