

Binary Adsorption of Vapours in Active Carbons Described by the Dubinin Equation

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ABSTRACT: It is shown that the use of the Dubinin–Radushkevich isotherm within the framework of the Myers–Prausnitz theory provides a satisfactory description of the adsorption of mixtures of chlorobenzene + carbon tetrachloride vapours by active carbons. This approach can be extended to other systems and full use can be made of the advantages of Dubinin's theory. The experimental data was obtained by Headspace-GC, a rapid and reliable technique.

INTRODUCTION

The present paper is part of a study dealing with the industrial elimination of toxic vapours from air by active carbon beds. The ultimate goal is the prediction of adsorption under dynamic conditions, as achieved for single components by computer simulations (Lavanchy *et al.* 1991; Laduguie *et al.* 1992; Lavanchy *et al.* 1993). We show that the combination of the Dubinin–Radushkevich equation with the theory for mixed-gas adsorption (Myers and Prausnitz 1965; Van Ness 1969; Myers and Valenzuela 1986) leads to interesting results, in view of the fact that the Dubinin isotherm contains parameters related separately to the solid and to the adsorptive. Therefore, a limited set of data is required to describe binary adsorption over a wide range of pressure and temperature.

In order to illustrate the possibilities of this approach, the system $C_6H_5Cl + CCl_4$ has been chosen. It contains typical organic vapours with different saturation pressures. Their ratio is practically 1:10 near room temperature and therefore the system may be regarded as a typical case in the general study of toxic vapour elimination. It was also decided to use the Headspace-GC technique in our laboratory (Spiez) to determine the experimental adsorption data. The possibilities and the limitations of this relatively simple technique, used with a number of active carbons, will also be described.

THEORETICAL

The theory for the volume filling of micropores, developed by Dubinin in the late 1940s, is a major contribution for the description of adsorption by microporous solids (Dubinin 1975, 1989; Dubinin and Stoeckli 1980; Stoeckli 1995). In its modern formulation, the fundamental relation of the theory is the equation of Dubinin and Astakhov,

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$$N_a = N_{a0} \exp[-(A/\beta E_0)^n] \quad (1)$$

where $A = RT \ln(p_s/p)$.

The quantity N_a is the amount adsorbed at relative pressure p/p_s and N_{a0} is the limiting amount adsorbed in the micropores. The latter is related to the actual micropore volume $W_0 = N_{a0} V_m$, where V_m represents the molar volume of the liquid-like adsorbate. The characteristic energy of adsorption E_0 depends on the solid and β is a scaling factor called the affinity coefficient of the adsorptive. By convention, the reference vapour is benzene and $\beta(C_6H_6) = 1$. Various expressions have been proposed to calculate $\beta/\beta(C_6H_6)$, but an overall comparison of the experimental values shows that the ratio of parachores leads to a satisfactory agreement in the case of active carbons (Dubinin 1975; Wood 1992). Depending on the solid and on the type of micropores, the exponent n varies typically from 1.5 to 4–5, but in the case of typical industrial active carbons it is close to 2. This corresponds to the classical equation of Dubinin and Radushkevich used in the present study.

A major advantage of equation (1) is the presence of well-defined parameters, which correspond to the micropore system (E_0 and W_0) and to the adsorptive (β and p_s). With the exception of p_s , these parameters are temperature-independent and therefore a minimum set of data is required for the individual adsorption isotherms.

As shown elsewhere (Valenzuela and Myers 1989), it is possible to describe the adsorption equilibrium of binary vapour mixtures within a well-defined thermodynamic framework. Therefore, we shall only deal with the main features of this approach.

