

Adsorption of Phenolic Compounds from Aqueous Solutions, by Activated Carbons, Described by the Dubinin–Astakhov Equation

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Received October 16, 2000. In Final Form: March 6, 2001

It is shown that the adsorption of phenol and 3-chlorophenol from aqueous solutions, by basic active carbons and at an equilibrium solution pH below that of dissociation of the phenols, can be described by an equation of the DRK type with exponent $n = 4$. The principle of temperature invariance is fulfilled between 283 and 313 K, which means that predictions can be made on the basis of a characteristic energy, E_s , and of affinity coefficients, β_s , relative to phenol. This approach presents an advantage over the traditional Langmuir isotherm. Moreover, the comparison of the limiting amounts adsorbed by the different carbons suggests that phenol and 3-chlorophenol are adsorbed in a monolayer as observed for carbon blacks, except in the case of activated carbons with a low degree of activation in which molecular-sieve effects can take place. Similar conclusions are obtained from the enthalpies of immersion into the aqueous solutions and their comparison with graphitized carbon blacks.

Introduction

Adsorption of phenol and substituted phenols from aqueous solutions on activated carbons is one of the most studied of all liquid-phase applications of carbon adsorbents. An up-to-date exhaustive review has recently been published by Radovic et al.¹ Today, it is known that the adsorption process on carbon materials basically depends on several variables such as the pH of the solution, the electron-donating or electron-withdrawing properties of the phenolic compound, and the surface area of the adsorbent and its surface chemistry, which is determined by the nature of its oxygen surface functionalities and its surface charge. For example, oxidation of the surface decreases the density of π electrons on the carbon surface. This, in turn, reduces the π – π interactions with the phenol ring and the adsorption capacity. It follows that the adsorption process is a complex interplay of electrostatics and dispersive interactions.¹

To analyze the adsorption isotherms of phenolic compounds obtained at equilibrium, many authors use the Langmuir or Freundlich equations, which contains empirical parameters. Therefore, a more systematic approach is needed.

In the present study, we examine the adsorption of phenol and 3-chlorophenol from aqueous solutions, within the framework of Dubinin's theory,^{2,3} because it can be applied to the adsorption of a number of solutes from aqueous solutions.⁴ The present study also considers the

enthalpy of immersion $\Delta_i H$ of carbons into aqueous solutions of phenolic compounds. This thermodynamic function is related to Dubinin's theory and it reflects the transfer of the solute from the solution onto the carbon. It will be shown that adsorption is limited to the coating of the total surface of the carbon, S_{tot} , which consists of the micropore walls, S_{mi} , and the external (nonmicroporous) surface area, S_{ext} . This is already suggested by the fact that the adsorption isotherm is of type I and the limiting amount is smaller than the amount required to fill the micropore volume, W_0 , of the carbons.

Theory

The fundamental expression of Dubinin's theory is the Dubinin–Astakhov (DA) equation,

$$N_a = N_{a0} \exp[-(A/E)^n] \quad (1)$$

where $A = RT \ln(p_s/p)$, N_a is the amount adsorbed (usually given in mol/g) at relative pressure p/p_s and temperature T , and N_{a0} is the limiting amount filling the micropores. From the limiting amount adsorbed, N_{a0} , it is possible to estimate the volume W_0 filled by the adsorbate, by using its molar volume V_m in the condensed state at the corresponding temperature and $W_0 = N_{a0} V_m$. E is the characteristic energy of the system, which depends on the solid and on the adsorbate. Dubinin's theory requires the temperature invariance of parameter E , at least over a reasonable temperature range, so that eq 1 can be used to predict adsorption equilibria of vapors, including water.⁵ The effect of the adsorbate itself is expressed by a factor β , called affinity coefficient, the reference being by conventional benzene and therefore $\beta(\text{C}_6\text{H}_6) = 1$. Under these circumstances, $E = \beta E_0$. For activated carbons, power n varies from approximately 1.5 to 3, and the most frequent

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(1) Radovic, L. R.; Moreno-Castilla, C.; Rivera-Utrilla, J. *Chem. Phys. Carbon* **2000**, 27, 227.

(2) Dubinin, M. M. *Carbon* **1989**, 27, 457.

(3) Stoeckli, F. In *Porosity in Carbons*; Patrick, J., Ed.; Arnold: London, 1995.

(4) Jaroniec, M.; Derylo, A. *J. Colloid Interface Sci.* **1981**, 84, 191.

