

## On the Adsorption, by Activated Carbons, of Some Sparingly Soluble Organics from Aqueous Solutions

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Dedicated to Professor *André Merbach* on the occasion of his 65th birthday

Activated carbons play an important role in the purification of air and of water. Whereas vapors are adsorbed by a micropore filling process, the removal of sparingly soluble species such as phenol and its derivatives is limited to the coating of the effective surface of the material. This reduces considerably the sorptive capacity of a given carbon, and a suitable description is needed to predict the corresponding equilibrium. It is shown that, in the case of phenol, its derivatives, and a few typical pollutants, the latter process can be described by an extension of the *Dubinin–Radushkevich–Kaganer (DRK)* equation. A major advantage of this approach is the possibility of calculating the adsorption equilibrium based on simple physicochemical properties of the adsorptives and on the structural characteristics of the activated carbon. It also appears that, by analogy with adsorption in the vapor phase, a scaling factor can be introduced for adsorption from solution.

**Introduction.** – Activated carbons [1][2] are mainly used for their sorptive capacity, which can be as high as 0.6–0.8 cm<sup>3</sup> per g of solid. This property is due to the presence of locally slit-shaped micropores (or nanopores, following the modern terminology) with dimensions between 0.4 and *ca.* 2 nm. However, as opposed to zeolites, the pore-size distributions are heterogeneous and depend on the precursor and on the activation process. Activated carbons possess an internal surface area  $S_{mi}$  corresponding to the walls of the micropores, which can be as high as 1500 m<sup>2</sup> g<sup>-1</sup>. On the other hand, the walls of the larger pores lead to a so-called external surface areas  $S_e$ , which can reach 100–200 m<sup>2</sup> g<sup>-1</sup>.

Depending on the situation, adsorption by activated carbons can follow two distinct patterns. Vapors are adsorbed by a process of micropore filling, whereas the removal from aqueous solutions of sparingly soluble compounds such as phenol and its derivatives [3] is limited to the coating of the micropore walls and of the external surface [4–9]. In the latter case, the adsorption capacity is therefore reduced. However, it appears that both mechanisms can be described within the framework of *Dubinin's* theory, with suitable modifications [1][2][4][6][10].

The present paper extends earlier work on the adsorption of phenol from aqueous solutions [7–9], by including a variety of carbons, ranging from a nonporous graphitized carbon black to materials with average micropores around 0.8 nm. For comparison purposes, data from some carbons from the literature [11–13] was included. The study also includes typical industrial carbons with so-called supermicropores (1.5 to 2 nm or  $E_0 < 16–17$  kJ mol<sup>-1</sup>), often used in large-scale filtration installations. This allows the extension of an earlier correlation [4][9] to the entire

spectrum of activated carbons and the inclusion of other sparingly soluble molecules. However, it is only a step in a more general scheme for the description of single and multiple adsorption based on *Dubinin's* theory, as opposed to other descriptions. The latter are often based on the *Langmuir*, *Freundlich*, *Langmuir–Freundlich*, and other adsorption isotherms [11–13].

**Theoretical.** – As discussed elsewhere [1][2][10], the adsorption of vapors by microporous solids corresponds to a volume filling process described by *Dubinin's* theory, developed in successive stages since 1947. It is based on the thermodynamic potential  $A = RT \ln(p_s/p)$ , and the fundamental expression is the *Dubinin–Astakhov* (*DA*) equation (see *Eqn. 1*), where  $N_a$  (in mmol g<sup>-1</sup>) is the amount adsorbed at relative pressure  $p/p_s$  and temperature  $T$ ,  $N_{ao}$  is the limiting amount filling the micropore volume  $W_o = N_{ao}V_m$ , assuming that  $V_m$  is close to the molar volume in the liquid state, and  $E$  is the so-called characteristic energy of the system. The latter can be written as  $E = \beta E_0$ , where  $\beta$  is the affinity coefficient of the adsorptive, benzene being the reference ( $\beta(C_6H_6) = 1$ ). These coefficients have been compiled by *Wood* [14], who also discusses the various correlations used to predict them. For most activated carbons, exponent  $n = 2$ , which corresponds to the classical *Dubinin–Radushkevich* (*DR*) equation. It is followed by most organic and inorganic vapors including H<sub>2</sub>O, but for the latter, the situation is somewhat more complicated, as shown by *Stoekli* and co-workers [15–17].

