

EXTENSION OF DUBININ'S THEORY TO ADSORPTION FROM FROM AQUEOUS SOLUTIONS

FRITZ STOECKLI*

*IMT-Chimie des Surfaces, Université de Neuchâtel. Rue Emile Argand 11,
CH-2009 Neuchâtel, Switzerland*

DASHA M. NEVSKAIA, EVA CASTILLEJOS-LOPEZ

*Departamento de Química Inorgánica, Facultad de Ciencias UNED, Paseo
Senda del Rey 9, 28040 Madrid, Spain*

TERESA A. CENTENO

Instituto Nacional del Carbón-CSIC. Apartado 73, 33080 Oviedo, Spain

Abstract. Adsorption of sparingly soluble organics from aqueous solutions, by activated carbons, can be described within the framework of Dubinin's theory by using a modified Dubinin–Radushkevich–Kaganer (DRK) equation, where relative pressures are replaced by relative concentrations. With respect to the descriptions based on the Langmuir model and similar expressions, this approach has the advantage that it allows predictions on the basis of simple physico-chemical properties of the solid and of the adsorbate. Preliminary experiments indicate that in the case of dilute binary mixtures, the model of independent coadsorption, based on the DRK equation, applies. However, more experimental evidence is needed to confirm this potentially very useful approach in filtration technology.

Keywords: Dubinin's theory; adsorption; aqueous solutions; binary mixtures

1. Introduction

The removal of sparingly soluble organics from aqueous solutions is a relatively important topic, in particular for the purification of drinking

* To whom correspondence should be addressed. Institut de Microtechnique-LCPS, rue Emile Argand 11, CH-2009 Neuchâtel, Switzerland; E-mail: fritz.stoeckli@unine.ch

water by activated carbon. So far, a variety of theoretical models have been proposed, which can reproduce accurately the experimental data.^{1,2}

However, a major shortcoming in the use of Langmuir- or Freundlich-based approaches is the fact that predictions are difficult, and even impossible in many cases, due to the complexity of the parameters used in these expressions. It is therefore necessary to find alternative descriptions, which provide a tool for quantitative or at least semi-quantitative predictions in filtration technology.

Active carbons are very efficient adsorbents and the adsorption of vapours is well described by Dubinin's theory,^{3,4} which uses relatively simple parameters and allows predictions over relatively wide pressure and temperature ranges. As shown in detail elsewhere,⁵⁻⁷ for relative concentrations $c_{eq}/c_s < 0.01-0.05$ (submonolayer conditions) adsorption of sparingly soluble species such as phenol and its derivatives can be described by the modified Dubinin-Radushkevich-Kaganer (DRK) equation.

$$N_a(T;p) = N_{am} \exp[-(A/E_s)^n] \quad (1)$$

where

$$A = RT \ln(c_s/c_{eq}) \text{ and } n \sim 2-4 \quad (2)$$

In the case of sparingly soluble species, N_{am} corresponds to the monolayer capacity of the walls of the micropores and not to the filling of these pores, as opposed to adsorption from the vapour phase. This means that the sorptive capacity of a microporous carbon is often smaller in the case of adsorption from dilute aqueous solutions, than from the vapour phase. This point is clearly illustrated by the adsorption of phenol from both phases.⁸

It appears that the principle of temperature invariance observed by Dubinin for micropore filling also applies here, as parameters n and E_s are practically constant over a range of 20°–30°.

One can also introduce specific scaling factors (surface affinity coefficients β_s) for E_s , to correlate the adsorption of different species relative to a reference solute (benzene or phenol). These properties are reflected in the logarithmic plot (Figure 1) for the adsorption of various phenolic compounds from aqueous solutions, at different temperatures and on three different activated carbons, with $n = 4$. As shown in the case of the DRK equation⁹ (adsorption of vapours by non-porous solids), exponent n is related to the heterogeneity of the surface and it appears that for certain systems $n = 3$ (or even 2) also provides a good fit.