(5) Stoeckli, F.; Jakubov, T. S.; Lavanchy, A. *J. Chem. Soc., Faraday Trans.* **1994**, 90, 783.

Table 1. Structural Characteristics of the Activated Carbons Derived from Equations 2 and 3 and Surface Basicity

carbon	W_o (cm ³ g ⁻¹)	E_o (kJ mol ⁻¹)	L (nm)	S_{mi} (m ² g ⁻¹)	S_e (m ² g ⁻¹)	S_{tot} (m ² g ⁻¹)	pH _{PZC}
PLW	0.45	23.9	0.86	1047	50	1097	9.0
AP-2.5	0.20	22.6	0.96	417	8	425	10.0
AP-5	0.24	19.8	1.29	372	32	404	10.2
AP-10	0.35	15.2	2.84	246	47	293	10.5
CP-5	0.41	17.0	1.93	425	52	477	10.1
CP-10	0.55	13.9	(4.32)	(255)	65	(320)	10.4

case, where $n = 2$, corresponds to the Dubinin–Radushkevich (DR) equation. On the basis of different experimental techniques, it has been shown³ that the characteristic energy E_o is related to the average width of the micropores by

$$L(\text{nm}) = 10.8/(E_o - 11.4 \text{ kJ/mol}) \quad (2)$$

Consequently, assuming slit-shaped micropores, the surface of their walls is approximately equal to

$$S_{mi}(\text{m}^2/\text{g}) = 2000 W_o(\text{cm}^3/\text{g})/L(\text{nm}) \quad (3)$$

Dubinin's theory can be extended to the adsorption of vapors on certain nonporous surfaces such as graphitized carbons blacks⁶ and manganese dioxide⁷ and the DR equation takes the form of the so-called Dubinin–Radushkevich–Kaganer (DRK) equation:^{8,9}

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

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

It has been shown⁴ that the preferential adsorption of various compounds from aqueous solutions, by activated carbons, follows an equation of the DRK type. With the present formalism, one obtains

$$N_a = N_{am} \exp\{-[RT \ln(c^*/c_{eq})/E_s]^2\} \quad (5)$$

In this expression, the vapor–solid adsorption potential $A = RT \ln(p_s/p)$ is replaced by a new thermodynamic potential, $RT \ln(c^*/c_{eq})$, where c^* is the saturation concentration of the adsorbed species and c_{eq} is the concentration at equilibrium, to which corresponds the amount adsorbed N_a . Equation 5 is similar to eq 4, but because adsorption takes place from an aqueous solution, there is no reason E_s should be related directly to the characteristic energy E_o of eq 1. On the other hand, E_s must be temperature-invariant, but this has not been examined systematically. At the present time, and in view of the fact that the adsorption isotherms of phenol and related compounds show a plateau, the majority of authors use Langmuir's equation adapted to solution work:

$$N_a = N_{am} B c_{eq} / (1 + B c_{eq}) \quad (6)$$

In this expression, B is a parameter that depends on the temperature and on the system and c_{eq} is the equilibrium concentration in the solution. Other expressions such as the Freundlich equation have also been used, but all these equations suffer from the shortcoming that the variation

of their main parameters with temperature cannot be predicted in a simple fashion, as opposed to Dubinin's equation. In light of eqs 1 and 4 an obvious generalization of eq 5 would be

$$N_a = N_{am} \exp[-(A_s/E_s)^n] \quad (7)$$

where A_s is the thermodynamic potential, $A_s = RT \ln(c^*/c_{eq})$, the reference state for the solute being either the saturated solution at temperature T or the pure solute itself (both have the same chemical potential). Equation 7 does not imply a specific model for adsorption from the solution.

In the case of preferential adsorption, the enthalpy of immersion of the solid into the solution reflects the transfer of the solute from the solution onto the solid. The energy balance involves demixing and the interaction between the solute and the surface, as discussed below (section 4).

Experimental Section

Solids. The study is based on well-characterized active carbons, PLW⁵ and AP-2.5, AP-5, AP-10, CP-5, and CP-10.¹⁰ Their main characteristics, E_o , W_o , S_{mi} , and S_{ext} , obtained from CO₂ adsorption isotherms, are given in Table 1, together with their pH_{PZC}. Data obtained by Leyva-Ramos et al.¹¹ with the activated carbon Filtrasorb 400 were also included. Graphitized carbon blacks N234-G, Hoechst,⁶ and Vulcan 3-G, with BET surface areas of 92, 54, and 71 m²/g were also considered for comparison in immersion calorimetry.