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

The strength of *Dubinin's* theory lies in the simplicity of the physicochemical parameters and in that both  $E$  and  $n$  are temperature-invariant (see, e.g., below *Fig. 1*). This means that the adsorption equilibrium can be predicted over a range of temperatures and pressures.

It has been shown in the early 1950s that adsorption of vapors by nonporous carbons, in the sub-monolayer region, can be described by a modified version of *Eqn. 1*, known as the *Dubinin–Radushkevich–Kaganer* equation (*DRK*) [18] (see *Eqn. 2*).

In this case, the limiting amount adsorbed corresponds to the monolayer capacity of the carbon surface, and the corresponding surface area  $S$  (in m<sup>2</sup> g<sup>-1</sup>) is given by *Eqn. 3*, where  $A_m$  is the molecular surface area of the adsorptive (typically  $45 \cdot 10^{-20}$  m<sup>2</sup> for phenol lying flat on the carbon surface [9]) and  $N_{AV}$  is *Avogadro's* number. As we have recently discussed [19], by analogy with *Eqn. 1*, the exponent  $n$  of the classical *DRK* equation can be different from 2, as it reflects the heterogeneity of the surface, as perceived by the adsorbate.

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

$$S = N_{am} A_m N_{AV} \quad (3)$$

As shown in detail elsewhere [2], on the basis of a variety of techniques including modelling of adsorption by Monte Carlo techniques [20][21], it appears that  $E_0$  is related to the average micropore width  $L_o$  (in nm) by *Eqn. 4*. It follows that, for ideally

slit-shaped micropores, the surface area of  $S_{mi}$  (in  $\text{m}^2 \text{g}^{-1}$ ) their walls is given by *Eqn. 5* ( $W_o$  in  $\text{cm}^3 \text{g}^{-1}$ ,  $L$  in nm). The external (nonmicroporous) surface area can be derived from a standard comparison plot of the nitrogen (77 K) or the benzene isotherm at room temperature against the corresponding isotherm on a nonporous carbon (*Sing's* so-called  $\alpha_s$ -plot) [22].

$$L_o = 10.8/(E_o - 11.4 \text{ kJ mol}^{-1}) \quad (4)$$

$$S_{mi} = 2000 W_o/L \quad (5)$$

Earlier work done in the Soviet Union [5][6][23], largely unknown in the West, has shown that adsorption from aqueous solutions could be described by an expression similar to the *DRK* equation (see *Eqn. 2*), where the relative pressure  $p/p_s$  is replaced by the relative concentration  $c/c^*$ ,  $c^*$  being the saturation concentration of the adsorptive at the given temperature. This assumption is justified by the fact that both  $RT \ln(p_s/p)$  and  $RT \ln(c^*/c)$  correspond to a change in chemical potential ( $-\Delta G$ ). More recently, it has been shown by *Stoekli* and co-workers [9] that the use of exponent  $n = 4$  provides a better overall fit than  $n = 2$  used by other authors [5][6][23]. This leads to the modified *DRK* equation for adsorption from aqueous solutions, *i.e.*, to *Eqn. 6*, where  $N_a$  is the amount adsorbed by the carbon at temperature  $T$  and equilibrium concentration  $c_{eq}$ ,  $N_{am}$  represents the monolayer capacity of the micropore surface  $S_{mi}$ , and  $E_s$  is an energy characterizing the system under investigation (solid and adsorbate). It appears that changing exponent  $n$  from 2 to 4 does not modify  $E_s$  significantly. As shown earlier and confirmed below,  $E_s$  is temperature-invariant, at least between 283 and 313 K.

