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Dynamic adsorption, in active carbon beds, of vapour mixtures corresponding to miscible and immiscible liquids

A. Lavanchy [a], F. Stoeckli [b,*]

[a] *NC Laboratory, CH-3700 Spiez, Switzerland*
[b] *Chemistry Department, Av. de Bellevaux 51, CH-2000 Neuchâtel, Switzerland*

Abstract

It is shown that the combined Myers–Prausnitz–Dubinin theory (MPD) can be extended to the adsorption of ternary mixtures from an air stream. When combined with a computer model developed for dynamic adsorption, it provides a satisfactory agreement with the experimental breakthrough curves in active carbon beds. On the other hand, as illustrated by a mixture of water and 2-chloropropane vapours, MPD is no longer valid when the corresponding liquids are not miscible. In this case, binary adsorption can be described with a relatively good precision by assuming independent co-adsorption of the vapours. This, in turn, leads to satisfactory previsions for dynamic adsorption.

Keywords: A. Activated carbon; C. adsorption; D. adsorption properties

1. Introduction

We have shown recently [1] that the dynamic adsorption of binary vapour mixtures from air by active carbon beds can be predicted by combining the new Myers–Prausnitz–Dubinin theory (MPD) [2,3] with a computer simulation model [4]. As illustrated below, this approach can now be extended to ternary mixtures of organic vapours in a stream of dry air. Full agreement has been found between the experimental breakthrough curves and the predictions for mixtures of 2-chloropropane, carbon tetrachloride and chlorobenzene in dry air, passing through an active carbon bed.

The vapour mixtures considered so far in static and dynamic adsorption all correspond to miscible liquids, and it was assumed that the same was true for the adsorbed phase. Consequently, the Myers–Prausnitz theory and its combination with Dubinin's theory were justified. However, in real filtration systems water is often present and it is known that in the liquid state it is not miscible with typical organic compounds. It follows that the MPD approach is no longer valid under these circumstances. In order to develop our current study of binary and multiple adsorption, it was therefore decided to examine the case of vapour mixtures corresponding to non-miscible liquids.

The present work refers to binary mixtures, typified by the system water and 2-chloropropane, for which MPD no longer applies. It appears that for moderate degrees of micropore filling, this system is described to a good first approximation by the independent co-adsorption of the two species. Under these circumstances, each vapour is adsorbed in the micropore volume left free by the other.

2. Theoretical

In view of the full descriptions of Dubinin's theory and of the MPD approach given previously [1–3], we shall limit ourselves to the essential information. Physical adsorption of single vapours by active carbons is

* Corresponding author.

described by the Dubinin–Astakhov Eq. (1):

$$N_a = N_{ao} \exp[-(A/E)^n]. \quad (1)$$

N_a represents the amount adsorbed at temperature T and relative pressure p/p_o; N_{ao} is the limiting amount adsorbed, usually given in kmol kg^{-1} of solid and related to the actual micropore volume accessible to the molecule, $W_o = N_{ao} V_m$, V_m being the molar volume of the adsorbate; $A = RT \ln(p_o/p)$. The quantity $E = \beta E_o$ contains two specific parameters, which depend on the adsorptive and on the solid. Moreover, for the adsorption of organic and many inorganic vapours by typical active carbons, exponent n is close to 2. This corresponds to the classical Dubinin–Radushkevich (DR) equation and a type I isotherm.

As shown earlier [5], the DA Eq. (1) contains an inflexion point which becomes apparent for small values of the ratio E/RT (typically around 1). Under these circumstances, the isotherm becomes S-shaped, which corresponds to a classical type V. It has been observed for the adsorption of water by active carbons with a small oxygen content on the surface. The corresponding characteristic energy E is in the range of 1–2 kJ mol^{-1}, as opposed to 16–25 kJ mol^{-1} in the case of benzene with its type I isotherm. For water, the exponent n varies from 2 to 7, which reflects the steepness of the isotherm at the inflexion point.

