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DYNAMIC ADSORPTION OF VAPOUR MIXTURES IN ACTIVE CARBON BEDS DESCRIBED BY THE MYERS–PRAUSNITZ AND DUBININ THEORIES

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Abstract—The adsorption of binary vapour mixtures from air by active carbon beds can be predicted with a good accuracy by adapting a model developed earlier for single vapours. This model is based on a semi-implicit finite difference scheme. Multiple adsorption of vapours is described by the combined theories of Myers–Prausnitz and of Dubinin (MPD), which have already been applied successfully to static adsorption. A good agreement is found between the predicted and the experimental breakthrough curves of the systems 2-chloropropane + chlorobenzene and carbon tetrachloride + chlorobenzene on two activated carbons at 298 K and under different experimental conditions.

Key Words—A. Activated carbon, C. adsorption, D. adsorption properties.

1. INTRODUCTION

The purification of air remains one of the major industrial applications of active carbons and therefore it is desirable to be able to predict the removal of effluents under dynamic conditions. This remains an important task in the case of mixtures of vapours, where the models developed for the adsorption of single components no longer apply, or lead only to approximations.

In this study, we present a new approach for the prediction of binary and multiple adsorption under dynamic conditions. It is based on the combination [1] of the Myers–Prausnitz [2–4] and Dubinin [5,6] theories (MPD) with a mathematical model used earlier for the adsorption of a single component from a stream of air [7]. The advantage of this approach is the fact that it provides analytical expressions for the description of the individual isotherms and therefore reduces the simulation time to an acceptable level. The validity of the model is illustrated by the comparison between the predicted and the experimental breakthrough curves obtained for the adsorption from air, under dynamic conditions, of 2-chloropropane + chlorobenzene and carbon tetrachloride + chlorobenzene vapour mixtures on active carbon beds at 298 K.

2. THEORETICAL

2.1 *Static adsorption*

Physical adsorption of vapours by active carbons is well described by Dubinin's theory for the volume filling of micropores [5,6]. Its fundamental expression is the Dubinin–Astakhov eqn (1)

$$N_a = N_{ao} \exp[-(A/\beta E_o)^n] \qquad (1)$$

where N_a represents the amount adsorbed at temperature T and relative pressure p/p_o; N_{ao} is the limiting amount adsorbed, given usually in mol g^{-1} of solid and related to the micropore volume accessible to the molecule, $W_o = N_{ao} V_m$, V_m being the molar volume of the adsorbate; $A = RT \ln(p_o/p)$; and β and E_o are specific parameters which depend on the adsorptive and on the solid. For typical active carbons of industrial origin, the exponent $n = 2$, which corresponds to the classical Dubinin–Radushkevich (DR) equation.

The major advantage of the DA eqn (1) is the limited number of parameters required to describe and to predict the adsorption over a wide range of pressures and temperatures. For this reason, it was already used in the mathematical model of Ladugie *et al.* [7], for the simulation of physical adsorption of a single vapour from air in a bed of active carbon. As described below, this model has been extended to the case of binary adsorption.

Binary and multiple adsorption of vapours under static and dynamic conditions has been considered by many authors [8–11], but the choice of models which can predict the equilibrium is still limited. For example, in the early 1950s, Bering and Serpinski proposed an empirical extension of the Dubinin–Radushkevich equation to multiple adsorption [12–16] and several systems could be described. However, its success was limited by the choice of a subsidiary equation needed to reduce the number of parameters and this approach was virtually abandoned. Later, Myers and Prausnitz [2–4] developed a useful model for multiple adsorption, which con-

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tains the isotherms of the pure components. However, the model is based on integrals of the adsorption isotherms divided by the pressure, which do not necessarily lead to analytical solutions. Therefore, one considered essentially the isotherms of Langmuir and of Toth [17]. They provide exact solutions, but have a limited predicative power, as opposed to the DA equation.

As described in detail elsewhere [1], in the model of Myers and Prausnitz the equilibrium pressures p_1 and p_2 and the mole fractions x_1 and x_2 of a binary mixture adsorbed by a solid are related formally by integrals Ψ involving the isotherms of the pure components. The equilibrium condition, which can be extended to several components, is

$$\Psi_1(p_1/x_1)=\Psi_2(p_2/x_2)=\Psi_i(p_i/x_i) \qquad (2)$$

As shown by Lavanchy *et al.* [1], in the case of the DA eqn (1), the function Ψ has an analytical solution

$$\Psi_i(p_i/x_i)=(W_o/V_{mi})(\beta_i E_o/RT)(1/n)\Gamma[1/n \; ((RT/\beta_i E_o)\ln(p_{oi}/(p_i/x_i)))^n] \qquad (3)$$

where Γ is the *incomplete Gamma* function $\Gamma[\alpha;u]=\int_u^\infty \exp[-t].t^{\alpha-1}\,dt$.