As observed for adsorption from the vapour phase, the characteristic adsorption energy E_s , depends on both the adsorbent and the adsorbate. It appears that in the case of aqueous solutions of phenol,⁵⁻⁷ E_s is practically equal to the characteristic energy of adsorption of benzene vapours E_o ,

which is a reference in adsorption by microporous carbons.³ For other species (i) removed from aqueous solutions, one finds specific scaling factors β_s relative to phenol and defined by

$$E_s(i) = \beta_s E_s(\text{phenol}) \quad (3)$$

Typical values are shown in Table 1, with the values observed for adsorption from the vapour phase or calculated as described elsewhere.

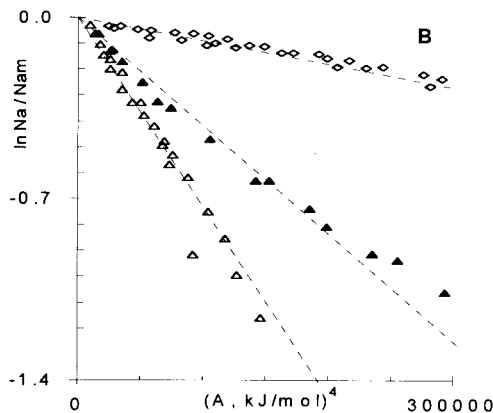


Figure 1. Logarithmic plot of Eq. (2) for the adsorption of various organics from aqueous solutions onto activated carbons: \circ carbon CP (phenol, 4-cresol, 3-chlorophenol, 3-aminophenol, 4-nitrophenol); \blacktriangle carbon PC (phenol, *m*-chlorophenol); \triangle carbon AC (phenol, aniline).

TABLE 1. Typical affinity coefficients β_s (average values) for the adsorption of sparingly soluble organics from aqueous carbons onto activated carbons. For comparison purposes, the affinity coefficients for adsorption from the vapour phase^{9,10} are also given (in the case of compounds with low vapour pressures, β is estimated¹⁰ from parachors or molar volumes).

Compound	$\beta_s = E_s/E_o$	β (vapour phase)	β_s/β
Phenol	1.03	1.09	0.95
3-chlorophenol	1.02	1.24	0.82
4-nitrophenol	0.90	1.20	0.75
Aniline	0.80	1.05	0.74
Benzene	0.54	1.00	0.54
Benzoic acid	0.80	1.04	0.77
Caffeine	1.28	1.85	0.69

These results show that predictions can be made for the removal of sparingly soluble organics by activated carbons at $c_{eq}/c_s < 0.05$, on the basis of relatively simple physico-chemical and structural properties. The latter are the characteristic energy E_o of the carbon, which varies typically between 30 kJ/mol (micropore width around 0.5 nm) and 16–17 kJ/mol

(supermicropores of ~ 2 nm) and the surface area of the micropore walls S_{mi} . This area can be assessed by different techniques, but in view of the good correlation observed with the adsorption of phenol from aqueous solutions based either on the solution isotherm or immersion calorimetry, the latter technique is now used to determine surface areas (see the contribution of Centeno and Stoekli in this volume). For example, on the basis of a molecular surface area of 45×10^{-20} m² (molecule lying flat on the carbon surface), the specific enthalpy $h_i(\text{phenol}) = -(0.109 \pm 0.03)$ J/m². Moreover, and in spite of the fact that phenol is excluded from the oxygen-containing surface sites, it appears that, due to a compensation effect, the enthalpy of immersion $\Delta_i H(\text{J/g})$ of a carbon into an aqueous solution of phenol (usually 0.4 M) leads to a good approximation of the total surface area by⁶

$$S_{tot} (\text{m}^2/\text{g}) = \Delta_i H(\text{phenol } 0.4 \text{ M})/h_i \quad (4)$$

This area corresponds to S_{mi} and the external surface S_e area found in larger pores and on the outside. Experiments with graphitized carbon blacks suggest a similar relation for caffeine solutions with $-(0.112 \pm 0.015 \text{ J/m}^2)$, but in view of the structure of this molecule, the technique is limited to micropores larger than 0.55–0.6 nm.