Careful studies have also shown that at low relative pressures water adsorption isotherms display an initial section of type I and its importance depends on the amount of oxygen [6,7]. Formally, the type IV isotherm may be considered as the sum of two contributions, of types I and V. Both sections satisfy the requirement of temperature invariance of the DA equation, and therefore the overall water adsorption isotherm can be described as a sum of DA equations of types I and V:

$$N_a = N_{ao}(\mathrm{I}) \exp\{-[A/E(\mathrm{I})]^{n(\mathrm{I})}\} + N_{ao}(\mathrm{V}) \exp\{-[A/E(\mathrm{V})]^{n(\mathrm{V})}\}. \quad (2)$$

In this equation, $N_{ao}(\mathrm{I})$ corresponds to the amount of water adsorbed on acidic and basic sites. Their saturation leads to the type I isotherm, with a characteristic energy $E(\mathrm{I})$ around 4–7 kJ mol^{-1} and exponent $n(\mathrm{I})$ between 1 and 2 [7].

The corresponding volumes, obtained by multiplying N_{ao} by the molar volume V_m of the adsorptive, are W_o, $W_o(\mathrm{I})$ and $W_o(\mathrm{V})$.

For vapours whose liquids are miscible, the model of Myers and Prausnitz [8–10] can be used. The adsorption equilibrium of vapours with pressures p_i and mole fractions x_i in the adsorbed phase is given by the condition that the specific integral functions ψ must be equal:

$$\psi_1(p_1/x_1) = \psi_2(p_2/x_2) = \psi_i(p_i/x_i). \quad (3)$$

These integrals contain the adsorption isotherms of the pure components and, as shown by [2], if one uses the DA Eq. (1), the function ψ_i has an analytical solution:

$$\psi_i(p_i/x_i) = (W_0/V_{mi})(\beta_i E_0/RT)(1/n)\Gamma(1/n; \{(RT/\beta_i E_0) \ln[p_{oi}/(p_i/x_i)]\}^n) \quad (4)$$

where Γ is the incomplete Gamma function $\Gamma[\alpha; u]$ [11].

In the case of immiscibility in the adsorbed state, a likely consequence of immiscibility in the liquid state, MPD no longer applies. However, as a first approximation, one may assume independent adsorption in the micropores. This means that the volume available for adsorption by a given adsorptive is not the total micropore volume W_o, but the volume left free by the other. In the case of water (1) and an organic vapour (2), one obtains the set of type IV and type I equations:

$$W_1 = N_{a1} V_{m1} = (W_o - W_2)((1-\theta) \exp\{-[A_1/E_1(\mathrm{I})]^{n1(\mathrm{I})}\} + \theta \exp\{-[A_1/E_1(\mathrm{V})]^{n1(\mathrm{V})}\}) \quad (5)$$

and

$$W_2 = N_{a2} V_{m2} = (W_o - W_1) \exp[-(A_2/E_2)^{n2}] \quad (6)$$

where θ is the fraction of the water adsorbed as type V isotherm:

$$\theta = W_o(\mathrm{V})/[W_o(\mathrm{I}) + W_o(\mathrm{V})] = W_o(\mathrm{V})/W_o. \quad (7)$$

The approach which is described here for the static adsorption of water and an organic vapour bears some similarity to the work of [12] and of [13], but it is less complicated.

To calculate the adsorption equilibrium for a given time/space point in the carbon bed, one may add the mass–balance relations:

$$m_1 = N_{a1} u1 \rho + c_1 \epsilon \quad (8)$$

$$m_2 = N_{a2} u2 \rho + c_2 \epsilon \quad (9)$$

where m = total mass of substance/unit volume of the bed (kg m^{-3}); u = molecular weight of the adsorptive (kg mol^{-1}); ρ = bulk density of the active carbon (kg m^{-3}); ϵ = void volume fraction of the active carbon bed; c = concentration of the adsorptive (kg m^{-3}).