Adsorption from Solutions. In the present study, we determined the adsorption of phenol at 298 and 313 K and of 3-chlorophenol at 298 K on active carbon PLW. The technique was identical to that used earlier for carbons of series AP and CP at 298 K.¹⁰ Basically, the adsorption isotherms were determined by using flasks containing 0.1 g of carbon/100 cm³ of phenolic solution of different initial concentrations. These solutions were kept in a thermostated shaker bath at 298 or 313 K for 15 days, a time sufficiently long to ensure adsorption equilibrium. The adsorption isotherms were determined without adding any buffer to control the pH, to avoid the introduction of any new electrolyte into the system. But in all cases the suspensions at equilibrium had a pH between 6 and 7, which is below the pH_{PZC} of the carbons.

Immersion Calorimetry. The enthalpies of immersion of active carbon PLW and of the nonporous carbon blacks (essentially N234-G) into the aqueous solutions of phenolic compounds (phenol and 3-chlorophenol) were determined at 293 K with a calorimeter of the Tian-Calvet type, as described in detail elsewhere.^{12,13}

In the case of activated carbon PLW, samples of 0.040 to 0.150 g were used. They were previously outgassed at a dynamic vacuum of 10⁻⁵ Torr and at a temperature not higher than 383 K. The enthalpies of immersion were determined by using 0.4 M solutions for phenol and 0.2 M for 3-chlorophenol. In the case of carbon black NG234-G, the concentrations were mainly around

(10) Moreno-Castilla, C.; Rivera-Utrilla, J.; López-Ramón, M. V.; Carrasco-Marín, F. *Carbon* **1995**, *33*, 845.

(11) Leyva-Ramos, R.; Soto-Zuñiga, J. H.; Mendoza-Barrón, J.; Guerrero-Coronado, R. M. *Adsorp. Sci. Technol.* **1999**, *17*, 533.

(12) Bansal, R. C.; Donnet, J. B.; Stoeckli, H. F. *Active Carbon*; Dekker: New York, 1988.

(13) Carrasco-Marín, F.; Mueden, A.; Centeno, T. A.; Stoeckli, F.; Moreno-Castilla, C. *J. Chem. Soc., Faraday Trans.* **1997**, *93*, 2211.

(6) Hugli-Cleary, D.; Stoeckli, F. *Carbon* **2000**, *38*, 1309.

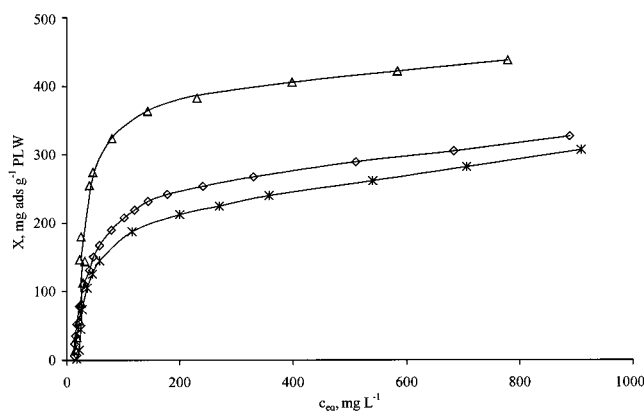
(7) Stoeckli, F.; Hugli-Cleary, D.; Centeno, T. A. *J. Eur. Ceram. Soc.* **1998**, *18*, 1177.

(8) Kaganer, M. G. *Dokl. Akad. Nauk SSSR* **1952**, *116*, 603.

(9) Rudzinski, W.; Everett, D. H. In *Adsorption of Gases on Heterogeneous Surfaces*; Academic Press: London, 1992.

Table 2. Adsorption of Phenol and 3-Chlorophenol from Aqueous Solutions by the Activated Carbons

carbon	compound	T (K)	E_s (kJ mol ⁻¹)	β_s	eq 7	
					$N_{am} \times 10^{-3}$ (mol g ⁻¹)	S_m (DRK) (m ² g ⁻¹)
PLW	phenol	298	19.1	1.00	3.75	1016
	phenol	313	19.1	1.00	3.62	981
	3-chlorophenol	298	18.9	0.99	3.50	1050
Filtrisorb 400	phenol	283	21.1	1.00	1.98	537
	phenol	298	21.1	1.00	2.00	542
	phenol	313	21.1	1.00	2.00	542
AP-2.5	phenol	298	23.6	1.00	1.28	347
	3-chlorophenol	298	26.6	1.13	0.57	171
AP-5	phenol	298	27.5	1.00	1.67	453
	3-chlorophenol	298	27.5	1.00	1.51	453
AP-10	phenol	298	29.9	1.00	1.80	488
	3-chlorophenol	298	31.1	1.04	1.68	504
CP-5	phenol	298	27.4	1.00	2.20	596
	3-chlorophenol	298	29.1	1.06	1.74	522
CP-10	phenol	298	30.5	1.00	2.55	691
	3-chlorophenol	298	28.7	0.94	2.20	660