$$N_a = N_{am} \exp\{-[RT \ln(c^*/c_{eq})/E_s]^4\} \quad (6)$$

So far, the validity of *Eqn. 6* has been established for the adsorption of unbuffered phenol and some of its derivatives on a few typical activated carbons [7–9]. However, as shown earlier, in the case of oxidized carbons, the monolayer capacity  $N_{am}$  for phenol (and probably its derivatives) is reduced by the selective adsorption of  $\text{H}_2\text{O}$  on the oxygen-containing complexes of the surface [8]. It was also established that the enthalpy of formation of a monolayer over the entire surface, from the aqueous solution, could be obtained by immersion calorimetry [2][9], provided that the liquid phase contains a sufficient amount of solute. It appeared that the net enthalpy of transfer of phenol from the solution onto the carbon surface is on average  $-31.2 \text{ kJ mol}^{-1}$ . Assuming a molecular surface area of  $45 \cdot 10^{-20} \text{ m}^2$ , it was found that the creation of a monolayer corresponds to  $h_i(\text{phenol}) = -0.115 \text{ J m}^{-2}$ . This means that the total monolayer capacity  $N_{am \text{ tot}}(\text{phenol})$  (in  $\text{mmol g}^{-1}$ ), or the total surface area of the carbon  $S_{\text{tot}} = S_{mi} + S_e$  (in  $\text{m}^2 \text{g}^{-1}$ ) can be determined by immersion calorimetry into dilute aqueous solutions of phenol (*e.g.*, 0.4M). The corresponding relationships are given by *Eqns. 7* and *8* ( $\Delta_i H$  in  $\text{Jg}^{-1}$ ). This approach, not limited to phenol, should provide a test for self-consistency as discussed below.

$$N_{am \text{ tot}}(\text{phenol}) = -\Delta_i H/31.2 \text{ kJ mol}^{-1} \quad (7)$$

$$S_{\text{tot}} = -\Delta_i H / 0.115 \text{ Jm}^{-2} \quad (8)$$

As shown in the case of phenol and some of its derivatives adsorbed from unbuffered solutions onto a limited number of activated carbons [9][13], Eqn. 6 is valid over a relatively wide temperature range (typically from 283 to 313 K). Consequently, with the help of  $N_{\text{am}}$  and of  $c^*$ , it is possible to predict the adsorption equilibrium of a given agent adsorbed from an aqueous solution. At low concentrations, adsorption takes place essentially on the micropore walls, as predicted by Eqn. 6. The external surface area  $S_e$  is coated only at relatively high concentrations, which is the case for immersion calorimetry. Moreover,  $S_e$  is only a fraction of the total surface area available to the adsorbate. It follows that, if the initial conditions are known (amount of carbon, concentration and volume of liquid in contact with the solid), the combination of Eqn. 6 with a mass-balance leads to the residual concentration of the agent in the liquid.

**Experimental.** – The present study is based on a variety of activated carbons and a nonporous carbon black *N-234G*. The main characteristics of the solids are given in Table 1. The experimental techniques used for immersion calorimetry, the adsorption of vapors, and adsorption from aqueous solns. by using UV spectroscopy are described in detail in [2][9][11].

Table 1. Main Characteristics of the Carbons Used in the Present Study

Carbon	$E_0$ [kJ mol <sup>-1</sup> ]	$E_s$ [kJ mol <sup>-1</sup> ]	$W_0$ [cm <sup>3</sup> g <sup>-1</sup> ]	$S_{\text{mi}}$ [m <sup>2</sup> g <sup>-1</sup> ]	$S_e$ [m <sup>2</sup> g <sup>-1</sup> ]
<i>N234-G</i>	12.4	13.5	–	–	93
<i>N-125</i>	16.6	–	0.64	615	160
<i>CN 31</i>	16.9	18.8	0.35	355	90
<i>U03</i>	17.2	18.64	0.59	630	60
<i>PC-REF</i>	17.5	18.5	0.59	1045	50
<i>F02</i>	18.9	22.8	0.65	775	90
<i>BV46ox</i>	19.8	20.7	0.42	650	115
<i>XC-72</i>	21.3	22.0	0.06	120	120
<i>AP 2–5</i>	22.6	23.6	0.20	415	10