For given masses m_1 and m_2, the system of Eqs. (5), (6), (8) and (9) contains four unknowns, c_1, c_2, N_{a1} and N_{a2}, which can be found numerically using Newton's method.

3. Experimental

The experimental conditions were similar to those described in detail earlier [1] and we shall limit ourselves to the features relevant to the present study.

3.1. Active carbon

We used active carbon U03, with a mean grain diameter of 1 mm, a bulk density of 484 kg m^{-3} and an apparent density of 980 kg m^{-3}. The micropore volume $W_0 = 0.495 \times 10^{-3}$ m^3 kg^{-1} and the characteristic energy $E_0 = 16.95 \times 10^3$ J mol^{-1} are those obtained from the DR analysis ($n2 = 2$) of the benzene isotherms ($\beta = 1$) measured at 293 K by headspace gas chromatography (HS-GC) [2].

For water adsorption, the parameters of the DA equations corresponding to the type I and type V contributions are, respectively:

$$W_o(\mathrm{I}) = 1 \times 10^{-5} \text{ m}^3 \text{ kg}^{-1},$$

$$E(\mathrm{I}) = 4440 \text{ J mol}^{-1},\ n1(\mathrm{I}) = 2$$

and

$$W_o(\mathrm{V}) = 4.85 \times 10^{-4} \text{ m}^3 \text{ kg}^{-1},$$

$$E(\mathrm{V}) = 1180 \text{ J mol}^{-1},\ n1(\mathrm{V}) = 2.55.$$

It is interesting to point out that the enthalpy of immersion of this carbon into water at 293 K calculated from the type I and type V isotherms [5,7] is -32.2 J/g, in close agreement with the experimental value of -31.5 J/g.

3.2. Adsorbates

The parameters of the adsorbates, required for the calculations and the simulations, are given in Table 1. In the case of the three organic vapours, the carrier gas was dry air, with a viscosity of 17.9×10^{-6} N s m^{-2}.

3.3. Experimental procedure

In the case of the ternary mixtures, dry air loaded with the required amounts of organic vapours was sent through a glass tube of 0.03 m in diameter and filled with active carbon up to a height of 0.059 m. The flow rate was usually close to 0.14 m s^{-1}.

The test temperature was 298.2 K and the pressure 1013×10^2 N m^{-2}. The outlet concentrations were analysed in cycles of 1–2 minutes by IR spectroscopy, using a gas cell of 20 m pathlength.

In the case of water and 2-chloropropane, the same procedure applies, with three differences. The test temperature was set to 295.2 K. The air was humidified to the test concentration by passing a defined fraction of the dry air flow through a saturation column of 1.4 m length and 0.08 m diameter filled with glass Raschig rings. Prior to the experiment, the active carbon bed was pre-conditioned during a period of 48 ± 15 hours, with a stream of air (approximately 2 m^3 per hour), containing the same degree of humidity as in the subsequent experiment with the organic vapour.

3.4. Computer simulations

For the ternary mixture, and for the mixture of water and 2-chloropropane vapours, the same procedure was used, as described earlier [1]. A new "miscibility" flag is used to select the appropriate algorithm. In the case of active carbon pre-conditioned with wet air, two additional parameters must be added, namely the initial water load and the concentration.

As pointed out earlier, the predictions of the model and the experimental results are totally independent.