**Figure 1.** Adsorption isotherms of phenol at 298 K (◇) and at 313 K (*), and 3-chlorophenol (△) at 298 K, from aqueous solutions onto carbon PLW.

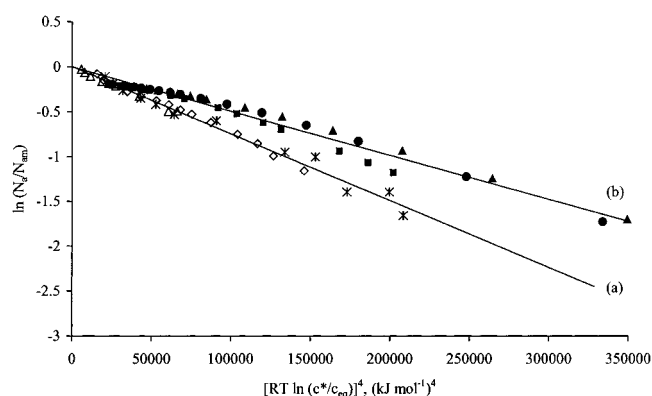
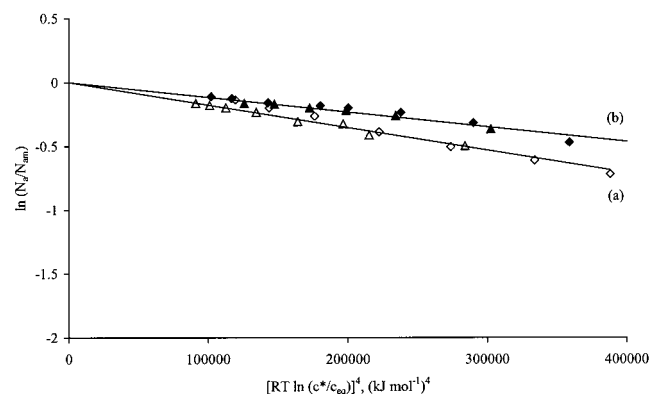
0.04 M. Experiments were also performed with carbon blacks Hoechst and Vulcan 3-G to test for self-consistency.

Results and Discussion

First, it has been known for a long time,¹⁴ and confirmed by many authors,¹ that in the case of phenol adsorption from aqueous solutions there is a decrease in the surface coverage of the activated carbons when their surface acidity increases. For this reason we have chosen activated carbons with basic surface properties, as shown by their pH_{PZC} . Second, the solution pH at equilibrium was between 6 and 7 in the case of adsorption on activated carbons PLW and those of the series AP and CP, which was below the pH_{PZC} of the carbons. Under these conditions the phenols used will be undissociated,¹⁰ and it is expected that the interactions between the phenols and the surface of the carbons will be of a dispersive nature only.

The data for the adsorption of the phenolic compounds by the various carbons is given in Table 2. As a matter of interest, we also included the data of Leyva-Ramos et al.¹¹ for the adsorption of phenol from aqueous solutions at 283, 298, and 313 K by Filtrasorb 400.

The equilibrium isotherms of phenol (298 and 313 K) and 3-chlorophenol (298 K) adsorbed from aqueous solutions by active carbon PLW are shown in Figure 1.

**Figure 2.** (a) Generalized DRK plots for the adsorption of phenol at 298 K (◇) and 313 K (*), and 3-chlorophenol (△) at 298 K, from aqueous solutions onto carbon PLW. (b) Generalized DRK for the data of Leyva-Ramos et al. for phenol at 283 K (■), 298 K (●), and 313 K (▲) on a typical activated carbon.**Figure 3.** Generalized DRK plots for the data of Moreno-Castilla et al. for the adsorption of phenol (◇) and 3-chlorophenol (△) at 298 K from aqueous solutions onto carbons CP-5 (a) and closed symbols for CP-10 (b).