Consequently the equilibrium equation can be obtained by combining eqn (2) and eqn (3) with the mass balance and other relations of the general theory of Myers and Prausnitz.

This approach, called MPD (Myers, Prausnitz and Dubinin), has been tested successfully for the static adsorption of binary mixtures, such as chlorobenzene + carbon tetrachloride [1] and, more recently 1,2-dichloroethane + benzene, on a typical industrial active carbon at room temperature. It was therefore obvious to include this approach in the numerical simulation model proposed by Ladugie *et al.* [7], based on the DA eqn (1) and already describing successfully the adsorption of a single vapour from a stream of air. We shall describe briefly the main features of the model.

2.2 *The adsorption model*

The mathematical model, described in detail elsewhere [7], is based on a semi-implicit finite difference scheme. For each space/time element, a system of coupled non-linear equations describing the main physical relations is solved. The parameters taken in account are:

(1) The mass conservation for each compound. Neglecting axial diffusion effects leads to a one-dimensional model.

(2) Mass transfer relationship. It is a linear rate model, based on a fluid film resistance. The mass transfer coefficient is calculated from the film diffusion coefficient, itself obtained from the relation proposed by Fuller, Schettler and Giddings [8]. It has been observed that the overall mass transfer rate decreases with increasing load and therefore a linear reduction of the film diffusion coefficient has been introduced. In the present simulations, it was assumed that this factor varied from 0.01 (no adsorption) to 1 (maximum load).

(3) Binary adsorption of the vapours, which is calculated by using eqns (2) and (3) with exponent $n=2$ and corresponding to the classical DR equation. The additional conditions are

$$\sum_i (x_i/N_{ai})-(1/N_t)=0 \qquad (4)$$

$$N_i^m=N_t x_i \qquad (5)$$

where N_{ai} and N_i^m are respectively the amounts of vapour (i) adsorbed alone or from the mixture, at relative pressures p_i/p_{oi} and $N_t=\Sigma N_{ai}$.

(4) Energy conservation, a parameter which can be omitted in the case of isothermal adsorption. This hypothesis reduces the simulation time by a factor of nearly 3.

3. EXPERIMENTAL

3.1 *Activated carbons*

The properties of the two commercially based solids are given in Table 1. The micropore volumes W_o and the characteristic energies E_o have been obtained from the DR treatment of benzene isotherms measured by HS-GC (head space gas chromatography [1]) at 293 K. It is well-known that these parameters depend on the adsorptive properties, but in the case of strongly activated carbons, characterized by wide pores, the use of a reference adsorbate such as benzene, is sufficient. This illustrates the advantage of Dubinin's theory, and consequently of the MPD approach.

3.2 *Adsorbates*

The organic vapours were chosen in order to include a wide range of saturation pressures and to avoid any form of chemical reaction. Their main properties required for the simulation are given in

Table 1. Main characteristics of the adsorbents

Activated carbons	Description	Micropore volume, W_o ($m^3\,kg^{-1}$)	E_o ($J\,mol^{-1}$)	Mean grain diameter (m)	Bulk density ($kg\,m^{-3}$)	Apparent density ($kg\,m^{-3}$)
U03 (U)	Coal based, granular	0.495×10^{-3}	16.95×10^3	1.0×10^{-3}	484	980
Norit-125 (N)	Peat based, extruded (L = 2–5 mm)	0.55×10^{-3}	16.24×10^3	1.25×10^{-3}	460	690

Table 2. Parameters required for the simulations

Adsorptive	Molecular mass ($kg\ mol^{-1}$)	Diffusion volume ($m^3\ mol^{-1}$)	Liquid density at 25°C ($kg\ m^{-3}$)	Volatility at 25°C ($kg\ m^{-3}$)	Affinity coefficient, β
2-chloropropane (IPC)	78.5×10^{-3}	82.9×10^{-6}	8.558×10^{2}	2.177	0.93
Carbon tetrachloride (TCK)	153.8×10^{-3}	94.5×10^{-6}	1.584×10^{3}	9.439×10^{-1}	1.05
Chlorobenzene (CLB)	112.56×10^{-3}	108.2×10^{-6}	1.105×10^{3}	7.221×10^{-2}	1.18

Table 2. The carrier gas was dry air, with a viscosity of 17.9×10^{-6} N s m^{-2}.

