

Binary Adsorption of Vapours in Active Carbons Described by the Combined Theories of Myers–Prausnitz and Dubinin (II)

F. Stoeckli^{1*}, D. Wintgens¹, A. Lavanchy² and M. Stöckli² (1) Chemistry Department of the University, CH-2000 Neuchâtel, Switzerland. (2) NC-Laboratory, CH-3700 Spiez, Switzerland.

ABSTRACT: The new MPD method, described recently, has been applied to the adsorption of benzene + 1,2-dichloroethane vapours by a typical active carbon at 293 K. A total of 102 experiments have been carried out for adsorbed mole fractions between 0.06 and 0.94. Good agreement was found between the experimental and calculated values of the selectivity of the carbon for benzene, which decreased as the mole fraction of benzene increased. This variation reflects the heterogeneity of the carbon, which is taken into account by the DR equation. Although the liquid mixture is ideal, deviations from Raoult's law are observed in the adsorbed state, indicating a clear preference for benzene. The values of the activity coefficients obtained from the liquid/solid equilibrium improve the fit of the MPD method.

INTRODUCTION

As shown recently by Lavanchy *et al.* (1996), the binary adsorption of vapours in active carbons can be described by a combination of the theories of Myers–Prausnitz and Dubinin (MPD). Results have already been reported for the static adsorption of the system chlorobenzene + carbon tetrachloride by a typical industrial active carbon at 298 K. This system had been chosen in view of the large differences between the vapour pressures of the two components (a ratio of 1:10 near 298 K), which represents a realistic case in industrial filtration.

The MPD formalism has also been applied successfully to the calculation of the dynamic adsorption of different systems by active carbon beds and an excellent agreement has been found between the experimental and calculated breakthrough curves (Lavanchy and Stoeckli 1997).

In order to extend our study of binary adsorption within the framework of MPD and to test the experimental technique, we examined the system benzene + 1,2-dichloroethane adsorbed by a typical active carbon at 293 K. This system was chosen in view of the fact that the liquid mixture is almost ideal near room temperature (Coulson *et al.* 1948; Kipling and Tester 1952). Moreover, Blackburn *et al.* (1957) determined the surface activity coefficients of this mixture on the basis of adsorption from the liquid state, measured earlier by Kipling and Tester (1952). These experiments corresponded to the limiting case where the micropores are completely filled by the adsorbed mixture. On the other hand, adsorption from the vapour phase usually corresponds to an incomplete filling of the micropores, but a comparison can still be made with the liquid/solid equilibrium.

As described below, at low concentrations the activity coefficients in the adsorbed state, γ^a , are smaller than unity for both components, which reflects the influence of the carbon on the system. This has been observed for adsorption from the liquid and the vapour phases (Minka and Myers 1973; Costa *et al.* 1981; Myers 1983).

*Author to whom all correspondence should be addressed.

THEORETICAL

As shown by Myers and others (Myers and Prausnitz 1965; Van Ness 1968; Valenzuela and Myers 1989), the adsorption equilibrium of different species requires that the following integrals of the individual isotherms $n_i(p)$ must be equal,

$$\Psi_i(p_i^0) = \int_0^{p_i^0} n_i(p)/p \, dp \quad (1)$$

By analogy with the case of liquid mixtures, the vapour pressure of an adsorbed component i , p_i , is related to the pressure p_i^0 through

$$p_i = x_i^a \gamma_i^a p_i^0 \quad (2)$$

where x_i^a is the mole fraction of i in the adsorbed mixture and γ_i^a is the corresponding activity coefficient. The pressure p_i^0 depends on the total amount adsorbed and becomes equal to the saturation pressure p_{si} when the whole micropore system is filled by the adsorbed mixture. Under these circumstances, the equilibrium between the adsorbed mixture and the liquid leads to

$$x_i^a \gamma_i^a = x_i^l \gamma_i^l \quad (3)$$

In the case of microporous solids, the most convenient isotherm is given by the Dubinin–Astakhov equation (Dubinin 1989; Stoeckli 1995),

$$N_a = N_{a0} \exp[-(A/\beta E_0)^n] \quad (4)$$

where $A = RT \ln(p_i/p)$. The quantity N_a (usually in mmol/g of solid) is the amount adsorbed at pressure p 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 depending on the adsorptive (it is equal to unity for benzene, by convention).