Let us assume that a mixture of m vapours is adsorbed under equilibrium conditions. The amounts adsorbed (given in mol/g of solid) are n_i with the corresponding mole fractions

$$x_i = n_i/n_t \quad (2)$$

where $n_t = \sum n_i$. In the vapour phase with mole fractions y_i and a total pressure P the partial pressures of the component i is

$$p_i = y_i P \quad (3)$$

By analogy with the case of liquid mixtures, the partial pressures p_i may be related to formal reference states of the individual adsorbates, characterised by pressures p_i^0 , and defined through

$$p_i = x_i \gamma_i p_i^0 \quad (4)$$

The quantities γ_i are the activity coefficients of the substances in the adsorbed mixture, which are not known a priori. If one assumes, to a first approximation, that the mixture is ideal, the quantities γ_i are equal to unity. In the case of liquid mixtures, the reference pressures p_i^0 correspond to the saturation pressures of the liquids p_{si} , whatever the composition of the mixture. However, in the case of co-adsorption, p_i^0 is neither equal to p_{si} nor a constant. It corresponds to an adsorbed amount n_i^0 , given by the individual adsorption isotherms $n_i = n_i(T; p_i)$,

$$n_i^0 = n_i(T; p_i^0) \quad (5)$$

The amounts n_1^0, n_2^0, \dots define the reference states of the adsorbates in the mixture of $n_1 + \dots + n_m + \dots + n_m$ mol/g. As shown elsewhere (Myers and Prausnitz 1965; Valenzuela and Myers 1989),

these reference states, and therefore the pressures p^o_i , play a key role in the description of mixed adsorption. They are linked through the thermodynamic property that the following integrals of the individual isotherms, i.e.

$$\Psi_i(p^o_i) = \int_0^{p^o_i} \frac{n_i(p)}{p} \cdot dp \quad (6)$$

must be equal for every component. With the upper limit of integration such that $\sum x_i = 1$, where x_i is given by equation (4), it appears that

$$\sum p_i/\gamma_i p^o_i = 1 \quad (7)$$

This provides the formal link between the reference states and the adsorbed mixture. In the case of an ideal mixture, one obtains x_i directly from the condition that $\Psi_1(p^o_1) = \dots = \Psi_i(p^o_i) = \dots = \Psi_m(p^o_m)$. The amounts n_i are calculated from the subsidiary conditions that

$$1/n_i = x_1/n^o_1 + \dots + x_i/n^o_i + \dots + x_m/n^o_m \quad (8)$$

and

$$n_i = x_i n_t \quad (9)$$

In their work, Valenzuela and Myers (1989) used successfully as local isotherms the expressions proposed by Toth (1971) and by Honig and Reyerson (1952). However, these equations contain temperature-dependent constants and, therefore, one must determine the individual adsorption isotherms at the temperature of the mixed adsorption. Moreover, the meaning of the specific parameters of these equations is not as well defined as in the case of the Dubinin–Astakhov equation (1), which predicts n^o_i for a given adsorbate on the basis of data obtained with another vapour. Therefore, we introduced the Dubinin–Radushkevich equation (1) with $N_{j0} = W_o/V_{mi}$ into equations (5) and (6), which leads to

$$n^o_i = (W_o/V_{mi}) \exp[-\{(RT/\beta_i E_o) \ln(p_s/p^o_i)\}^2] \quad (10)$$

and (see Appendix)

$$\Psi_i(p^o_i) = (W_o/V_{mi})(\beta_i E_o/RT)(\pi^{1/2}/2)[1 - \operatorname{erf}\{(RT/\beta_i E_o) \ln(p^o_i/p_s)\}] \quad (11)$$