The data have been analyzed in terms of the extended DRK equation (7), with a variable exponent n . As shown for example in Figures 2 and 3, one obtains very good overall fits for the plots of $\ln(N_0/N_{am})$ versus $[RT \ln(c^*/c_{eq})]^4$. (The values of N_{am} are obtained from the plots for the experimental data.) The power $n = 4$ may be surprising at first, but it appears that this value extends the fit of the experimental over a wider range of relative

Table 3. Limiting Volumes of Phenol Adsorbed by the Activated Carbons at 293 K ($V_m = 89 \text{ cm}^3 \text{ mol}^{-1}$)

carbon	Filtrisorb						
	PLW	400	AP-2.5	AP-5	AP-10	CP-5	CP-10
$N_{\text{am}} \times 10^{-3}$ (mol g^{-1})	3.75	1.98	1.28	1.67	1.80	2.20	2.55
$N_{\text{am}} \times V_m$ ($\text{cm}^3 \text{ g}^{-1}$)	0.33	0.18	0.11	0.15	0.16	0.20	0.23
W_0 ($\text{cm}^3 \text{ g}^{-1}$)	0.45		0.20	0.24	0.35	0.41	0.55

concentrations c_{eq}/c^* than $n = 2$. For example, in the case of phenol on carbon PLW at 298 K (Figure 1), the domain corresponds to $0.0004 < c_{\text{eq}}/c^* < 1$, whereas the use of $n = 2$ limits the linear section to $c_{\text{eq}}/c^* > 0.001$.

The data for phenol adsorbed on PLW at 298 and 313 K and on the carbon of Leyva-Ramos et al. 293, 298, and 313 K shows that the requirement for temperature invariance is fulfilled near room temperature. This suggests that eq 7 can be used to predict the adsorption of phenol with a constant value of E_s , given in Table 2. For 3-chlorophenol one obtains slightly different values for E_s , but a finer analysis shows that they can be correlated with $E_s(\text{phenol})$ by introducing a shifting factor, β_s , similar to the affinity coefficient β used in eq 1. In this case, if phenol is taken as the reference,

$$\beta_s = E_s/E_s(\text{phenol}) \quad (8)$$

β_s for 3-chlorophenol, derived for the different carbons and given in Table 2, takes an average value of 1.03 ± 0.10 .

As shown in Tables 1 and 2, it appears that the characteristic energies E_s and E_0 vary in opposite directions. This is surprising, but it should be kept in mind that these parameters reflect two different mechanisms: E_0 corresponds, by definition, to the adsorption of benzene vapor filling the micropore volume W_0 . E_s , on the other hand, is associated with the transfer of phenol from aqueous solutions onto the surface of the carbon (see below). Moreover, the chemistry of the surface also plays a role in the adsorption of phenol.¹ However, no definite explanation can be offered at this stage and the correlation between E_s and other parameters needs further investigation.

At this stage, it appears that the adsorption of phenol and 3-chlorophenol from aqueous solutions can be fitted to the extended DRK equation (7) in which parameter E_s depends on the energy of interaction between the phenol and the given carbon. It is also related to the heat of immersion of the carbon into the phenol solution and to the affinity coefficient β_s . This is a clear advantage over both the Langmuir equation and the Freundlich equation, whose parameters have no simple physical meaning.

More information is also provided by the limiting amounts of phenol and 3-chlorophenol adsorbed by the different activated carbons. As illustrated by Figure 1, and confirmed by the fits to the DRK or the Langmuir¹⁰ equations, adsorption from solution is limited and N_{am} could correspond to a monolayer. The data of Table 2 also suggests that the limiting amounts N_{am} of phenol adsorbed by the solids correspond to smaller equivalent volumes than required to fill the micropores: Using the molar volume of 89 cm^3 of solid phenol at 293 K, one obtains the equivalent volumes $N_{\text{am}} \times V_m$ given in Table 3, which are always smaller than W_0 . For carbons PLW and CP-10, two limiting cases, one obtains 0.33 and 0.23 cm^3/g as opposed to micropore volumes W_0 of 0.45 and 0.55 cm^3/g . Moreover, these calculations do not take into account the

adsorption of phenol on the external surface S_e , approximately $(3.2 \times 10^{-6} \text{ mol/m}^2) \times (50 \text{ m}^2/\text{g}) = 0.16 \times 10^{-3} \text{ mol/g}$ or an equivalent volume of 0.01 cm^3/g . One may therefore postulate that the adsorption of phenol and 3-chlorophenol by activated carbons, and under the experimental conditions specified above, could follow a similar pattern, with the coating of the micropore walls and of the external surface by a monolayer, rather than the filling of the micropores.

