

ADSORPTION OF VAPOUR MIXTURES IN ACTIVE CARBONS DESCRIBED BY THE MYERS- PRAUSNITZ-DUBININ METHOD

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Introduction

At the present time, the description of single vapour adsorption by porous and non-porous solids has reached a high degree of sophistication and a variety of approaches are available in the literature [1]. On the other hand, the description of mixed adsorption has not been as rapid in the area of industrial filtration, where simple and reliable predictions are required to deal with the elimination of vapour mixtures from air.

This paper presents and discusses the recent work of the authors in the field of mixed adsorption by active carbons, based on the combination of the theories of Myers and Prausnitz and of Dubinin, and known as the MPD approach [2,3]. Although experimental and theoretical work is still in progress, success has already been reported in the prediction of binary adsorption under static and dynamic conditions [4]. For the latter, the new approach was combined with a simulation model developed earlier [5] and adapted to multicomponent systems. In this approach, the relatively simple -but efficient- theory proposed by Dubinin more than 50 years ago, plays a key role.

Dubinin's theory

Developed in successive stages between 1947 and 1970, this approach is summed up by the equation of Dubinin and Astakhov (DA) [6,7],

$$N_a = N_{ao} \cdot \exp\left[-\left(\frac{A}{\beta \cdot E_o}\right)^n\right] \quad (1)$$

N_a is the amount of vapour adsorbed at temperature T and relative pressure p/p_s , and A is the thermodynamic potential $A = RT \ln(p_s/p)$. Parameters β (affinity coefficient) and E_o (characteristic energy) depend respectively on the vapour and on the solid. In the case of active carbons, exponent n is usually close to 2, but depending on the type of micropore system, n may vary between 3 (homogeneous) to 1.5 (strongly activated and therefore very heterogeneous system). The case where $n=2$ corresponds to the classical equation of Dubinin and Radushkevich (DR), postulated in 1947 [7,8].

Provided that no molecular sieve effects are present, it appears that the limiting amount adsorbed, N_{ao} is related to the total volume of the micropore system $W_o = N_{ao} V_m$, where V_m is the molar volume of the adsorbate in the liquid state. Molecular sieve effects, present in special carbons or at low degrees of activation (burn-off), confirmed the small dimensions of the micropores associated with Dubinin's theory. It has also been shown that these pores are slit-shaped, locally at least [9] and in the case of the DR equation, their average width L is given by

$$L(\text{nm}) = \frac{10,8}{(E_o - 11,4 \text{ kJ mol}^{-1})} \quad (2)$$

It follows that the surface area of the micropore walls is approximately

$$S_{mi}(\text{m}^2 \text{ g}^{-1}) = \frac{2000 W_o(\text{cm}^3 \text{ g}^{-1})}{L(\text{nm})} \quad (3)$$

It has been shown by Stoeckli, Jakubov and Lavanchy [10] that the DA equation (1) also describes type V isotherms when $E = \beta E_o$ is around 1-2 kJ mol⁻¹, as opposed to 15-25 kJ mol⁻¹ in the classical case of type I isotherms. The case of type IV water isotherms, as a sum of type I and V isotherms, has also been considered [11,12]. Consequently, it is now possible to include in the formalism of Dubinin's theory the description of water adsorption by active carbons.

Dubinin's theory is based on the thermodynamic potential $A = RT \ln(p_s/p)$ and therefore it has important consequences in the field of immersion calorimetry [9].

As discussed in detail elsewhere [13], it follows that this theory is a very useful tool for the characterization of active carbons, as for the prediction of single vapour adsorption.

The simplicity of the parameters used in the theory is one of its advantages and it has led to the successful combination with the formalism developed by Myers and Prausnitz for binary and multiple adsorption, as discussed below.

The new MPD approach

In 1952, Bering and Serpinski proposed an empirical relation, based on the Dubinin-Radushkevich equation, to describe the adsorption equilibrium of binary vapour mixtures on active carbons [14]. In the modern formalism it becomes

$$N_{\text{tot}} = \left(\frac{W_o}{\sum x_i V_{mi}} \right) \exp \left\{ - \frac{\left[\sum x_i RT \ln \left(\frac{p_i}{p_i^o} \right) \right]^2}{\left[\sum E_o x_i \beta_i \right]^2} \right\} \quad (i = 1, 2) \quad (4)$$

where N_{tot} is the total amount adsorbed and x_i represents the mole fraction of species (i)

This approach had a limited success, owing to the choice of an unsatisfactory subsidiary equation, and the case of binary and multiple adsorption remained a challenge.