It appears that the Dubinin–Radushkevich equation provides a relatively simple expression for the integrals $\Psi_i(p^o_i)$ and the problem of mixed adsorption by active carbons can be solved. A general algorithm has been proposed to deal with the ideal adsorption of several components (Myers and Valenzuela 1986; Valenzuela and Myers 1989). In the case of binary adsorption, illustrated below, the calculations are relatively simple. If the composition of the vapour phase and therefore the equilibrium pressures p_1 and p_2 are known, the model of an ideal adsorbed mixture ($\gamma_i = 1$) implies that

$$p^o_1 = p_1/x_1 \quad \text{and} \quad p^o_2 = p_2/x_2 \quad (12)$$

Since $x_1 + x_2 = 1$, it follows that

$$\psi_1(p_1/x) = \psi_2[p_2/(1-x)] \quad (13)$$

By using equation (11) for the individual adsorbates, one obtains the unknown mole fractions x and $1-x$. The reference pressures p°_1 and p°_2 , calculated from equation (12), lead to the quantities n°_1 and n°_2 given by equation (10). Finally, the amounts n_i adsorbed in the micropores are obtained from equations (8) and (9).

The general problem in filtration technology — the adsorption of a known vapour mixture by a given active carbon — can also be dealt with along these lines. The calculations of the final equilibrium, characterized by x_i , y_i , $n^{(v)}_i$ and $n^{(a)}_i$, the mole fractions and the amounts present in the two phases, require the use of mass balances for the individual adsorptives.

At this stage it should also be emphasized that the approach outlined in the present paper is not limited to active carbons. It can be extended to microporous solids like zeolites described by the Dubinin–Astakhov equation (1) with different values of the exponent n . A mathematical development similar to that given in detail in the Appendix, but based on the incomplete Gamma function (Gradshteyn and Ryzhik 1980), leads to the general expression

$$\gamma_i(p^{\circ}_i) = (W_o/V_{mi})(\beta_i E_o/RT) \cdot (1/n) \cdot \Gamma[1/n; (A_i \ln p_s/p^{\circ}_i)^n] \quad (14)$$

where, formally, $\Gamma[\alpha; u] = \int_u^{\infty} \exp(-t) \cdot t^{\alpha-1} dt$.

Moreover, in the case of active carbons, the model may also include water as a component of the mixture, since the Dubinin–Astakhov equation can be used to describe the adsorption of water (Stoekli *et al.* 1994).

EXPERIMENTAL

The adsorption of pure carbon tetrachloride and chlorobenzene vapours and of their mixtures was carried out at 298 K on active carbon U-02 of industrial origin. Its main characteristics are given in Table I.

TABLE I. Structural Characteristics of Active Carbon U-02 and of the Adsorptives at 298 K

Adsorptive		CCl ₄ (298 K)	C ₆ H ₅ Cl (298 K)	Used for calc.
Micropore volume	W_o (m ³ /kg)	0.467×10^{-3}	0.468×10^{-3}	0.468×10^{-3}
Characteristic energy	E_o (J/mol)	16.68×10^3	15.45×10^3	16.1×10^3
Affinity coefficient	β	1.05	1.19	
Saturation pressure p_s	(Pa)	15251	1596	
Molar volume (liquid)	V_m (m ³ /mol)	97.08×10^{-6}	102.25×10^{-6}	

There are slight differences between the characteristic energies of the adsorbates derived from the classical Dubinin–Radushkevich plots of the adsorptives and therefore the average E_o value was used in the calculations outlined above. The table also contains the relevant information on the adsorptives themselves.

The bulk of the adsorption measurements for the pure vapours and for their mixtures was carried out with the Headspace-Gas Chromatography technique, which is relatively simple and rapid, and so, of great help in research and routine work.

Approximately 0.5–0.6 g of freshly outgassed active carbon was introduced into vials of known volume ($12.50 \pm 0.05 \text{ cm}^3$), which were sealed off with a Teflon-coated septum held by an aluminium ring. At a given working temperature (in the present case 298 K), calibrated amounts of the pure liquids or their mixture (approximately 0.5–3 mmol) were introduced automatically with a syringe through the septum. The experimental conditions were such that a large proportion of the adsorbate was eventually found in the micropores and in any case no liquid phase was present. As shown by independent gravimetric experiments, the presence of dry air in the vials had no significant influence on the adsorption of vapours such as carbon tetrachloride and chlorobenzene by active carbons.