3.3 *Experimental procedure*

Dry air, challenged with the required amounts of organic vapours, was sent through a glass tube of 0.03 m in diameter and filled with the active carbon up to a height of 0.059 m. The flow rate was usually 0.14 m s^{-1}. The outlet concentrations were analyzed in cycles of 1–2 minutes, by IR spectroscopy and using a gas cell of 20 m path length. The gas flow system and the adsorption bed were thermostatted at 295.15 ± 0.2 K and the relative error was estimated to be within 2%.

3.4 *Computer simulations*

The simulations were carried out on a AXP 8400, 300 MHz, 0.5 GB memory computer, assuming isothermal conditions. The required computing time was usually less than 20 minutes for a whole system. It is important to emphasize that modelling was based exclusively on the data of Table 1 and Table 2,

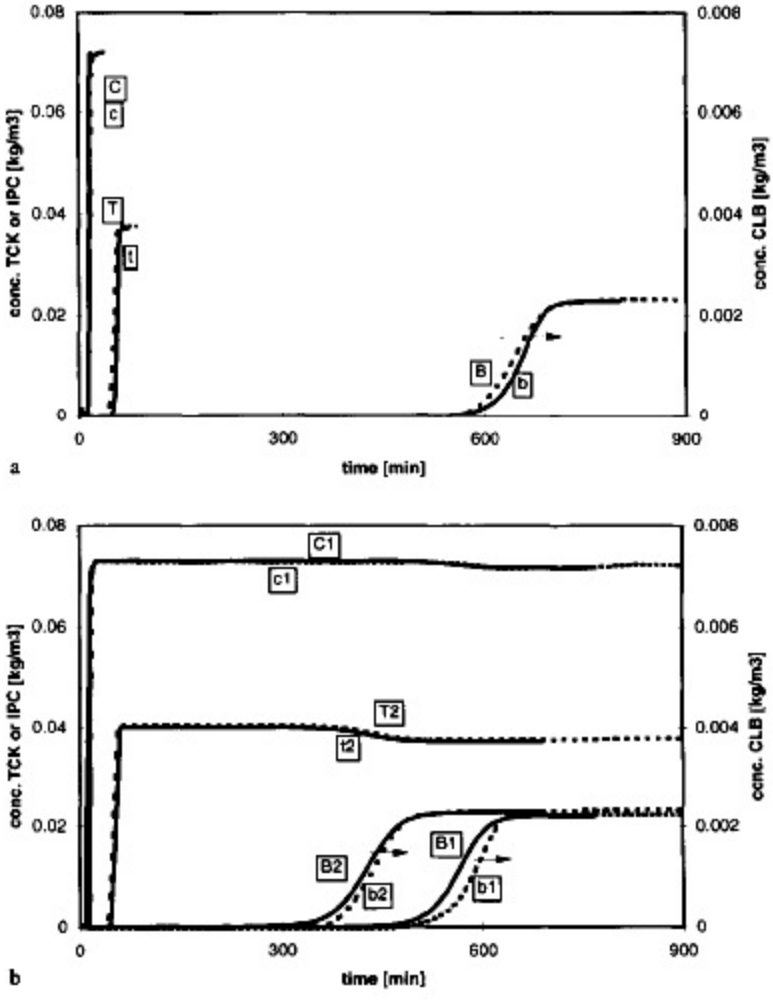

Fig. 1. (A) Calculated and experimental breakthrough curves for pure vapours of 2-chloropropane (C/c), chlorobenzene (B/b) and carbon tetrachloride (T/t) in a stream of air, on a bed of carbon U03. The standard conditions and the symbols are given in the text (Section 4). (B) Breakthrough curves for the binary mixtures of 2-chloropropane + chlorobenzene (1) and carbon tetrachloride + chlorobenzene (2), under the same standard conditions.

the dimensions of the filter and the flow rate. This means that no parameter fitting was attempted to obtain a better agreement with the experimental data. Consequently, the calculated and the experimental results, discussed below, are independent.