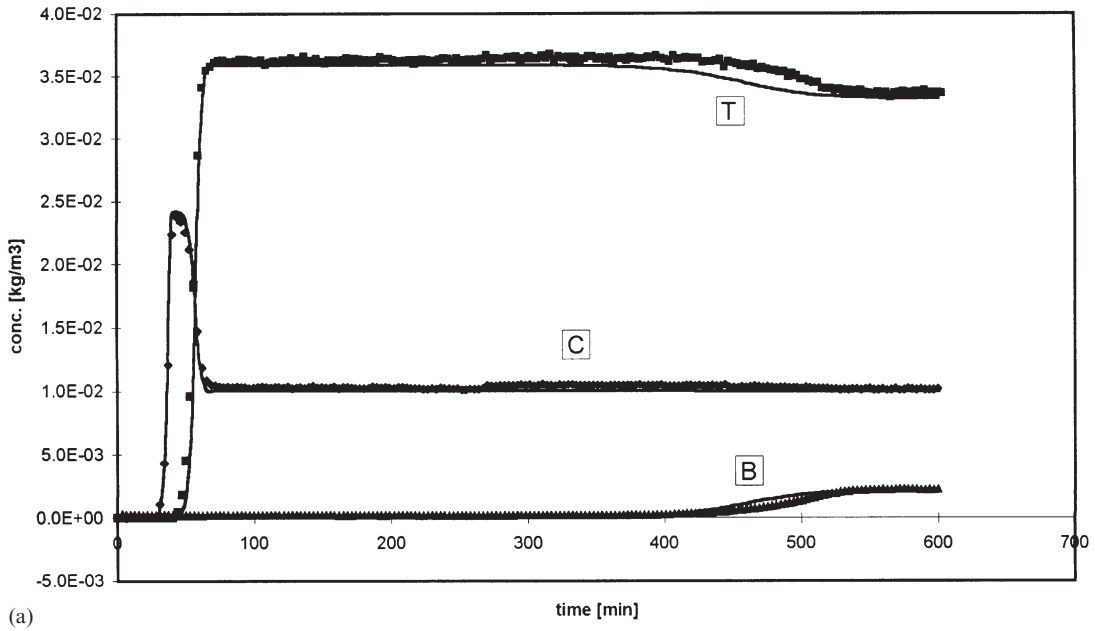
4. Results and Discussion

The results of the simulations are compared with the experimental data in Figs. 1–3 and in Table 2. The figures show the concentrations of the individual vapours at the outlet of the filter as a function of the time (breakthrough curves).

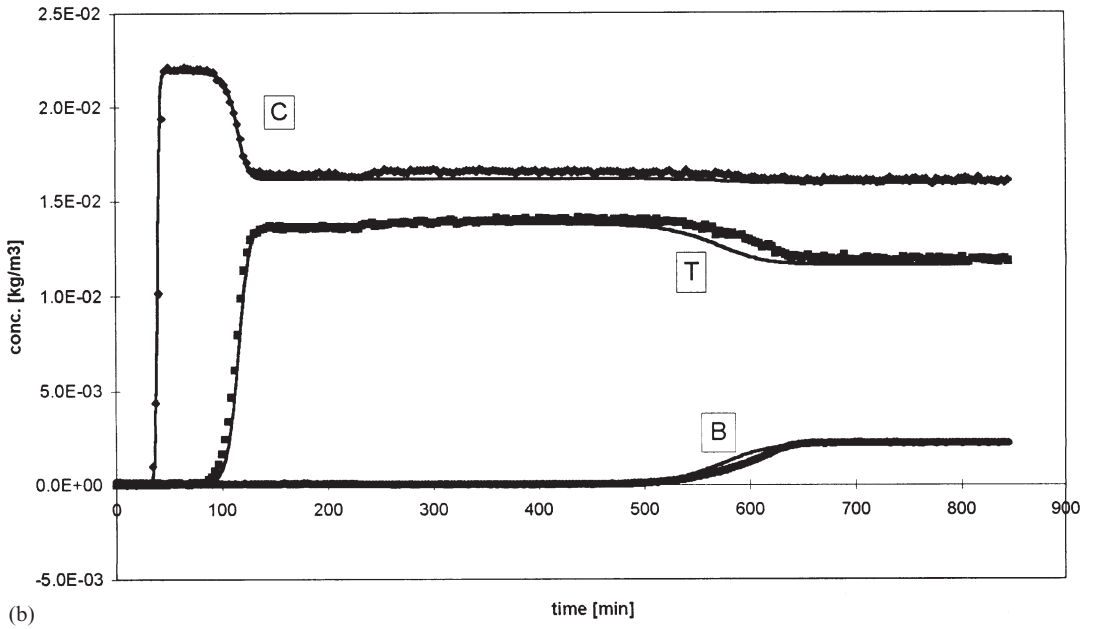
Fig. 1(a,b) shows the breakthrough curves for the ternary mixtures of carbon tetrachloride (T)+ chlorobenzene (B)+2-chloropropane (C). The solid lines correspond to the simulations and the points are the individual experimental results.

