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^3 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 $m^2 g^{-1}$. 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 $m^2 g^{-1}$.

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^{-1}), 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^{-1}) 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 β 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_2O, but for the latter, the situation is somewhat more complicated, as shown by *Stoeckli* and co-workers [15–17].

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

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^2 g^{-1}) is given by *Eqn. 3*, where A_m is the molecular surface area of the adsorptive (typically $45 \cdot 10^{-20}$ m^{-2} 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.

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

$$S = N_{am}\, A_m\, N_{AV} \tag{3}$$

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 $m^2\ g^{-1}$) their walls is given by *Eqn. 5* (W_o in $cm^3\ g^{-1}$, 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 α_S-plot) [22].

$$L_o = 10.8/(E_0 - 11.4\ \text{kJ mol}^{-1}) \tag{4}$$

$$S_{mi} = 2000\ W_o/L \tag{5}$$

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 *Stoeckli* 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 and 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.

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

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 H_2O 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 kJ mol^{-1}. Assuming a molecular surface area of $45 \cdot 10^{-20}\ m^2$, it was found that the creation of a monolayer corresponds to $h_i(\text{phenol}) = -0.115\ J\ m^{-2}$. This means that the total monolayer capacity $N_{am\ tot}$ (phenol) (in mmol g^{-1}), or the total surface area of the carbon $S_{tot} = S_{mi} + S_e$ (in $m^2\ g^{-1}$) 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 Jg^{-1}). This approach, not limited to phenol, should provide a test for self-consistency as discussed below.

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

$$S_{tot} = -\Delta_i H/0.115\ \mathrm{Jm}^{-2} \tag{8}$$

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_{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^{-1}]	E_S [kJ mol^{-1}]	W_0 [cm^{3}g^{-1}]	S_{mi} [m^{2}g^{-1}]	S_e [m^{2}g^{-1}]
N234-G	12.4	13.5	–	–	93
N-125	16.6	–	0.64	615	160
CN 31	16.9	18.8	0.35	355	90
U03	17.2	18.64	0.59	630	60
PC-REF	17.5	18.5	0.59	1045	50
F02	18.9	22.8	0.65	775	90
BV46ox	19.8	20.7	0.42	650	115
XC-72	21.3	22.0	0.06	120	120
AP 2–5	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 β(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^2, the limiting capacity N_{am} leads to a surface area of 93 m^2 g^{-1}, in very good agreement with the BET surface area (N_2; 78 K) of 92 m^2 g^{-1}. The low value of E_S(phenol) = 13.2 kJ mol^{-1} implies that, with respect to the micropore walls, adsorption on the external surface S_e of an activated