4. RESULTS AND DISCUSSION

The results of the simulations are compared with the experimental data in Figs 1–5. They show the concentrations of the individual vapours at the exit of the filter, as functions of time (breakthrough curves) and under different conditions, as discussed below. Unless specified otherwise, the following parameters are kept constant throughout the simulations and define standard conditions:

(1) the relative inlet concentrations p/p_o for 2-chloropropane (0.036), carbon tetrachloride (0.040) and chlorobenzene (0.032);
(2) linear flow rate of 0.14 m s^{-1};
(3) active carbon U03 with a bed depth of 0.059 m.

Moreover, in all figures the following conventions are adopted:

- capital letters and full lines correspond to calculated concentrations;
- lower case letters and broken lines correspond to experimental values for the three adsorbates, 2-chloropropane (C/c), chlorobenzene (B/b) and carbon tetrachloride (T/t).

The experimental procedure and the computer simulations were first tested with the pure vapours, under standard conditions, as show in Fig. 1(A). As expected from earlier work, one observes a good agreement between the calculated and the experimental data. The breakthrough time for chlorobenzene is much longer than for the other two components, which provides a good test of the model.

The second stage, illustrated by Fig. 1(B), corres-

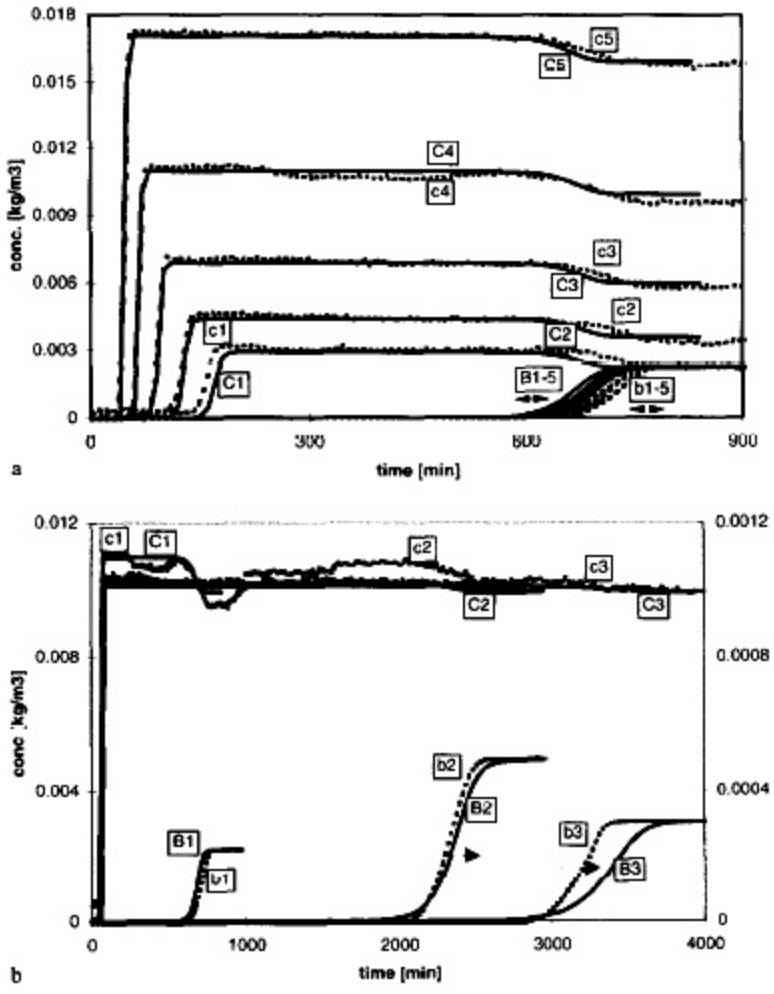

Fig. 2. Calculated and experimental breakthrough curves for the mixtures of 2-chloropropane and chlorobenzene in air, on carbon U03. (A) Constant relative inlet concentration of chlorobenzene = 0.036 in the 5 mixtures (B1/b1 to B5/b5) and variable concentrations for 2-chloropropane, 0.001 (C1/c1), 0.0018 (C2/c2), 0.003 (C3/c3), 0.005 (C4/c4) and 0.008 (C5/c5). (B) Constant inlet concentration for 2-chloropropane = 0.005 and variable for chlorobenzene, 0.036 (B1/b1), 0.008 (B2/b2) and 0.005 (B3/b3).