As we previously (Lavanchy *et al.* 1996), the use of the classical DR equation leads to an analytical solution for equation (1),

$$\Psi_i(p_i^0) = (W_0/V_m)(\beta E_0/RT)(\pi^{1/2}/2)[1 + \operatorname{erf}\{(RT/\beta E_0) \ln(p_i^0/p_{si})\}] \quad (5)$$

Taking into account equation (2) and assuming an ideal adsorbed state, the adsorption equilibrium for a binary mixture of vapours is given by the condition

$$\Psi_1(p_1/x_1^a) = \Psi_2(p_2/x_2^a) \quad (6)$$

From this, the mole fractions x_1^a and $x_2^a = 1 - x_1^a$ can be calculated by an iterative procedure, the partial pressures p_1 and p_2 being known. Finally, the actual amounts adsorbed, n_1^a and n_2^a , are obtained as described elsewhere (Lavanchy *et al.* 1996; Myers and Prausnitz 1965).

EXPERIMENTAL

The adsorption of the pure components, benzene and 1,2-dichloroethane, was carried out at 293 K on carbon U-02, a typical active carbon of industrial origin, used in the previous study. The main characteristics of the adsorptives and of the solid (DR equation) are given in Table 1.

Parameters E_0 and W_0 were obtained from the individual adsorption isotherms, determined under the same experimental conditions as the mixture (Headspace-Gas Chromatography, described earlier). It appears that slightly different values of W_0 and E_0 are obtained, which is probably due to structural factors and to the presence of air.

TABLE 1. Structural Characteristics of Carbon U-02 and of the Adsorptives at 293 K

Adsorptive	C_6H_6 (293 K)	$1,2-C_2H_4Cl_2$ (293 K)
Micropore volume, W_{oi} (m^3/kg)	0.448×10^{-3}	0.482×10^{-3}
Characteristic energy, E_o (J/mol)	17.0×10^3	15.6×10^3
Affinity coefficient, β	1.000	0.912
Saturation pressure, p_s (Pa)	9.985×10^3	8.339×10^3
Thermal expansion coefficient, α (1/K)	1.132×10^{-3}	1.165×10^{-3}
Molar volume (liquid), V_m (m^3/mol)	88.97×10^{-6}	78.92×10^{-6}

For the system benzene + 1,2-dichloroethane adsorbed on carbon U-02, the vapour/solid equilibrium was determined at 293 K by using the Headspace-Gas Chromatography technique described in detail previously (Lavanchy *et al.* 1996) by adding 0.5–3 mmol of liquid to 0.5–0.6 g of carbon contained in vials of known volume ($12.50 \pm 0.05 \text{ cm}^3$). The equilibrium pressures and the amounts adsorbed were determined from standard GSC chromatography techniques. A total of 102 experiments were performed on this system, covering the range of mole fractions $0.06 < x^s < 0.93$. The total amounts adsorbed (0.9–5.4 mmol/g) correspond to adsorbed volumes W_{ads} between 0.08 and $0.44 \text{ cm}^3/g$.

The liquid/solid equilibrium at 293 K was examined separately by a classical technique based on the change of refractive index in the solution and the mass balance between the two phases. This allows the determination of the affinity coefficients γ_{LS}^a of the two components in the adsorbed phase in equilibrium with the liquid mixture for the composition range $0.1 < x^s < 0.95$.