In 1965, Myers and Prausnitz [15,16] proposed a general formalism to deal with the adsorption equilibrium of two or more components between the vapour phase and the solid. Their approach led to the general criterion summed up by the condition that

$$\Psi_1 = \Psi_2 = \dots = \Psi_i \quad (5)$$

where the functions Ψ are integrals of the isotherms of individual components of the mixture,

$$\Psi_i = \int_0^{p_i^o} \frac{N_i(p)}{p} dp \quad (6)$$

By analogy with the case of liquid mixtures, the vapour pressure p_i of an adsorbed component (i) is related to a formal reference pressure p_i^o through

$$p_i = x_i \cdot \gamma_i \cdot p_i^o \quad (7)$$

where x_i is the mole fraction of component (i) in the adsorbed phase and γ_i the corresponding activity coefficient.

As shown by Lavanchy et al. [2,3], it is possible to find an analytical solution to integral (6), when using the Dubinin-Astakhov (1) equation for $N_i(p)$. Taking into account equation (7), one obtains finally

$$\Psi_i = \left(\frac{W_{oi}}{V_{mi}} \right) \left(\frac{\beta_i E_{oi}}{RT} \right) \left(\frac{1}{n} \right) \cdot \Gamma \left[\frac{1}{n}; \left[\left(\frac{RT}{\beta_i E_{oi}} \right) \cdot \ln \left(\frac{p_{si} x_i \gamma_i}{p_i} \right) \right]^n \right] \quad (8)$$

where Γ is the „incomplete“ Gamma function. For the special case of the DR equation,

$$\Psi_i = \left(\frac{W_{oi}}{V_{mi}} \right) \left(\frac{\beta_i E_{oi}}{RT} \right) \left(\frac{\sqrt{\pi}}{2} \right) \cdot \left\{ 1 - \operatorname{erf} \left[\left(\frac{RT}{\beta_i E_{oi}} \right) \cdot \ln \left(\frac{p_{si} x_i \gamma_i}{p_i} \right) \right] \right\} \quad (9)$$

It appears that the combination of Dubinin's theory with the formalism of Myers and Prausnitz provides an analytical expression, from which the equilibrium in the adsorbed phase can be calculated, provided that either the activity coefficients γ_i are known, or by assuming ideality in the adsorbed state. Since the equilibrium pressures p_i are known, or can be calculated on the basis of a mass balance in the system, it is possible to obtain x_i and the amounts N_i adsorbed in the micropores, by using a procedure described by Valenzuela and Myers [16]. It is based on two subsidiary equations,

$$\frac{1}{N_{\text{tot}}} = \frac{x_1}{N_i^{\circ}} + \dots + \frac{x_i}{N_i^{\circ}} \quad (10)$$

and

$$N_i = x_i N_{\text{tot}} \quad (11)$$

where N_{tot} is the total amount adsorbed and N_i° the amount of species (i) adsorbed alone at the formal pressure p_i° . Taking into account equation (7), this means that

$$N_i^{\circ} = \left(\frac{W_o}{V_{mi}} \right) \cdot \exp \left\{ - \left[\frac{RT \ln \left(\frac{x_i p_{si}}{p_i} \right)}{\beta_i E_o} \right]^2 \right\} \quad (12)$$

This new approach is called MPD (Myers-Prausnitz-Dubinin) and its possibilities are illustrated in the next section.

Adsorption of mixtures under static and dynamic conditions

The MPD method has been tested with different systems [2-4], under static and dynamic conditions. The adsorption of benzene + 1,2-dichloroethane vapours by a typical active carbon [3] provides an interesting example for the study of static equilibrium, the liquid mixture itself being ideal at room temperature. The experimental conditions, based on the so-called Headspace-Gas Chromatography technique, are described in detail elsewhere[2]. Separate experiments were also carried out on the solid-liquid equilibrium, leading to $\gamma_{i,LS}^a$, the activity coefficients in the adsorbed state at complete micropore-filling (see Table 2). Therefore, all the relevant parameters (N_i , N_{tot} , x_i , p_i and $\gamma_{i,LS}^a$) were available, which allowed us to check the validity of the MPD approach (Table 1).