After equilibration at constant pressure and temperature, the sampling of the vapour phase by standard gas chromatography techniques led to the composition and the partial vapour pressures p_i . Finally, the amounts adsorbed, n_i , were obtained from mass balance. Since chlorobenzene has a low volatility, its concentration in the gas phase was subject to relatively large errors for mole fractions $x < 0.2$ – 0.3 .

In order to determine the best experimental conditions for mixed adsorption, the following five different procedures were tested with active carbon U-02 under standard conditions (2.5 and 0.39 mmol of chlorobenzene and carbon tetrachloride and 0.70 g of carbon):

- (a) The two components were injected simultaneously as a liquid mixture of known composition.
- (b) CCl_4 was added directly after $\text{C}_6\text{H}_5\text{Cl}$.
- (c) The order of injection was reversed.
- (d) CCl_4 was added only 30 min after $\text{C}_6\text{H}_5\text{Cl}$.
- (e) The order of injection was reversed.

In every case, five experiments were carried out and the equilibrium was examined after 15 h, although separate determinations showed that equilibrium was virtually attained within 2 h. It appears that all techniques led to similar results, which indicates that the same final state was reached as far as the given adsorbates are concerned. Although procedure (a) led to a smaller scatter of the results, procedures (b) and (c) were preferred for the large number of experiments performed in this study in view of the technical advantages resulting from the successive injections of the pure components. In this case, the ratio of the equilibrium pressures $p(\text{C}_6\text{H}_5\text{Cl})/p(\text{CCl}_4)$ was $(26.0 \pm 2.1) \times 10^{-3}$ for the standard experiment.

An overall evaluation of the experimental data showed that the adsorbed amounts n_i were known to within 0.5%. The individual equilibrium pressures p_i showed a larger uncertainty (up to 20% in some cases). However, the influence of such an uncertainty on the calculation of the adsorption equilibrium was reduced by the presence of a $\ln(p_i)$ term in equations (10) and (11). As shown below, the observed accuracy was sufficient to test the model based on an ideal adsorbed mixture.

RESULTS AND DISCUSSION

Table 2 gives a set of typical experimental results obtained by the Headspace-GC technique for the binary adsorption of CCl_4 and $\text{C}_6\text{H}_5\text{Cl}$ on carbon U-02, as well as the values calculated on the

basis of an ideal mixture for the adsorbed state ($\gamma_i = 1$ in all cases). The table also includes the selectivity of the carbon for chlorobenzene relative to carbon tetrachloride defined (Valenzuela and Myers 1989) as the ratio

$$s_{1,2} = (x_1/y_1)/(x_2/y_2) \quad (15)$$

With the exception of the mole fractions of chlorobenzene $x(1)$ below 0.3, where its concentration in the gas phase is small and therefore subject to large errors, it appears that the experimental and calculated values of n_i and x_i are in good agreement. The same is true for the selectivity $s_{1,2}$ of the active carbon for chlorobenzene relative to carbon tetrachloride, which is around 20. These results show that the model of Myers and Prausnitz with the Dubinin-Radushkevich equation leads to a satisfactory description in the case of adsorptives with rather different vapour pressures.

The use of the Dubinin-Radushkevich equation for the individual adsorption isotherms also presents a great advantage over other expressions, because it contains well-defined parameters related to the solid and to the adsorptives. Therefore, it is possible to predict to a good degree of approximation the behaviour of the individual vapours and of their mixtures over a wide range of temperatures and relative pressures. Dubinin's theory requires a minimum of information on the solid, its characteristic energy E_0 and the accessible micropore volume W_0 , which can be obtained, in principle, from the isotherm of a reference vapour (N_2 at 77 K or, preferably, an organic vapour like CH_2Cl_2 or benzene at room temperature). The problem of molecular sieve effects can be assessed through the value of parameter E_0 , which is related to the average micropore width L (Stoeckli 1995). On the other hand, the data needed for potential adsorbates (V_m , β and p_s) does not even require preliminary adsorption measurements, since the affinity coefficient β itself can be calculated from other molecular properties (Dubinin 1975; Wood 1992).