Table 1
Specific parameters of the adsorbates

Adsorptive	Molecular mass (kg mol^{-1})	Diffusion volume (m^3 mol^{-1})	Liquid density (25°C) (kg m^{-3})	Volatility (25°C) (kg m^{-3})	Affinity coefficient β (—)
2-Chloropropane	78.5×10^{-3}	82.9×10^{-6}	8.558×10^2	2.177	0.93
Carbon tetrachloride	153.8×10^{-3}	94.5×10^{-6}	1.584×10^3	9.439×10^{-1}	1.05
Chlorobenzene	112.56×10^{-3}	108.2×10^{-6}	1.105×10^3	7.221×10^{-2}	1.18
			(22°C)	(22°C)	
2-Chloropropane	78.5×10^{-3}	82.9×10^{-6}	8.595×10^2	1.960	0.93
Water	18.02×10^{-3}	12.7×10^{-6}	9.96×10^2	1.945×10^{-2}	—



(a)



(b)

Fig. 1. Calculated and experimental breakthrough curves for the ternary mixture of carbon tetrachloride (T)+chlorobenzene (B) and 2-chloropropane (C) in a stream of dry air, on a bed of active carbon U03 at 298 K. (a) Relative concentrations of 0.040 (T), 0.005 (C) and 0.036 (B). (b) Relative concentrations of 0.014 (T), 0.008 (C) and 0.036 (B).

The relative inlet concentrations ($c_i/c_s = p/p_{sat}$) are 0.040 (T), 0.005 (C), 0.036 (B) in Fig. 1(a), and 0.014 (T), 0.008 (C), 0.036 (B) in Fig. 1(b).

These results show that in the range of relatively low inlet concentrations, as used here, the combination of the simulation model with the MPD theory leads to very good prediction for the breakthrough curves of the three vapours present in the stream.

Mixtures of water and 2-chloropropane, two immiscible adsorbates, have been used to test the model of independent co-adsorption described in Section 2. Fig. 2 shows the breakthrough curve of 2-chloropropane with