Table 1. 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. Selected data from ref. [3]. The MPD calculations are based on the hypothesis of an ideal adsorbed state (N_{tot} given in $mmol\ g^{-1}$).

p_1 (Pa)	p_2 (Pa)	y_1	N_{tot}	N_{tot}	x_1	x_1
exp.	exp.	exp.	exp.	calc.	exp.	calc.
7.23	196.28	0.036	4.163	4.029	0.101	0.057
1.38	21.35	0.061	2.213	2.232	0.202	0.139
37.65	325.54	0.104	4.628	4.448	0.203	0.144
14.14	91.48	0.134	3.503	3.423	0.291	0.221
222.38	848.10	0.208	5.194	5.128	0.293	0.234
64.20	179.18	0.264	4.122	4.044	0.410	0.356
0.31	0.96	0.243	0.917	0.689	0.500	0.566
158.70	249.60	0.389	4.369	4.379	0.504	0.469
0.70	1.69	0.293	1.193	0.930	0.617	0.597
67.84	73.44	0.480	3.625	3.547	0.614	0.607
43.94	29.64	0.597	3.133	3.038	0.714	0.734
28.64	10.08	0.740	2.706	2.578	0.825	0.853
203.71	51.62	0.798	4.039	3.908	0.829	0.853
20.81	3.69	0.849	2.461	2.282	0.899	0.925
839.53	95.67	0.898	4.666	4.670	0.905	0.911

As shown in the table, the assumption of an ideal adsorbed state ($\gamma_i^a = 1$) leads to a relatively good agreement between the calculated and the observed total amounts adsorbed N_{tot} . On the other hand, for the mole fractions x_i the agreement is satisfactory only for $x_i > 0.25-0.30$, which reflects the non-ideality of the adsorbed state. This is confirmed by the comparison of the activity coefficients γ_{MPD}^a recalculated from the MPD equation (8) by using the experimental values of x_i and assuming that Raoult's law holds for the other component. As shown in Table 2, these values are close to those obtained for the solid-liquid equilibrium, where the liquid mixture fills the entire micropore volume W_o of the carbon.

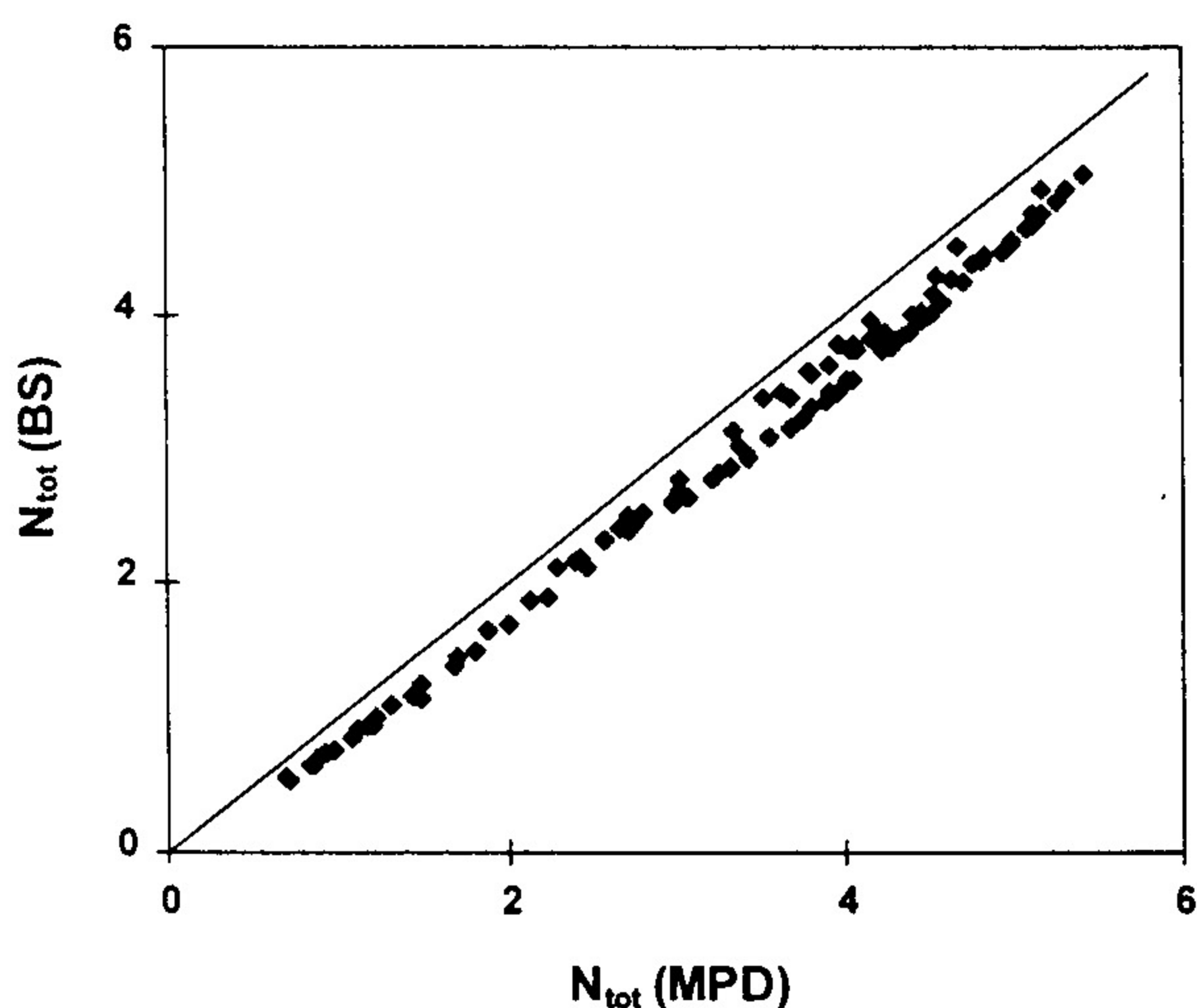
Table 2. Average activity coefficients γ_{MPD}^a of benzene and 1,2-dichloroethane (DCE) adsorbed in carbon U-02 at 293 K, calculated from the experimental values of x^a and assuming that Raoult's law holds for the solvent. The activity coefficients γ_{LS}^a correspond to the adsorbed state in equilibrium with the liquid mixture, also at 293 K.