In the low concentration range, Eq. (1) corresponds to adsorption on the micropore walls, where the adsorption energy is higher than on the external surface area. Typically, E_o is around 11 kJ/mol for non-porous carbons, and the adsorption of phenol from an aqueous solution onto graphitized carbon black N234-G leads to $E_s(\text{phenol}) = 13$ kJ/mol. This experiment confirms that adsorption on the open surface, also limited to a monolayer, becomes effective only at relatively high relative concentrations. In Figure 1, this corresponds to an additional section, not shown, at the upper end of the graph ($c_{eq}/c_s > 0.05\text{--}0.1$). On the other hand, in calorimetric experiments, the concentration is high enough (0.4 M) to form a monolayer on S_{tot} .

2. Binary Adsorption from Aqueous Solutions

Following the success obtained with the adsorption of single species, it is tempting to extend the Dubinin-based approach to binary and, hopefully, to multiple adsorption. The advantage is obvious, as it should allow predictions for the simultaneous removal of organics from water on the basis of simple parameters and over a range of temperatures. Obviously, within the framework of the modified DRK theory, the situation should correspond to the submonolayer region and describe the final stages of purification of water.

A convenient working hypothesis is the model of independent coadsorption, which assumes that each species is adsorbed according to its DRK

equation (1), but only on the surface area left free by the other component. In the case of binary adsorption, this corresponds to the set of coupled equations

$$N_{aA} = [N_{amA} - N_{aB} (N_{amA} / N_{amB})] \exp\{-[RT \ln(c_s / c_{eq})_A / E_{sA}]^n\} \quad (5)$$

$$N_{aB} = [N_{amB} - N_{aA} (N_{amB} / N_{amA})] \exp\{-[RT \ln(c_s / c_{eq})_B / E_{sB}]^n\} \quad (6)$$

The subsidiary condition, leading to the pre-exponential terms, is

$$S_{mi} = N_{amA} \cdot A_{mA} \cdot N_{Av} = N_{amB} \cdot A_{mB} \cdot N_{Av} \quad (7)$$

where A_{mA} and A_{mB} are the molecular surface areas of species A and B and N_{Av} is Avogadro's number.

In the case of a single species, exponent $n = 4$ often provides a good fit.⁵⁻⁷ However, it is not a prerequisite, as n probably reflects the heterogeneity of the surface. As discussed elsewhere,⁹ this is clearly the case with the original DRK equation, where the fixed value $n = 2$ is responsible for the discrepancy often observed between the monolayer capacities $N_{am}(\text{DRK})$ and $N_{am}(\text{BET})$. Exponent n may therefore vary from carbon to carbon and it is possible to obtain a better overall fit with $n = 3$ or even 2.

The set of Eqs. (5) and (6) is potentially interesting, provided that two requirements are fulfilled:

1. The principle of temperature invariance of E_s and n applies, which allows predictions over a range of concentrations and temperatures
2. The parameters E_{sA} and E_{sB} should be the same as those obtained for the adsorption of the individual species.

At this stage, the analysis of the phenol + aniline mixture in water, adsorbed by activated carbon AC at 298 K¹ and 313 K (new data) provides a first and interesting illustration of the potentiality of the present approach.

The analysis of the nitrogen adsorption isotherm at 77 K, using the Dubinin–Radushkevich equation, leads to a micropore volume $W_o = 0.418 \text{ cm}^3/\text{g}$, and a characteristic energy $E_o = 23.0 \text{ kJ/mol}$. With the help of the correlations^{3,4}

$$L_o(\text{nm}) = 10.8 / (E_o - 11.4 \text{ kJ/mol}) \quad (8)$$

$$S_{mi}(\text{m}^2/\text{g}) = 2500 W_o(\text{cm}^3/\text{g}) / L_o(\text{nm}) \quad (9)$$

one obtains respectively $L_o = 0.93 \text{ nm}$ and $S_{mi} = 898 \text{ m}^2/\text{g}$.