**Results and Discussion.** – Fig. 1 shows the logarithmic plot of Eqn. 1 with  $n = 2$  for the adsorption of typical organic vapors by carbon *PC-REF*. The data also includes phenol at 307 K, and it appears clearly that the mechanism corresponds to the volume filling of the micropores. Similar observations were made for the adsorption of phenol vapors at 306 and 319 K for carbon *F02*. With respect to benzene, the average affinity coefficient  $\beta(\text{phenol}) = 1.0$ , which is in good agreement with the prediction of 1.08 based on the ratio of the parachors [14]. On the other hand, as illustrated by Fig. 2, and in agreement with earlier determinations, the adsorption of phenol from an unbuffered aqueous solution at 298 K by carbons *PC-REF* and *F02* follows Eqn. 6, with the  $E_s$  values listed in Table 1. This is also the case for the nonporous graphitized carbon black *N-234G*. Assuming a molecular surface area of  $45 \cdot 10^{-20}$  nm<sup>2</sup>, the limiting capacity  $N_{\text{am}}$  leads to a surface area of 93 m<sup>2</sup> g<sup>-1</sup>, in very good agreement with the BET surface area (N<sub>2</sub>; 78 K) of 92 m<sup>2</sup> g<sup>-1</sup>. The low value of  $E_s(\text{phenol}) = 13.2$  kJ mol<sup>-1</sup> implies that, with respect to the micropore walls, adsorption on the external surface  $S_e$  of an activated

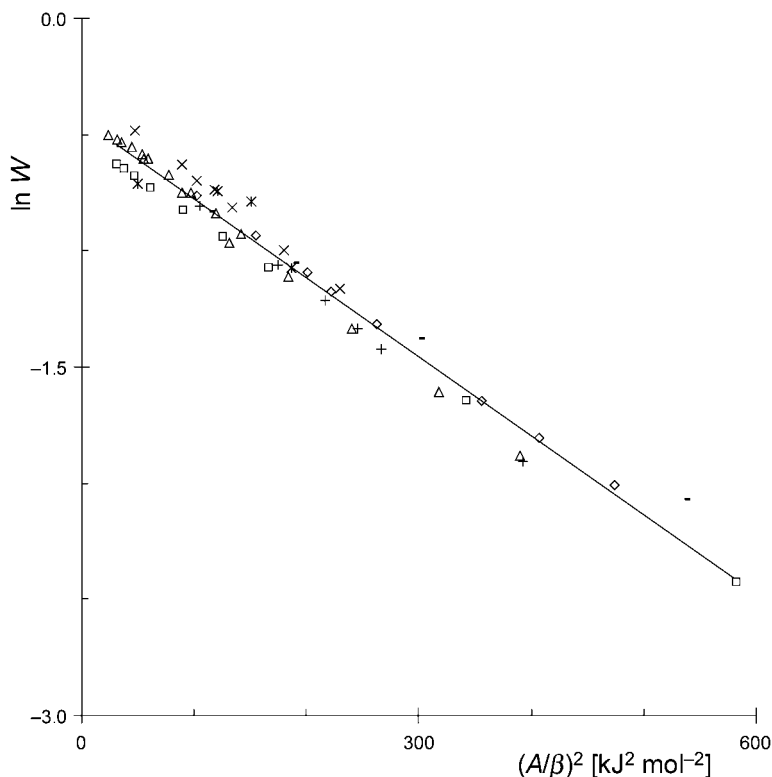


Fig. 1. Logarithmic Dubinin-Raduskevich plot for the vapor adsorption of benzene at 293 K ( $\square$ ), and 301 K ( $-$ ), of 1,2-dichloroethane at 293 K ( $\triangle$ ) and 306 K ( $\times$ ), of chloroform at 293 K ( $\square$ ) and 306 K ( $+$ ), and of phenol at 307 K ( $*$ ) on activated carbon PC-REF

carbon becomes important only at high relative concentrations (typically  $c_{eq}/c^* > 0.05$ ). This means that in the case of activated carbons used for the removal of traces from aqueous solutions, adsorption effectively occurs only on the micropore walls and follows Eqn. 6.

For the eight carbons used in this study, Eqn. 6 for adsorption by the micropore walls leads to the values of  $E_S(\text{phenol})$  also given in Table 1. Defining a solution affinity coefficient relative to the adsorption of the standard vapor benzene,  $\beta_s = E_S/E_0$ , it appears that  $E_S(\text{phenol})/E_0 = 1.08 \pm 0.06$ . This value is practically equal to the affinity coefficient for adsorption in the vapor phase and, furthermore, for the nonporous carbon black N234-G,  $E_S(\text{phenol})/E_0 = 1.07$ . This means that the characteristic adsorption energy of phenol from aqueous solutions is practically the same as for the vapor phase. It follows that, for or any activated carbon with micropores wider than ca. 0.8 nm, adsorption from aqueous solutions can therefore be described by Eqn. 6, where  $E_S = (1.05 \pm 0.07)E_0$ .