$x^a(C_6H_6)$	0.091	0.155	0.194	0.238	0.280	0.359	0.793	0.836	0.898
$\gamma^a(C_6H_6)_{MPD}$	0.494	0.569	0.605	0.703	0.717	0.762	1.000	1.000	1.000
$\gamma^a(C_6H_6)_{LS}$	0.416	0.475	0.515	0.563	0.612	0.706	1.011	1.011	1.007
$\gamma^a(DCE)_{MPD}$	1.000	1.000	1.000	1.000	1.000	1.000	0.867	0.808	0.728
$\gamma^a(DCE)_{LS}$	1.019	1.046	1.067	1.091	1.112	1.146	0.916	0.861	0.780

The relatively good agreement found throughout between the experimental and the calculated total amounts adsorbed, N_{tot} , is probably due to a compensation effect in the range $x < 0.3$ and $x > 0.7$.

It is also interesting to compare the predictions for N_{tot} based on MPD, with those obtained through the Bering-Serpinski equation (4), using the experimental data for x_i and p_i . This correlation, shown in Figure 1 (below), indicates that equation (4) is a good assumption and confirms that the limited success of this approach is caused by the subsidiary equation used by these authors. It appears that a combination of the Bering-Serpinski equation (4) with equations (10)-(12) might be an alternative to MPD. The possibility of a formal link between the two approaches is under investigation and results will be published in due course.

Figure 1. Comparison of the total amounts adsorbed N_{tot} calculated with the Bering-Serpinski equation (4), using the experimental data for x_i and p_i given in Table 1, and the values obtained from the MPD method.