However, a controversy has been going on for some time about the use of phenol adsorption from aqueous solutions to determine the surface area of carbonaceous materials.¹ This is due to the fact that this process may also depend, to some extent, on the surface chemistry of the carbon and on the pH of the solution. Furthermore, there are also some discrepancies about the value of the cross-sectional area of the phenol molecule when it is adsorbed in a flat position. Thus, Teng et al.¹⁵ used a value of $30.2 \times 10^{-20} \text{ m}^2$, Boehm et al.¹⁶ $40 \times 10^{-20} \text{ m}^2$, Coughlin et al.¹⁷ $41.2 \times 10^{-20} \text{ m}^2$, and Singh¹⁸ $52.2 \times 10^{-20} \text{ m}^2$. Recently, Lyklema¹⁹ used a cross-sectional area of $45 \times 10^{-20} \text{ m}^2$, and with this value, he found an area of 380 m^2 for a carbon with a BET (N_2) area of about 1000 m^2 , indicating that this is still so high as to suggest contributions from pores.

In the present study we used the value of $45 \times 10^{-20} \text{ m}^2$ for the molecular area of phenol and $49.8 \times 10^{-20} \text{ m}^2$ for 3-chlorophenol, adjusted by MMX force-field calculations.²⁰ Using these values, we come to the conclusion that under the present conditions the adsorption of phenol and of 3-chlorophenol is limited to the coating of the total surface of the carbon, S_{tot} . This surface consists of the micropore walls, S_{mi} , and the external (nonmicroporous) surface area, S_{ext} . Evidence for this mechanism is provided by two different approaches discussed below and based on the adsorption capacities and on immersion calorimetry.

The first approach is based on the comparison of the monolayer capacities N_{am} with the total surface area S_{tot} of the carbons, known from other techniques. Thus, taking into account the cross-sectional area of the phenols, the limiting adsorption capacities N_{am} obtained from the DRK plots and given in Table 2 lead to the equivalent total surfaces areas $S_{\text{m}}(\text{DRK})$ given in the same table. It appears that, for each carbon, the values obtained with both phenolic compounds are in good agreement, except for sample AP-2.5 in which the differences found in $S_{\text{m}}(\text{DRK})$ obtained with phenol and 3-chlorophenol can be due to the low degree of activation of this sample.¹⁰ It has been shown²¹ for this type of carbon molecular sieve effect can be present, which reduces the accessibility of the micropore system for the substituted phenols. As shown in Table 4, for activated carbons PLW, AP-2.5, AP-5, and CP-5 the average values of $S_{\text{m}}(\text{DRK})$ are in good agreement with the values of $S_{\text{tot}} = S_{\text{mi}} + S_e$, given in Table 1 and derived from the structural parameters E_0 , W_0 , using eqs 2 and 3. The systematically lower values of S_{tot} predicted for carbons AP-10 and CP-10 may reflect a limitation of eq 2 in the case of carbons with large micropore width. Under

(15) Teng, H.; Hsieh, C. T. *Ind. Eng. Chem. Res.* **1998**, *37*, 3618.

(16) Boehm, H. P.; Gromes, W. *Angew. Chem.* **1959**, *71*, 65.

(17) Coughlin, R. W.; Ezra, F. S.; Tan, R. N. *J. Colloid Interface Sci.* **1968**, *28*, 386.

(18) Singh, D. D. *Ind. J. Chem.* **1971**, *9*, 1369.

(19) Lyklema, J. *Fundamentals of Interface and Colloid Science. Volume II. Solid-Liquid Interfaces*; Academic Press: London, 1995.

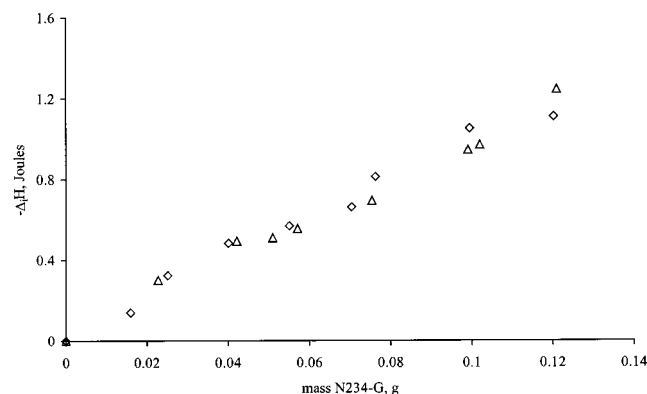
(20) PC Model Molecular Modeling Software for PC. Version 3, Serena Software, 1989.