The adsorption isotherms of the single species at 298 and 313 K provide the best fits for Eq. (1) with $n = 3$, rather than $n = 4$, where a slight upward curvature is observed in the logarithmic plots. This leads to the values of N_{am} and E_s given in Table 2. They correspond to the domain of relative concentrations c_{eq}/c_s between 5×10^{-5} and 0.01.

TABLE 2. Parameters of Eq. (1) with $n = 3$ for the single adsorption from unbuffered aqueous solutions by carbon AC ($E_o = 23.0$ kJ/mol and $S_{mi} = 898$ m²/g) at 298 and 313 K.

Adsorbate (single)	Phenol	Aniline
$E_s(298 \text{ K})$ (kJ/mol)	22.9 ± 0.4	17.9 ± 0.4
$E_s(313 \text{ K})$ (kJ/mol)	23.7 ± 0.5	18.0 ± 0.5
N_{am} (298 K) (mmol/g)	3.16 ± 0.07	3.14 ± 0.07
N_{am} (313 K) (mmol/g)	3.12 ± 0.07	3.00 ± 0.07
S_{mi} (average) (m ² /g)	848 ± 20	–

This data is coherent and suggests average surface affinity coefficients $\beta_s(\text{phenol}) = 1.01 \pm 0.04$ and $\beta_s(\text{aniline}) = 0.78 \pm 0.04$, in agreement with other determinations.⁷ Moreover, the molecular surface area of 45×10^{-20} m² obtained for phenol adsorbed on graphitized carbon blacks, leads to a micropore surface area of 848 m²/g, which is in reasonable agreement with the value derived from Eq. (9). The difference may be ascribed to the presence of surface oxygen, on which water is preferentially adsorbed in unbuffered solutions. The data also suggests that the molecular surface area of aniline is close to the value observed for phenol, as expected.

The analysis of the data for binary adsorption based on Eqs. (5) and (6) using again $n = 3$ and the values for $N_{am}(\text{phenol})$ and $N_{am}(\text{aniline})$ of Table 2, leads to the best fit values of E_s given in Table 3.

TABLE 3. Values of $E_s(\text{phenol})$ and $E_s(\text{aniline})$ for binary adsorption at 298 and 313 K.

Adsorbate (in the mixture)	Phenol	Aniline
$E_s(298 \text{ K})$ (kJ/mol)	22.5 ± 0.5	18.1 ± 0.5
$E_s(313 \text{ K})$ (kJ/mol)	22.3 ± 0.5	18.1 ± 0.5

These values are in good agreement with those obtained for the single adsorption (Table 2) and suggest that for the present binary system the adsorption equilibrium between 298 and 313 K could have been predicted with a reasonable accuracy by using the structural parameters of the carbon ($E_o = 23.0$ kJ/mol and $S_{mi} = 898$ m²/g), with the affinity coefficients β_s of Table 1 and the saturation concentrations of phenol and aniline found in standard tables. The correlation between the experimental and amounts adsorbed in the submonolayer region and the values calculated using the best fits for E_s and N_{am} is shown in Figure 2. The data corresponds to

adsorption in the submonolayer region, with $N_a(\text{phenol}) + N_a(\text{aniline})$ below 2–2.5 mmol/g.

Obviously, the uncertainty on β_s introduces a corresponding uncertainty in the amounts adsorbed. However, the approach outline here and based on the extended DRK equation provides a good estimate, as opposed to the Langmuir-based models, where the parameters cannot be determined “a priori” or extrapolated to other temperatures.