RESULTS AND DISCUSSION

Table 2 shows a selection of typical results obtained for the mixed adsorption of benzene + 1,2-dichloroethane vapours by active carbon U-02 at 293 K. The best fit is obtained if one uses the individual values W_{oi} and E_{oi} of the adsorptives as requested by the theory. (In the case of the system $C_6H_5Cl + CCl_4$, examined previously, the micropore volumes W_{oi} and the characteristic energies E_{oi} were much closer and it was possible to use average values, respectively $0.468 \times 10^{-3} \text{ m}^3/kg$ and 16.1 kJ/mol .)

The data listed in Table 2 show that the calculated and experimental values of the total amounts adsorbed, n_{tot} , are in good agreement. This may be regarded as a first test of the MPD approach. Table 2 also gives information on the selectivity of the carbon for benzene relative to 1,2-dichloroethane, a quantity defined (Valenzuela and Myers 1989) by the ratio

$$s_{1,2} = (x_1^s/y_1)/(x_2^s/y_2) \quad (7)$$

The calculated and experimental values of $s_{1,2}$ show the same trend and it appears that the selectivity is highest for small values of $x^s(C_6H_6)$ and small amounts adsorbed n_{tot} , or the corresponding volume W_{ads} . The variation of $s_{1,2}$ with x^s can be explained in terms of the heterogeneity of the adsorbent (Myers 1983; Sircar 1991) and of the influence of the pore size, as illustrated by the simulations of Tan and Gubbins (1992). In the final analysis, the two approaches are complementary since pore sizes and adsorption energies are related. This has been examined by different authors, for example Stoeckli (1974), Everett and Powl (1976), Stoeckli *et al.* (1982), Horvath and Kawazoe (1983), and Rudzinski and Everett (1992).

TABLE 2. Experimental and Calculated Data for the Mixed Adsorption of C_6H_6 (1) and $C_2H_4Cl_2$ (2) Vapours by Active Carbon U-02 at 293 K*

p_1 (Pa) exp.	p_2 (Pa) exp.	y_1 exp.	n_{tot} (mol/kg) exp.	n_{tot} (mol/kg) calc.	x_1 exp.	x_1 calc.	$s_{1,2}$ exp.	$s_{1,2}$ calc.	W_{sk} (cm ³ /g) exp.
1.15	44.88	0.025	2.781	2.797	0.109	0.053	4.77	2.20	0.222
7.23	196.28	0.036	4.163	4.029	0.101	0.057	3.06	1.64	0.333
1.38	21.35	0.061	2.213	2.232	0.202	0.139	3.92	2.51	0.179
37.65	325.54	0.104	4.628	4.448	0.203	0.144	2.20	1.45	0.375
14.14	91.48	0.134	3.503	3.423	0.291	0.221	2.66	1.84	0.287
222.38	848.10	0.208	5.194	5.128	0.293	0.234	1.58	1.16	0.425
0.51	2.97	0.147	1.107	1.077	0.407	0.375	4.00	3.49	0.092
64.20	179.18	0.264	4.122	4.044	0.410	0.356	1.94	1.54	0.342
0.31	0.96	0.243	0.917	0.689	0.500	0.566	3.12	4.06	0.077
158.70	249.60	0.389	4.369	4.379	0.504	0.469	1.60	1.39	0.367
0.70	1.69	0.293	1.193	0.930	0.617	0.597	3.88	3.58	0.102
67.84	73.44	0.480	3.625	3.547	0.614	0.607	1.72	1.67	0.308
43.94	29.64	0.597	3.133	3.038	0.714	0.734	1.68	1.86	0.270
479.90	244.14	0.663	4.672	4.633	0.715	0.708	1.27	1.23	0.402
28.64	10.08	0.740	2.706	2.578	0.825	0.853	1.65	2.05	0.236
203.71	51.62	0.798	4.039	3.908	0.829	0.853	1.23	1.47	0.352
20.81	3.69	0.849	2.461	2.282	0.899	0.925	1.58	2.19	0.216
839.53	95.67	0.898	4.666	4.670	0.905	0.911	1.09	1.17	0.411

*The MPD calculations are based on the hypothesis of an ideal adsorbed state. W_{sk} is given in cm³/g.