(21) Caturia, F.; Martin-Martinez, J. M.; Molina-Sabio, M.; Rodriguez-Reinoso, F.; Torregrosa, R. *J. Colloid Interface Sci.* **1988**, *124*, 528.

Table 4. Structural Parameters of the Carbons Based on Adsorption of Phenol and 3-Chlorophenol from Aqueous Solutions

carbon	PLW	Filtrisorb 400	AP-2.5	AP-5	AP-10	CP-5	CP-10
E_s (kJ mol ⁻¹)	19.1	21.1	23.6	27.5	29.9	27.4	30.5
S_m (DRK) (m ² g ⁻¹)	1016	540	347 ^a	453	496	559	676
$S_{mi} = S_m$ (DRK) - S_o (m ² g ⁻¹)	966		339	421	449	507	611
$L = 2000 W_o/S_{mi}$ (nm)	0.93		1.18	1.14	1.56	1.62	1.80
L from eq 2 (nm)	0.86		0.96	1.29	2.84	1.93	4.32

^a Surface area obtained from phenol adsorption.

**Figure 4.** Enthalpies of immersion of carbon N234-G into aqueous solutions of phenol (◇) and 3-chlorophenol (△) at 293 K.

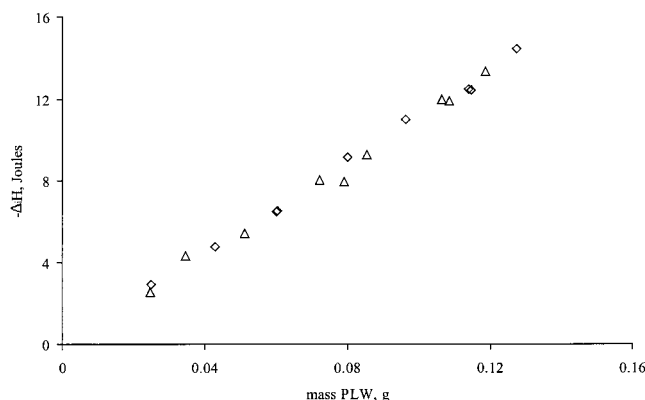
these circumstances, a better approximation can be obtained for the average width L of ideally slit-shaped pores by using the quantity $S_{mi} = S_m$ (DRK) - S_o and the micropore volume W_o of the carbon. As seen in Table 4, in the case of carbons AP-10 and CP-10, the values of L based on this approach show some differences with the predictions of eq 2. However, as pointed out earlier,³ this equation becomes less accurate for $L > 1.7$ – 2.0 nm ($E_o < 16$ – 17 kJ/mol), probably due to the fact that the micropores are no longer slit-shaped. This problem will be dealt with separately, in a new assessment of eq 2.

The second approach to the adsorption of phenolic compounds from aqueous solutions by activated carbons is based on the comparison of the enthalpies of immersion of the activated carbon and of a nonporous carbon black (N234-G) into the aqueous solutions. This technique has already been applied successfully to the case of caffeine,^{3,22,23} a molecule with limited solubility in water, showing a strong affinity for carbon and adsorbed as a monolayer. In the present case, the reference is carbon black N234-G with a BET surface area of 92 m²/g, but some experiments were carried out with carbons blacks Hoechst (54 m²/g) and Vulcan 3-G (71 m²/g) to cross check the technique.

As illustrated by Figure 4, the enthalpies of immersion of carbon N234-G into solutions of phenol and 3-chlorophenol at 293 K are linear functions of the amount of carbon. (This behavior is valid up to a point where a break is observed, which corresponds to the depletion of the solution.) For both phenolic compounds adsorbed by N234-G, the gradients correspond to specific enthalpies h_i of -0.109 ± 0.003 J/m² (phenol) and -0.107 ± 0.002 J/m² (3-chlorophenol). In the case of carbon blacks Hoechst and Vulcan 3-G, one obtains specific enthalpies of -0.103 and -0.124 J/m² for phenol, with similar uncertainties.

(22) Stoeckli, F.; Frangière, M.; Huguenin, D.; Depraz, M.; Ballerini, L. *Carbon* **1989**, *26*, 915.

(23) Ballerini, L.; Huguenin, D.; Rebstein, P.; Stoeckli, F. *J. Chim. Phys.* **1990**, *87*, 1709.