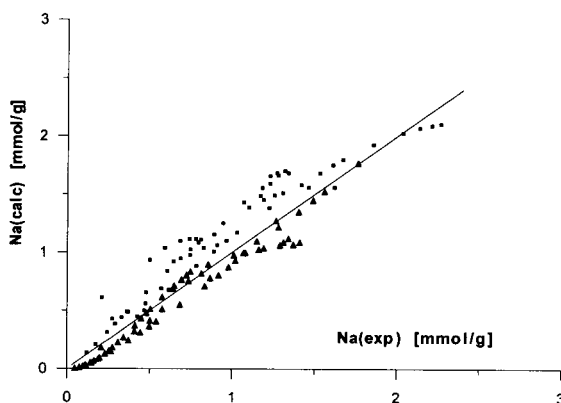


Figure 2. Correlation between the calculated and experimental amounts of phenol (■) and aniline (▲) adsorbed from binary mixtures in water, by active carbon AC, at 298 and 313 K.

3. Conclusions

The present study shows that Dubinin’s theory can be extended to the adsorption, by activated carbons, of sparingly soluble organics from aqueous solutions. The basic equation is a modified Dubinin–Raduskevich–Kaganer equation, where relative pressures are replaced by relative concentrations and the exponent n around 3–4. The principle of temperature invariance of parameters E_s and n has been established for single adsorption of a variety of organics and predictions can be made for a range of concentrations and temperatures.

Preliminary studies on binary systems in water, for example, phenol + aniline adsorbed by a typical industrial active carbon, suggest a similar pattern in the submonolayer region. In this case, the model of independent coadsorption can be applied and, with a good approximation, the individual isotherms are those obtained for single adsorption. This extension must be confirmed by a systematic study of more systems and special attention should be given to the value of exponent n , probably on the basis of a refined analysis of the carbon itself.

The approach outlined here is of great relevance to filtration technology, where semi-quantitative and quantitative predictions can be made on the basis of relatively simple physico-chemical properties of the adsorbates and the structural parameters of the carbon.

References

1. D.M. Nevskaja, E. Castillejos-López, A. Guerrero-Ruiz, and V. Muñoz, Effect of the Surface chemistry of carbon materials on the adsorption of phenol-aniline mixtures from water, *Carbon* 42(3), 653–665 (2004).
2. R. Leyva-Ramos, J. Zoto-Zuñiga, J. Mendoza Barron, and R.M. Guerro Coronado, Adsorption of phenol from aqueous solutions onto activated carbon. Effect of solvent, temperature and particle size, *Adsorpt. Sci. Technol.* 17(7), 533–543 (1999).
3. F. Stoeckli, in: *Porosity in Carbons*, edited by J. Patrick (E. Arnold, London, 1995), pp. 67–97.
4. F. Stoeckli and T.A. Centeno, On the determination of surface areas in activated carbons, *Carbon* 43(6), 1184–1190 (2005).
5. F. Stoeckli, M.V. López-Ramón, and C. Moreno-Castilla, Adsorption of phenolic compounds from aqueous solutions, by activated carbons, described by the Dubinin-Astakhov equation, *Langmuir* 17(11), 3301–3306 (2000).
6. E. Fernández, D. Hugi-Cleary, M.V. López-Ramón, and F. Stoeckli, Adsorption of phenol from dilute and concentrated aqueous solutions by activated carbons, *Langmuir* 19(23), 9719–9723 (2003).
7. D. Hugi-Cleary, A. Slassi, and F. Stoeckli, *Helv. Chim. Acta* 88, 470–477 (2005).
8. F. Stoeckli and D. Hugi-Cleary, *Russ. Chem. Int. Ed.* 50(11), 2060–2063 (2001).
9. D. Hugi-Cleary, S. Wermeille, and F. Stoeckli, *Chimia* 57(10), 611–615 (2003).
10. G.O. Wood, Affinity coefficients of the Polanyi/Dubinin adsorption isotherm equations, *Carbon* 39(3), 343–356 (2001).