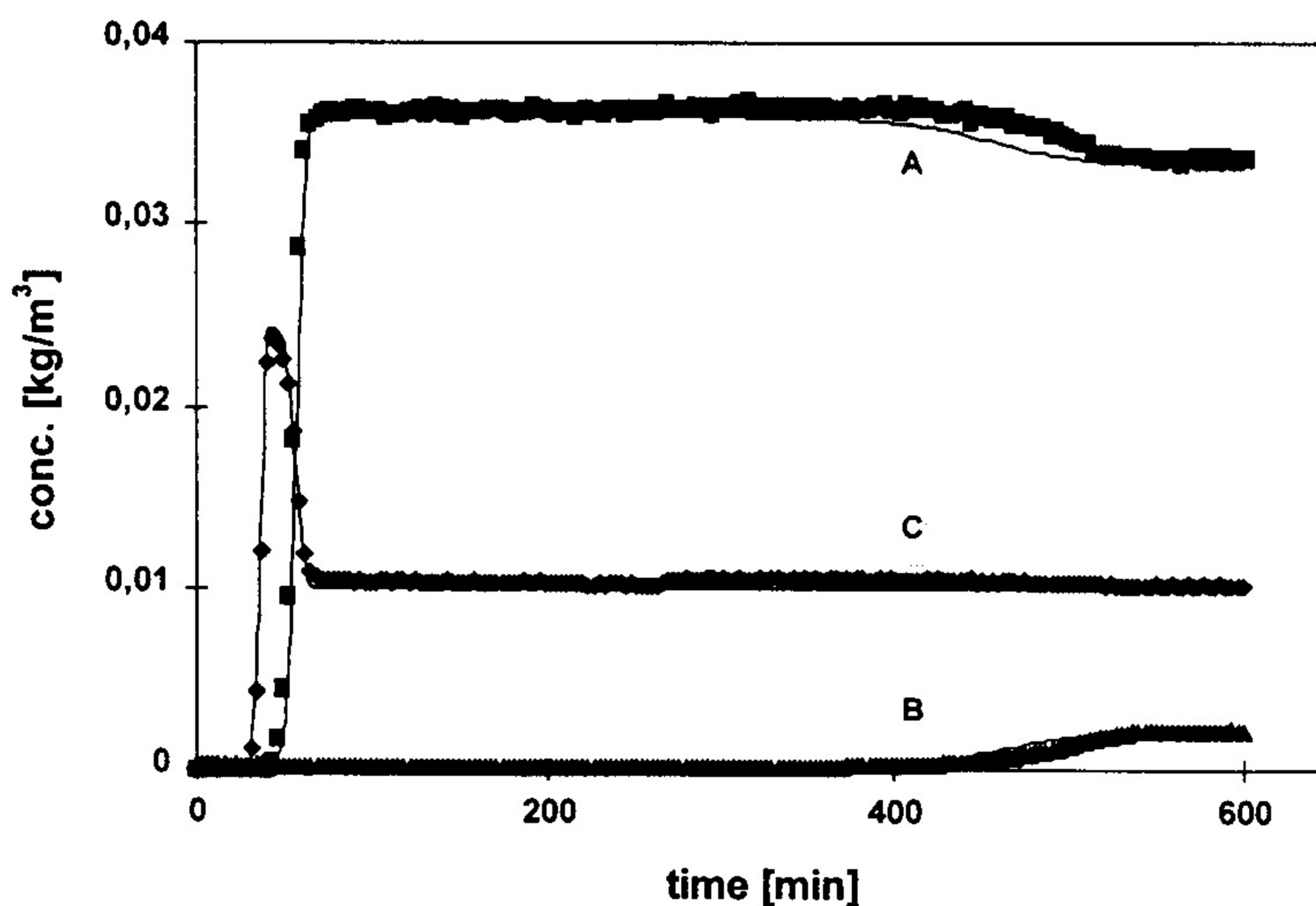
These results show that the new MPD approach is of great help in the prediction of adsorption equilibrium for vapour mixtures. However, the non ideality of the adsorbed state remains a variable to be considered, in particular in the region of Henry's law.

The MPD approach has also been considered in the problem of filtration processes, where vapours are removed under dynamic conditions from a stream of air passing over active carbon beds. For single vapours, success had already been achieved by using the DR equation in connection with a computer simulation model proposed by Ladugie *et al.* [5]. Consequently, the MPD formalism has been adapted to an extended version of the model [4] and success has been reported for a variety of binary mixtures.

Recently, the behaviour of the ternary mixture of carbon tetrachloride, chlorobenzene and 2-chloropropane over an active carbon bed has been investigated. As shown in Figure 2, a very

good agreement is observed between the calculated breakthrough curves and the experimental data. Surprisingly, the assumption of an ideal adsorbed state does not seem to have a great influence on the final result. This had also been observed for the binary systems.

Figure 2. Breakthrough curves for a mixture of carbon tetrachloride (A), chlorobenzene (B) and 2-chloropropane (C), in a stream of dry air and over carbon U-02 at 293 K. The relative concentrations c/c_0 are 0.04, 0.005 and 0.036. The curves correspond to the simulations and the points to the experimental data.



Conclusions

We have shown that the combination of Dubinin's theory with the formalism developed by Myers and Prausnitz leads to interesting developments in the prediction of binary and multiple adsorption under static and dynamic conditions. For the latter case, it was also necessary to develop and to adapt a specific model to be used in the computer simulation.

The success obtained here -and in particular the prospects of the new MPD approach- are a direct consequence of the simplicity of Dubinin's theory and its basic equation (1), which requires a limited number of parameters to describe adsorption over a large range of pressures

and temperatures. Moreover, these parameters are readily available. It is therefore remarkable, that Dubinin's theory, which has been proposed more than fifty years ago, still leads to interesting and useful achievements in adsorption science and in filtration technology.

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