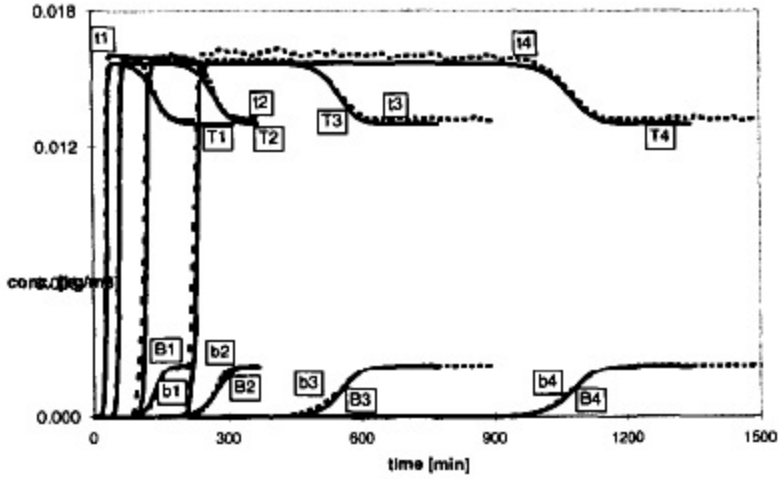

Fig. 3. Calculated and experimental breakthrough curves for the standard mixture of carbon tetrachloride (T/t) and chlorobenzene (B/b) in air, as a function of the depth of the carbon bed U03, 15 mm (1), 29 mm (2), 61 mm (3) and 115 mm (4).

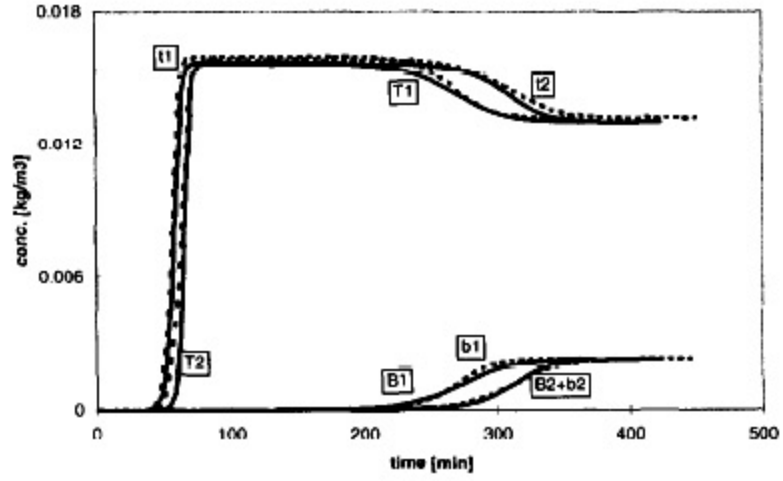

Fig. 4. Calculated and experimental breakthrough curves for the standard mixture of carbon tetrachloride (T/t) and chlorobenzene (B/b) on carbon beds U03 (1) and Norit-125 (2).

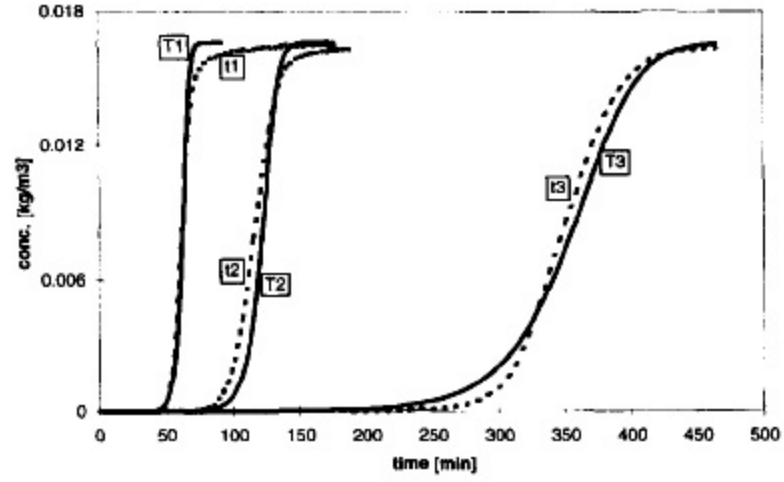

Fig. 5. Calculated and experimental breakthrough curves of pure carbon tetrachloride (T/t) in air with a relative inlet concentration of 0.02 and for flow rates of 0.48 m s^{-1} (T1/t1), 0.13 m s^{-1} (T2/t2) and 0.011 m s^{-1} (T3/t3).