It has been shown that a good fit can be obtained for $s_{1,2}$ by using a Langmuir equation with either a two-site model (Myers 1983) or an energy distribution (Sircar and Myers 1988; Sircar 1991). From a formal point of view, the latter is in agreement with our approach based on Dubinin's theory, since it can be shown that its fundamental equation (4) results from an integral transform of a local isotherm and an adsorption energy distribution (Stoekli *et al.* 1982; Rudzinski and Everett 1992). The variation of $s_{1,2}$ with the degree of micropore filling, θ , is also a direct consequence of the variation of the adsorption potential with the degree of micropore filling, $\theta = W_{ads}/W_{sk}$, as predicted by Dubinin's theory.

This illustrates the advantage of using the Dubinin-Radushkevich equations in the framework of the Myers-Prausnitz approach to describe multiple adsorption in microporous carbons. Moreover, the Dubinin-Astakhov equation allows additional flexibility through its variable exponent n .

In spite of the good agreement observed for the selectivity $s_{1,2}$, Table 2 reveals systematic deviations between the calculated and experimental mole fractions for $x^a < 0.3-0.4$. Since the deviations are larger than the experimental uncertainties, one may assume that Raoult's law is not followed in the adsorbed state, as observed for the adsorption from the liquid mixture (Kipling and Tester 1952). Consequently, equation (6) should take the form

$$\psi_1(p_1/(\gamma_1^a x_1^a)) = \psi_2(p_2/(\gamma_2^a x_2^a)) \quad (8)$$

There are two additional unknowns, γ_1^a and γ_2^a , and therefore equation (8) is not sufficient even if the pressures and the compositions are known. However, a first estimate can be obtained by assum-

ing that g_2^a , the activity coefficient of 1,2-dichloroethane, is close to unity for $x_2^a > 0.6-0.7$ and equation (8) becomes

$$\Psi_1(p_1/(\gamma_1^a x_1^a)) = \Psi_2(p_2/x_2^a) \quad (9)$$

By introducing the experimental data for the mole fractions x_1^a and $x_2^a = 1 - x_1^a$ (Table 2), equation (9) can be solved for g_1^a , the activity coefficient of benzene at mole fractions $x_1^a < 0.35$. A symmetrical procedure can be applied to 1,2-dichloroethane at mole fractions $x_2^a < 0.25$ to calculate g_2^a . The two sets of approximate activity coefficients, g_{MPD}^a , are given in Table 3. It appears, that to a first approximation, g_{MPD}^a does not depend on the degree of micropore filling q . The accuracy of these coefficients lies within 10% and it appears that at low concentrations they are both smaller than unity.

Table 3 also shows the values of the activity coefficients γ_{LS}^a obtained from the study of the liquid/solid equilibrium. It appears that the values obtained for the regions of low concentrations are very similar to γ_{MPD}^a . This suggests that in the adsorbed phase the activity coefficient depends more on the composition than on the degree of micropore filling θ , at least for $\theta > 0.1$. The activity coefficients γ_{LS}^a obtained in this study are similar to those reported by Blackburn *et al.* (1957) on the basis of the work of Kipling and Tester (1952). The latter investigated the liquid/solid equilibrium for the mixture of benzene + 1,2-dichloroethane adsorbed on an activated coconut charcoal. Although no information is available for this carbon, it may be assumed that it was similar to our material and had relatively wide pores.