**Figure 5.** Enthalpies of immersion of active carbon PLW into aqueous solutions of phenol (◇) and 3-chlorophenol (△) at 293 K.**Table 5. Adsorption and Immersion Calorimetry Results for Carbon PLW**

phenol	temp (K)	$N_{am} \times 10^{-3}$ (mol g ⁻¹)	S_m (DRK) (m ² g ⁻¹)	$S_m = \Delta_i H/h_i$ (m ² g ⁻¹)
phenol	298	3.75	1016	1037
phenol	313	3.62	981	
3-chlorophenol	298	3.50	1050	1047

The enthalpies of immersion of carbon PLW into solutions of phenol and 3-chlorophenol follow a similar pattern (see Figure 5), with specific enthalpies of respectively -113.0 ± 1.0 and -112.0 ± 1.4 J/g of carbon. As shown in Table 5, using the specific enthalpies obtained with carbon N234-G and on the basis of a BET surface area of 92 m²/g, one obtains equivalent surface areas S_m of 1037 ± 9 and 1047 ± 13 m²/g for carbon PLW. These values are in good agreement with the surface areas S_m (DRK) obtained from the liquid adsorption isotherms (Tables 2 and 4).

It is also interesting to point out that, in the case of carbon black N234-G, the surface density of phenol of 3.18×10^{-6} mol/m² and the specific enthalpy of immersion of -0.109 J/g lead to a molar enthalpy of $-0.109/3.18 \times 10^{-6} = -34.3$ kJ/mol for the transfer of phenol from the solution onto the carbon surface. For carbon PLW, the ratio $\Delta_i H/N_{am} = -(113 \text{ J/g})/(3.75 \times 10^{-3} \text{ mol/g}) = -30.1$ kJ/mol. For another typical activated carbon, not used in the present study, one obtains a ratio $\Delta_i H/N_{am}$ of -30.0 kJ/mol. These values are very close and suggest a similar process for the adsorption on porous and nonporous carbons, leading to a single layer of phenol on the micropore walls and on the open surface. In this respect, the behavior of phenol is similar to that of caffeine, reported earlier.^{3,22,23} Moreover, these enthalpies are in good agreement with the energy of -25 kJ/mol obtained by Salvador and Merchán²⁴ for the adsorption of phenol from an aqueous solution, by a typical active carbon, on the basis of a new type of kinetic experiments (thermally programmed adsorption and desorption).

(24) Salvador, F.; Merchán, M. D. *Carbon* **1996**, *34*, 1543.

It is also interesting to point out that the adsorption of 3-aminophenol, 4-cresol, and 4-nitrophenol onto carbons AP-2.5, AP-5, AP-10, CP-5, and CP-10, described earlier,¹⁰ seems to follow a pattern similar to that of phenol and 3-chlorophenol and one obtains the following affinity coefficients relative to phenol taken as a reference,

$$\beta_s(3\text{-aminophenol}) = 0.84 \pm 0.15$$

$$\beta_s(4\text{-cresol}) = 0.87 \pm 0.04$$

$$\beta_s(4\text{-nitrophenol}) = 0.84 \pm 0.07$$

$$\beta_s(3\text{-chlorophenol}) = 1.03 \pm 0.10$$

This suggests some regularity in the process, but as pointed out elsewhere,^{1,10} the pH of the solution has an influence on the monolayer capacity N_{am} .

Conclusions

The present study, based on adsorption from aqueous solutions and on immersion calorimetry, shows that phenol

and 3-chlorophenol are adsorbed as monolayers by both porous and nonporous carbons displaying basic surface properties and provided that the pH is below that of dissociation of the compounds. (Obviously, this does not necessarily apply to carbons with low degrees of activation, where molecular-sieve effects often reduce the accessibility of the micropore system.) It also appears that adsorption from aqueous solutions can be described by an extended DRK equation, in the present case with exponent $n = 4$, and covering the domain of relative concentrations c_{eq}/c^* between 10^{-4} and 1. The principle of temperature invariance being fulfilled over a certain range of temperature, the adsorption equilibrium from solution can be described by eq 7 between 283 and 313 K. In the case of phenol, this approach requires a single adjustable parameter, E_s , depending on the activated carbon. However, as pointed out above, the correlation between E_s and other parameters needs further investigation.

As suggested by earlier data,¹⁰ it is likely that under suitable conditions the present approach can be extended to other phenolic compounds.

LA0014407