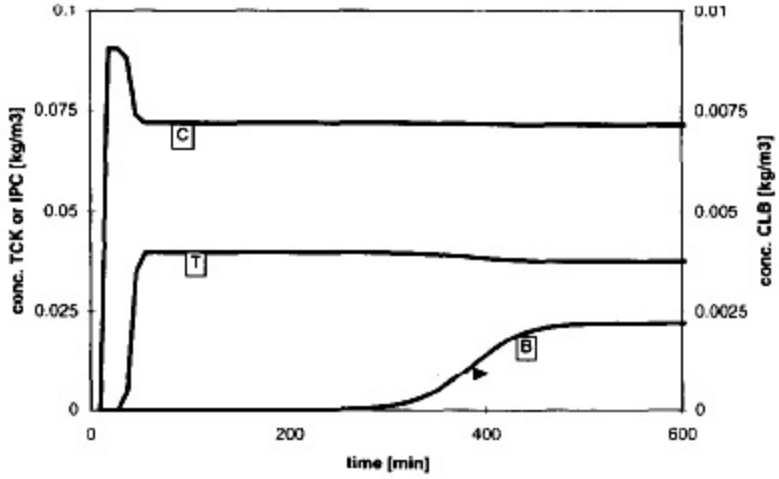

Fig. 6. Predicted breakthrough curves for a mixture of 2-chloropropane (C), carbon tetrachloride (T) and chlorobenzene (B) in air, with relative inlet concentrations of 0.036, 0.040 and 0.032, on carbon bed U03.

ponds to the mixtures of 2-chloropropane + chlorobenzene (1) and to carbon tetrachloride + chlorobenzene (2), with the same inlet concentrations as in Fig. 1(A). In spite of the different breakthrough times of the components, the simulations lead to good agreements with the experimental values.

Figure 2(A) and (B) correspond to the mixture of 2-chloropropane + chlorobenzene, using different inlet concentrations. The first real discrepancy between calculated and observed breakthrough times appears for mixture (3) in Fig. 2(B), where the relative concentration of 2-chloropropane is only 0.005. This is not too surprising in view of the long time required for the breakthrough of this vapour (more than 2 days). The difference is in the shape of the outlet concentration, the breakthrough itself starting practically as expected.

Figure 3 illustrates the effect of the bed depth on the breakthrough times for the mixture of carbon tetrachloride + chlorobenzene under standard conditions. The calculated and observed curves are in very good agreement.

Figure 4 shows the effect of the adsorbent on the breakthrough of the same mixture as before. The calculated curves are different for carbons U03 (1) and Norit-125 (2), but in agreement with the experimental data. This illustrates the influence of the active carbon bed, characterized by its parameters E_0 and W_0 of the Dubinin equation.

The effect of the change in flow rate (0.011, 0.13 and 0.48 m s^{-1}) on the breakthrough of pure carbon tetrachloride in air is shown in Fig. 5. In all cases, one observes a satisfactory agreement between the calculated and the experimental values. This means that the flow rate is correctly taken into account by the model.

The different systems and the variations of the parameters considered in this study show that the inclusion of the MPD approach in a relatively simple numerical sorption model lead to a satisfactory prediction of dynamic adsorption of organic mixtures by active carbons. The main advantage is the possibility to calculate the breakthrough curves for constant and variable inlet concentrations of the components. The latter correspond to industrial conditions and in most cases the outcome could not be predicted easily by laboratory experiments alone. Moreover, like MPD itself, the model discussed here is not limited to binary mixtures of organic vapours. Figure 6 shows for example the predictions for the mixture of the three vapours considered here and under the standard conditions defined above (the corresponding experimental results will be reported later).

In spite of the promising results described here, some limitations to the possibilities offered by the model should be pointed out. Firstly, it is restricted to physisorption. Secondly, in practice water vapour is always present in the system, which my cause unexpected difficulties. Although the adsorption of water by active carbons is described by the DA eqn (1) [18,19], it must first be shown to what extent the static adsorption of water mixed with other vapours is correctly described by the MPD approach. A major problem is the miscibility or the immiscibility of the corresponding liquids, which may strongly affect the behaviour in the adsorbed state. It also appears that water adsorption is very slow and diffusion controlled and its rate varies with the state of the carbon (oxygen containing groups). All these effects must be accounted for in further developments of the model and will be reported in due course.

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