This contrasts with the behavior of benzene itself, where it has been established by Choma *et al.* [23] that the characteristic energy  $E_S(\text{C}_6\text{H}_6)$  obtained for eight carbons is equal to  $(0.52 \pm 0.04)E_0$ . These authors used Eqn. 6 with exponent 2, but the change in

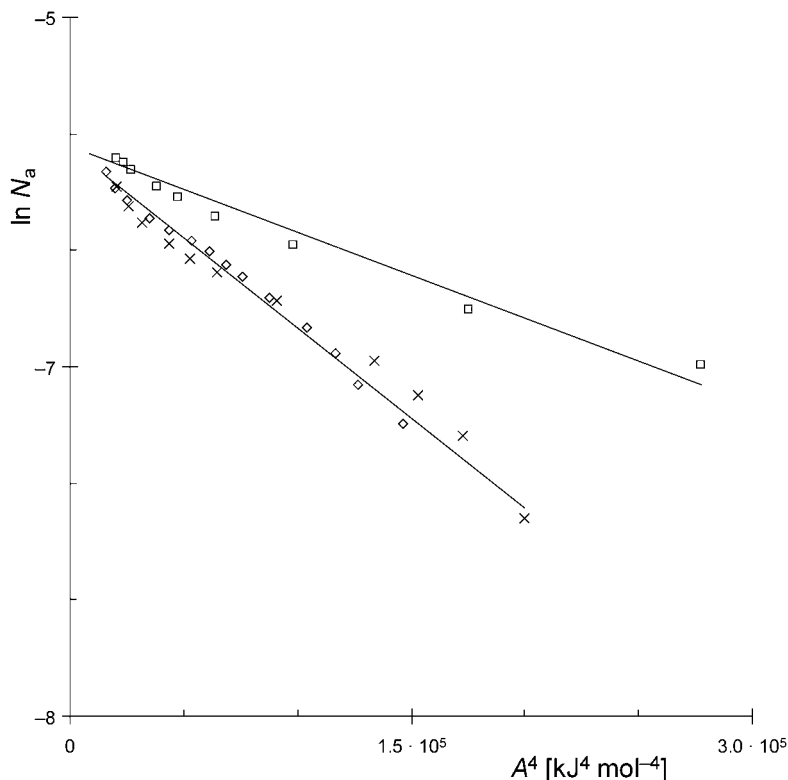


Fig. 2. Logarithmic plot of Eqn. 6 for the adsorption of phenol from aqueous solution on activated carbons F02 at 298 K ( $\square$ ) and PC-REF at 298 K ( $\diamond$ ) and 313 K ( $\times$ )

exponent does not modify significantly the value of  $E_S$ . Inspection of the data for  $E_S$  obtained for a number of sparingly soluble molecules in this study and from the analysis of data from the literature, given in Table 2, leads to solution affinity coefficients  $\beta_s = E_S/E_0$ , which are systematically smaller than the affinity coefficients  $\beta = E/E_0$  observed or calculated for adsorption from the vapor phase [14]. For example, the adsorption isotherms of caffeine from an aqueous solution by carbons F02 and N-125, studied in our laboratory, follow Eqn. 6 with characteristic energies  $E_S(\text{caffeine})$  of 25.1 and 20.4 kJ mol<sup>-1</sup>. These values lead to solution affinity coefficients  $\beta_s(\text{caffeine}) = E_S(\text{caffeine})/E_0$  of 1.33 and 1.23, whereas the prediction based on the empirical correlations suggested by Wood [14] suggest a value of ca. 1.8–1.9.