TABLE 3. Average Activity Coefficients, γ_{MPD}^a , of Benzene and of 1,2-Dichloroethane (DCE) Adsorbed in Carbon U-02 at 293 K, Calculated from the Experimental Values of x^a via Equation (9) and Assuming that Raoult's Law holds for the Solvent. The Activity Coefficients, γ_{LS}^a , Correspond to the Adsorbed State in Equilibrium with the Liquid Mixture, also at 293 K

$x^a(\text{C}_6\text{H}_6)$	0.091	0.155	0.194	0.238	0.280	0.359	0.793	0.836	0.869	0.898
$\gamma(\text{C}_6\text{H}_6)_{\text{MPD}}^a$	0.494	0.569	0.605	0.703	0.717	0.762	1.000	1.000	1.000	1.000
$\gamma(\text{C}_6\text{H}_6)_{\text{LS}}^a$	0.416	0.475	0.515	0.563	0.612	0.706	1.011	1.011	1.009	1.007
$\gamma(\text{DCE})_{\text{MPD}}^a$	1.000	1.000	1.000	1.000	1.000	1.000	0.867	0.808	0.750	0.728
$\gamma(\text{DCE})_{\text{LS}}^a$	1.019	1.046	1.067	1.091	1.112	1.146	0.916	0.861	0.817	0.780

The agreement between the calculated and experimental values of the mole fractions x^a can be improved by introducing into equation (8) the experimental, and therefore independent, values of the activity coefficients γ_{LS}^a . Under these conditions, as illustrated by Figure 1, the overall fit leads to a standard deviation $\sigma_x = \pm 0.03$, against ± 0.05 in the case of an ideal adsorbed state (Table 2).

The present study illustrates the possibilities offered by the MPD method for the prediction of static adsorption of vapour mixtures by active carbon beds and consequently by microporous adsorbents in general. This approach has already been applied to the description of dynamic adsorption by computer simulation, where a good agreement has been observed between the calculated and the experimental breakthrough curves for a number of binary vapour mixtures (Lavanchy and Stoeckli 1997).

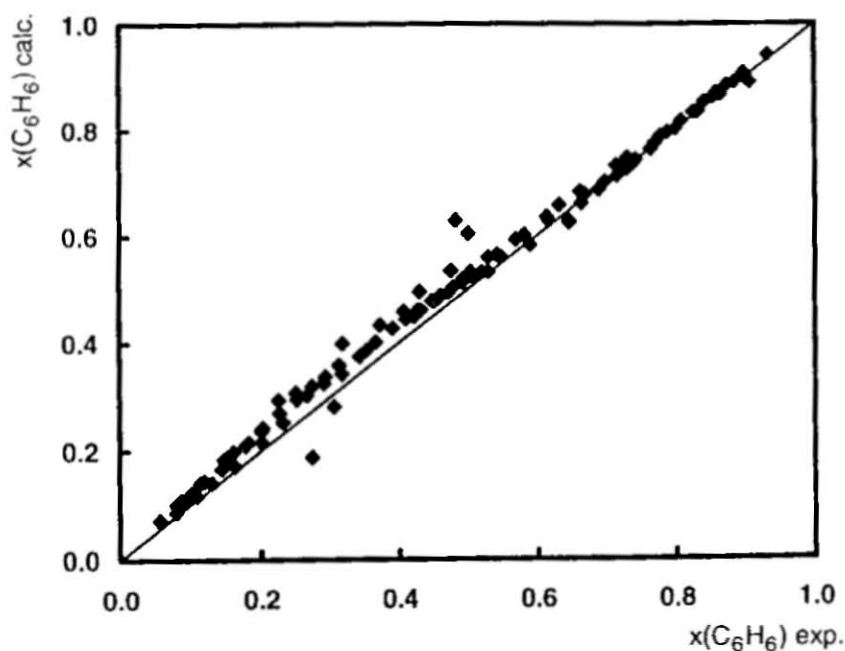


Figure 1. Correlation between the calculated mole fractions of benzene in the adsorbed state, using the activity coefficients γ_{LS}^* in equation (8), and the experimental values of x^* .

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