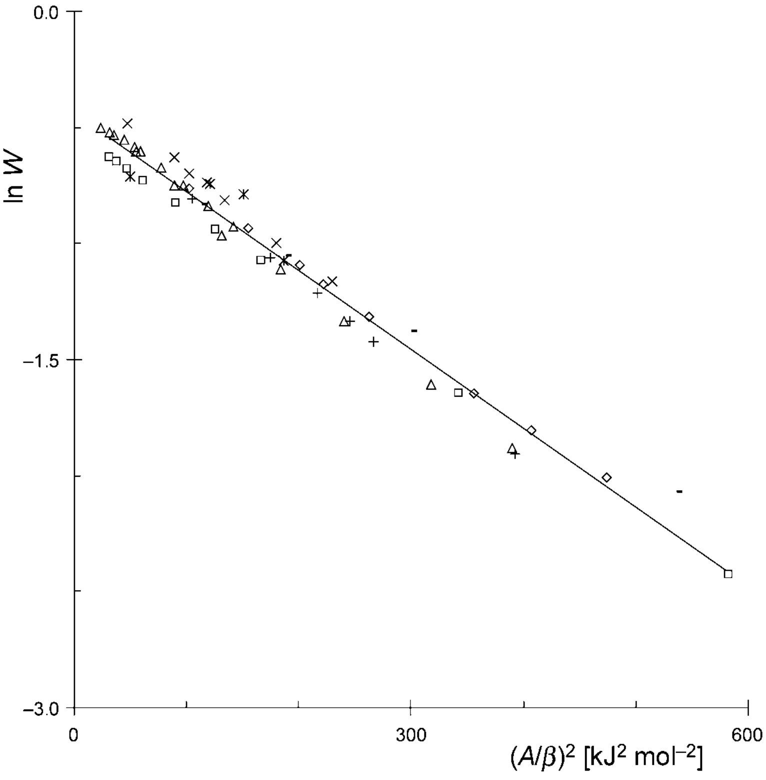

Fig. 1. *Logarithmic* Dubinin-Raduskevich *plot for the vapor adsorption of benzene at 293 K* (□), *and 301 K* (−), *of 1,2-dichloroethane at 293 K* (△) *and 306 K* (×), *of chloroform at 293 K* (Rl) *and 306 K* (+), *and of phenol at 307 K* (*) *on activated carbon* PC-REF

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(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 $E_S(C_6H_6)$ obtained for eight carbons is equal to (0.52 ± 0.04) E_0. These authors used *Eqn. 6* with exponent 2, but the change in

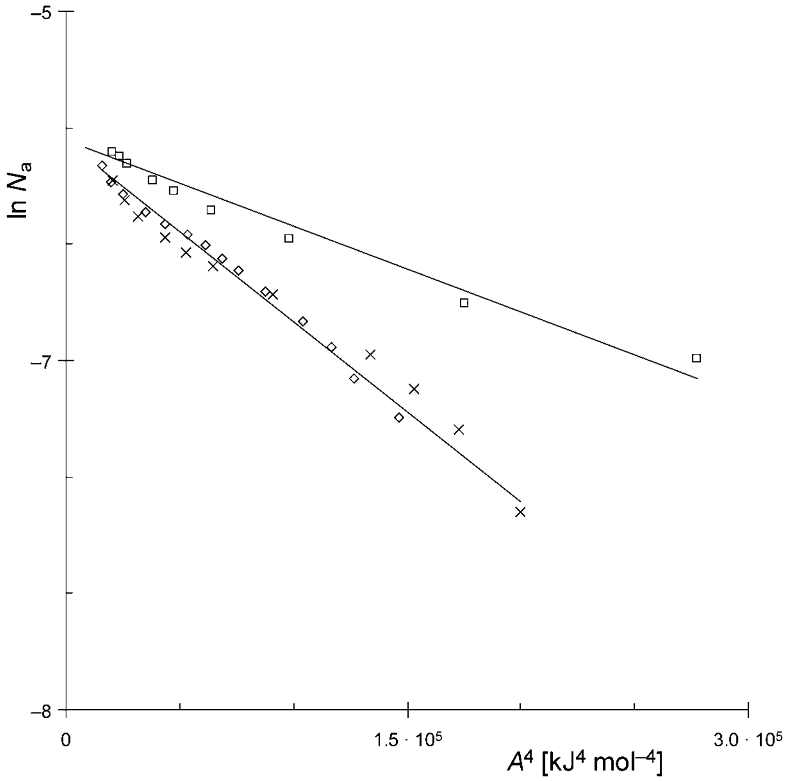

Fig. 2. *Logarithmic plot of* Eqn. 6 *for the adsorption of phenol from aqueous solution on activated carbons* F 02 *at 298 K* (□) *and* PC-REF *at 298 K* (◇) *and 313 K* (×)

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(caffeine) of 25.1 and 20.4 kJ mol^{-1}. These values lead to solution affinity coefficients β_s(caffeine) = E_S(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 β_S/β 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/$E_S(C_6H_6)$ was relatively close to β, and analysis of their data for benzene adsorbed from aqueous solution [5] shows that $E_S(C_6H_6)/E_0$ is approximately equal to 0.5, in agreement with the detailed work of *Choma et al.* [23].

Table 2. *Affinity Coefficients β_S for Adsorption from Unbuffered Aqueous Solutions, Relative to Benzene* (characteristic energy E_0) *and Values for Adsorption from the Vapor Phase, β*

	n[a])	$\beta_S = E_S/E_0$	β	β_S/β
Phenol (this work)	4	1.05 ± 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 ± 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

[a]) 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 βE_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 β_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*.

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

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^{-1} (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 β_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)

β. 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.

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