A first estimate of the data shown in Table 2 suggests that  $\beta_s/\beta$  varies between 0.5 and 0.8. This trend had already been pointed out by Koganovski *et al.* [6] for six compounds sparingly adsorbed on two carbons. These authors found that the ratio  $E_S/E_S(\text{C}_6\text{H}_6)$  was relatively close to  $\beta$ , and analysis of their data for benzene adsorbed from aqueous solution [5] shows that  $E_S(\text{C}_6\text{H}_6)/E_0$  is approximately equal to 0.5, in agreement with the detailed work of Choma *et al.* [23].

Table 2. Affinity Coefficients  $\beta_s$  for Adsorption from Unbuffered Aqueous Solutions, Relative to Benzene (characteristic energy  $E_0$ ) and Values for Adsorption from the Vapor Phase,  $\beta$

	$n^a$ )	$\beta_s = E_s/E_0$	$\beta$	$\beta_s/\beta$
Phenol (this work)	4	$1.05 \pm 0.10$	1.09	0.83–1.08
Phenol [11]	4	0.89–0.91	1.09	0.83–1.08
Caffeine (this work)	4	1.23–1.33	1.8–1.9	0.65–0.74
Benzene [23]	2, 3	$0.52 \pm 0.04$	1.0	0.46–0.56
Benzene [5]	2	0.48–0.65	1.0	0.46–0.56
Aniline [6][10]	2, 4	0.75–0.84	1.07	0.44–0.78
4-Chloroaniline [5][6]	2	0.52–0.72	1.36	0.38–0.53
4-Chlorophenol [6][9]	2, 4	0.84–1.06	1.24	0.68–0.85
Chloroform [5][6]	2	0.50–0.53	0.89	0.56–0.60

<sup>a</sup>) Exponent  $n$  used in Eqn. (6)

At this stage, it would appear that the characteristic energy  $E_s$  of a typical adsorbate is *ca.* 0.5–0.8 times  $\beta E_0$ , phenol itself being an exception. It is likely that the change in the affinity coefficient between the vapor phase and the aqueous solution reflects the influence of the solution on the adsorption process, and further systematic investigation is required. It also appears that the earlier data reported for  $\beta_s$  values observed with carbons *AP-5*, *AP-10*, *CP-5*, and *CP-10* [9] requires further analysis.

**Conclusions.** – At this stage, it appears that in the case of activated carbons with average micropore widths  $L_0 > 0.8$  nm, the adsorption of a number of sparingly soluble molecules from aqueous solutions could be described by a generalized relationship of Eqn. 6, *i.e.*, by Eqn. 9.

$$N_a = N_{am} \exp\{-[RT \ln(c^*/c_{eq})/\beta_s E_0]^4\} \quad (9)$$

The advantage of this approach, to be confirmed by further systematic experiments, is the simplicity of its parameters, and the fact that it can be used over a range of temperatures and relative concentrations. A carbon to be used in a filtration system is characterized by its energy  $E_0$ , micropore volume  $W_0$ , and surface areas  $S_{mi}$  and  $S_e$ . These parameters can be derived routinely from a single adsorption isotherm ( $N_2$  at 77 K or, preferably  $C_6H_6$  at room temperature). The monolayer capacity  $N_{am}$  of the microporous surface area, the relevant parameter for adsorption at low concentrations, can be determined from Eqn. 3. Alternatively, one may use the calorimetric approach based on Eqns. 7 or 8, with a correction for the external surface area  $S_e$ . Moreover, for higher concentrations (typically  $c_{eq}/c^* > 0.05$ ), adsorption on  $S_e$  can be taken into account by an additional equation, similar to Eqn. 9, where  $E_0 \approx 11–12$  kJ mol<sup>-1</sup> (typical values for graphitized carbon blacks) and by using the corresponding monolayer capacity  $N_{am}(S_e)$  obtained from Eqn. 3.

For sparingly soluble species in general, Eqn. 9 requires the knowledge of the surface affinity coefficients  $\beta_s$ , some of which are given in Table 2. With the exception of phenol where  $\beta_s = 1.05 \pm 0.07$ , these parameters correspond approximately to (0.5–0.8)

$\beta$ . The latter can be calculated easily from physical properties [14], but this correlation needs to be investigated further and refined. Results will be published in due course.

The authors wish to thank Dr. D. M. Nevskaiia (UNED, Madrid) for data on carbon NR-1 and the Swiss National Science Foundation for financial support (Project No 200020-101 460).

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