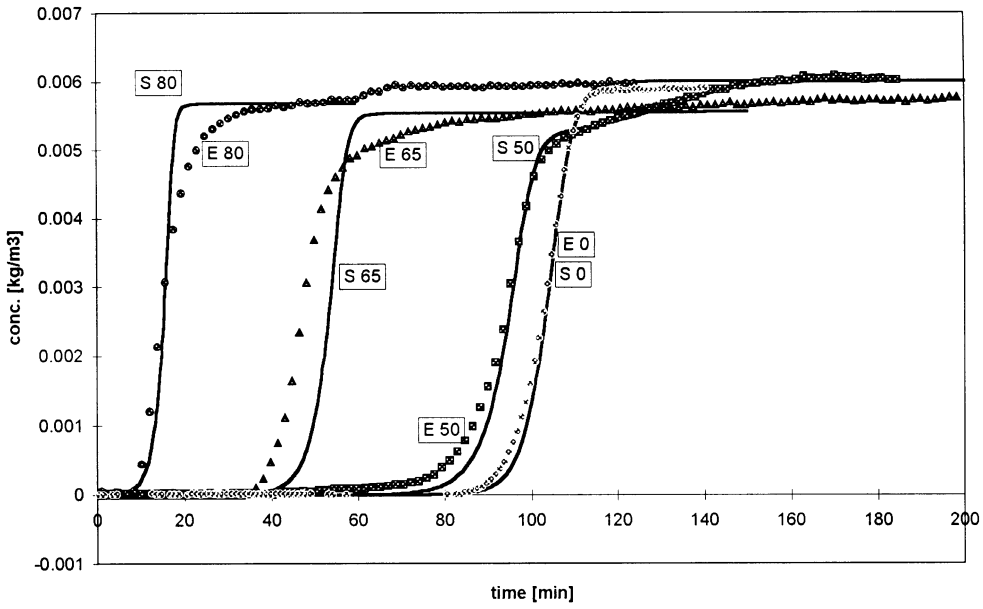


Fig. 2. Calculated and experimental breakthrough curves of 2-chloropropane at a relative inlet concentration $c_i/c_s = 0.003$, alone and in the presence of water vapour, on carbon bed U03 at 295 K. The degree of humidity of the air stream varies from 0 to 80%. The solid lines (S) correspond to the simulations, to be compared with the experimental points (E).

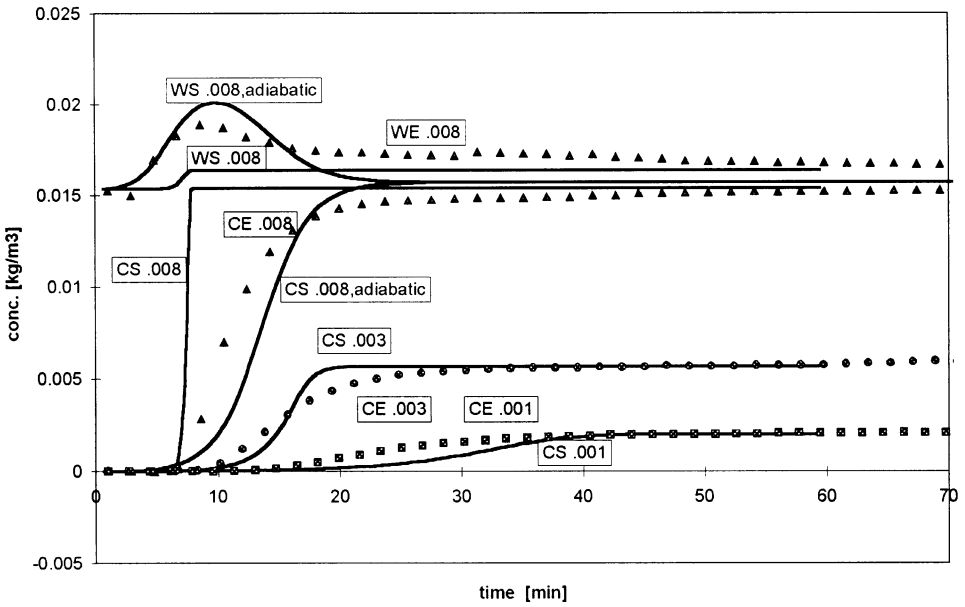


Fig. 3. Simulated (S) and experimental (E) breakthrough curves of water (WS, WE) and 2-chloropropane (CS, CE) at a constant humidity of 80%, in a stream of air, on carbon bed U03 at 295 K. The inlet concentrations of 2-chloropropane are 0.001, 0.003 and 0.008. For a relative inlet concentration of 0.008 2-chloropropane, the process is no longer isothermal (see text).

a relative inlet concentration of 0.003 and variable water contents, at 295 K. The breakthrough curves obtained from the computer simulations (S) are compared with the experimental results (E) at a relative humidity of 0, 50, 65 and 80%, the carbon bed having been preconditioned as described in Section 3.3.