As mentioned earlier, it is possible to extend the present development to the Dubinin-Astakhov isotherm (variable exponent n) and consequently to describe mixed adsorption for a variety of systems. In this case, the basic relation for the function $\psi_i(p^0)$ is given by equation (14). Work is currently being carried out along these lines and the results will be presented in due course.

The present study also illustrates the advantages of the Headspace-GC technique, which reduces the amount of work required in the study of adsorption systems with different components. It is rapid and of great help in routine work.

APPENDIX

In this section we outline the relatively complicated steps leading to equation (11). The starting point is the definition of ψ given by equation (6), which represents the integral of the adsorption isotherm of the pure component i divided by the pressure p_i . The combination of the general expression (6)

$$\psi = \lim_{z \rightarrow 0} \int_z^p \frac{n(p)}{p} \cdot dp$$

with the Dubinin-Radushkevich equation (10) leads to

$$n(p) = W \exp \left[- \left\{ A_i \ln \left(\frac{p_s}{p} \right) \right\}^2 \right] \quad (A1)$$

TABLE 2. Experimental and Calculated Data for the Mixed Adsorption of C_6H_5Cl (1) and CCl_4 (2) by Active Carbon U-02 at 298 K. Calculations Based on the Model of an Ideal Mixture

P_1 (Pa) exp.	P_2 (Pa) exp.	y_1 exp.	n_1 (mol/kg) exp.	n_1 (mol/kg) calc.	n_2 (mol/kg) exp.	n_2 (mol/kg) calc.	x_1 exp.	x_1 calc.	$s_{1,2}$ exp.	$s_{1,2}$ calc.
5.078	533.77	0.009	0.785	0.577	2.098	3.237	0.272	0.151	39.2	18.6
2.595	251.67	0.010	0.779	0.583	1.811	2.821	0.301	0.171	41.7	20.0
0.244	17.68	0.014	0.346	0.502	0.620	1.411	0.358	0.263	40.3	25.8
3.897	215.22	0.018	0.960	0.888	1.723	2.464	0.358	0.266	30.9	20.1
3.293	172.99	0.019	1.040	0.906	1.549	2.327	0.402	0.280	35.2	20.4
0.881	9.21	0.087	1.201	1.386	0.639	0.579	0.653	0.706	19.7	25.1
1.116	11.27	0.090	1.331	1.475	0.657	0.606	0.669	0.708	20.5	24.5
0.919	9.24	0.091	1.195	1.413	0.685	0.568	0.636	0.713	17.5	25.0
20.172	121.62	0.142	2.391	2.665	0.607	0.845	0.797	0.760	23.7	19.1
4.946	28.29	0.149	1.795	2.186	0.675	0.578	0.727	0.791	15.2	21.6
1.012	5.37	0.159	1.646	1.599	0.254	0.337	0.866	0.826	34.4	25.2
2.932	9.85	0.229	2.135	2.114	0.254	0.310	0.894	0.872	28.3	22.9
1.666	4.86	0.255	1.448	1.892	0.287	0.229	0.834	0.892	14.7	24.1
1.154	3.22	0.264	1.628	1.750	0.177	0.195	0.902	0.900	25.6	25.1
33.941	72.12	0.320	2.934	3.260	0.285	0.373	0.912	0.897	21.9	18.5
39.882	72.33	0.355	3.202	3.358	0.271	0.333	0.922	0.910	21.4	18.3
6.138	10.75	0.364	2.185	2.470	0.276	0.207	0.888	0.925	13.8	21.5
58.605	102.18	0.364	3.372	3.518	0.247	0.345	0.932	0.910	23.8	17.7
169.495	286.71	0.371	3.588	3.856	0.283	0.398	0.927	0.906	21.5	16.4
14.334	8.74	0.621	2.915	3.065	0.085	0.093	0.972	0.971	20.9	20.1