There appears to be relatively good agreement between the predictions of the simulations based on the

Table 2
Experimental and simulated breakthrough times of 2-chloropropane, for different relative humidities and inlet concentrations

Relative humidity (%)	Relative concentration c_i/c_s	Breakthrough time (min) ($c_{out}/c_{in}=0.1$)		Difference (%)
		Exp.	Sim.	
0	0.0011	180.0	194.0	7
0	0.003	95.0	97.0	2
0	0.008	46.0	46.0	0
0	0.036	14.0	13.0	−7
50	0.0011	167.0	177.0	6
50	0.003	83.0	86.0	4
50	0.008	43.0	41.0	−5
50	0.036	14.0	12.0	−15
65	0.0011	57.0	94.0	49
65	0.003	41.0	46.0	11
65	0.005	25.0	31.0	21
65	0.036	5.5	6.5	17
80	0.0011	16.0	19.0	17
80	0.003	11.0	11.5	4
80	0.008	7.5	7.0	−7
80	0.036	3.0	2.0	(−40)

simple model of independent co-adsorption and the experimental results. This is also illustrated by Table 2, which gives the experimental and calculated breakthrough times of 2-chloropropane for an outlet concentration corresponding to 1/10 of the inlet concentration, at various degrees of relative humidity. The largest differences are observed for the smallest inlet concentrations where experimental errors are considerable, and for a relative humidity of 65%. From an experimental point of view, this is not too surprising, since this concentration corresponds to the steep rise in the S-shaped water isotherm. In this range, even small variations of the humidity (1–2%) lead to large changes in the adsorption equilibrium.

By symmetry with the case of Fig. 2, Fig. 3 shows the breakthrough curves of water and of 2-chloropropane, at 295 K, obtained with variable inlet concentrations ($c_i/c_s=0.001$, 0.003 and 0.008) and a constant humidity of 80%. One observes a good agreement between the calculated and experimental breakthrough times of the two vapours, but for the highest inlet concentration of 2-chloropropane (0.008), the simulated (CS.008) and the experimental (CE.008) curves show deviations. The same is true for water (WS.008 and WE.008). These deviations probably reflect the non-isothermal conditions in the active carbon bed, not accounted for in the computer simulation. Modifications considering adiabatic conditions were introduced into the model, by assuming heat capacities of 900, 1809, 4230 and 1003 $J\,K^{-1}\,kg^{-1}$ for carbon, 2-chloropropane, water and air, and a heat transfer coefficient of 10.9 $J\,K^{-1}\,m^{-2}\,s^{-1}$ for the walls of the column. It appears that the simulated breakthrough curves for water (WS.008 adiabatic) and 2-chloropropane (CS.008 adiabatic) are much closer to the experimental curves.

In conclusion, it appears that numeric simulation of adsorption processes is possible for both miscible and immiscible mixtures. The first case is based on the MPD approach, whereas for vapours of immiscible liquids (e.g. water and an organic compound), one must apply the model of independent co-adsorption. As shown so far, when combined with our simulation model, both models lead to good predictions for dynamic adsorption of mixtures by active carbon beds. However, more experimental evidence must be provided, and in the case of miscible components the effect of the activity coefficient in the adsorbed state needs further investigation [3].

In our opinion, at high inlet concentrations the limited micropore volume remains a major problem, as it may lead to displacement of one component outside the micropore, into the meso- and macropores, or even into the interparticle volume. Experimentally, the condensation of water has been observed on the walls of the glass tube containing an active carbon bed pre-treated with air containing 80% relative humidity and subsequently challenged with a high concentration of carbon tetrachloride. The latter strongly displaces the water and often there is not enough micropore volume available for complete co-adsorption. Consequently, a new phase may appear outside the carbon adsorbent, which is not accounted for by the model.

The two models presented in this paper correspond to extreme situations, and the more general case of partly miscible compounds remains to be examined. This approach, which is currently under investigation,

involves a combination of the two models and results will be published in due course.

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