where $A_i = RT/\beta_i E_0$ and $W = W_0/V_{mi}$. With the substitution of variables

$$y = A_i \ln\left(\frac{p_s}{p}\right) \quad dy = -\frac{A_i}{p} dp \quad dp = -\frac{p}{A_i} dy$$

it follows that

$$\begin{aligned} \Psi &= \lim_{z \rightarrow 0} W \cdot \int_z^{p_s} \frac{e^{-\{A_i \ln(p_s/p)\}^2}}{p} \cdot dp \\ \Psi &= \lim_{z \rightarrow 0} W \cdot \int_{A_i \ln(p_s/z)}^{A_i \ln(p_s/p)} \left[\frac{e^{-y^2}}{p} \cdot \left(-\frac{p}{A_i}\right) \right] dy \end{aligned}$$

which can be written as

$$\Psi = -\lim_{z \rightarrow 0} \frac{W}{A_i} \cdot \int_{A_i \ln(p_s/z)}^{A_i \ln(p_s/p)} e^{-y^2} \cdot dy \quad (\text{A2})$$

In order to deal with the limit $z \rightarrow 0$, equation (A2) can be split into two contributions,

$$\Psi = -\left\{ \lim_{z \rightarrow 0} \frac{W}{A_i} \cdot \int_{A_i \ln(p_s/z)}^0 e^{-y^2} \cdot dy + \frac{W}{A_i} \cdot \int_0^{A_i \ln(p_s/p)} e^{-y^2} \cdot dy \right\} \quad (\text{A3})$$

which leads to

$$\Psi = \lim_{z \rightarrow 0} \frac{W}{A_i} \cdot \int_0^{A_i \ln(p_s/z)} e^{-y^2} \cdot dy - \frac{W}{A_i} \cdot \int_0^{A_i \ln(p_s/p)} e^{-y^2} \cdot dy \quad (\text{A4})$$

We see that

$$\Psi = \Psi_1 - \Psi_2 \quad (\text{A5})$$

and two separate integrals must be solved:

$$\Psi_1 = \lim_{z \rightarrow 0} \frac{W}{A_i} \cdot \int_0^{A_i \ln(p_s/z)} e^{-y^2} \cdot dy \quad (\text{A6})$$

and

$$\Psi_2 = \frac{W}{A_i} \cdot \int_0^{A_i \ln(p_s/p)} e^{-y^2} \cdot dy \quad (\text{A7})$$

With the definition of the 'error function':

$$\text{erf}(u) = \frac{2}{\sqrt{\pi}} \int_0^u e^{-t^2} \cdot dt \quad (\text{A8})$$

one obtains an integral related to ψ_1 and ψ_2 :

$$\int_0^u e^{-t^2} \cdot dt = \frac{\sqrt{\pi}}{2} \operatorname{erf}(u)$$

With the corresponding values of the limits $u = A_1 \ln(p_s/p)$ and $A_1 \ln(p_s/z)$, it follows that

$$\psi_1 = \frac{W}{A_1} \frac{\sqrt{\pi}}{2} \lim_{z \rightarrow 0} \operatorname{erf}[A_1 \ln(p_s/z)] \quad (\text{A9})$$

and

$$\psi_2 = \frac{W}{A_1} \frac{\sqrt{\pi}}{2} \operatorname{erf}[A_1 \ln(p_s/p)] \quad (\text{A10})$$

For ψ_1 , the limit $z \rightarrow 0$ leads to $\operatorname{erf}(\infty)$ which is equal to unity and integral (A4) becomes

$$\psi = \frac{W}{A_1} \frac{\sqrt{\pi}}{2} \{1 - \operatorname{erf}[A_1 \ln(p_s/p)]\} \quad (\text{A11})$$

This corresponds to equation (11) when p is replaced by p^0 , or p/x_1 .

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