Static Adsorption, by Activated Carbons, of Vapour Mixtures Corresponding to Immiscible Liquids

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ABSTRACT: It is shown that the static adsorption of benzene and water vapours by a typical industrial active carbon can be described by the model of independent co-adsorption proposed for compounds which are not miscible in the liquid state. The model assumes that the vapours are adsorbed according to their respective DA isotherms, each component using the micropore volume left unoccupied by the other. A good agreement is found between the calculated and the experimental adsorption, but in the case of water the model must take into account the decrease of the characteristic energy E(H₂O) with increasing co-adsorption of benzene. This behaviour is confirmed by earlier studies of water adsorption and of immersion calorimetry into water, following variable pre-adsorption of n-nonane.

INTRODUCTION

As shown recently (Lavanchy et al. 1996; Stoeckli et al. 1997), the adsorption of binary and ternary vapour mixtures by active carbon beds can be described successfully by combining the Dubinin equation with the theory of Myers and Prausnitz (1965). A major advantage of this new approach, called the Myers–Prausnitz–Dubinin (MPD) theory, lies in the simplicity of the parameters required to describe the adsorption of vapour mixtures over a wide range of pressures and temperatures. Moreover, the combination of MPD with a computer simulation model developed by Ladugie et al. (1992) extends the theory to the case of dynamic adsorption by active carbon beds (Lavanchy and Stoeckli 1997). This extension has been successful, and therefore an important step has been achieved in the field of industrial filtration.

However, in real systems, water is often present and it is well known that in the liquid state it is not miscible with typical organic and inorganic compounds. Static and dynamic experiments also show that water can be expelled from the micropore system of activated carbons, which indicates that the adsorbates are not miscible in the adsorbed state. This means that the MPD approach is no longer valid and a new model must be considered to describe the simultaneous adsorption of vapours corresponding to immiscible liquids (for example, benzene and water). The present study presents an approach based on the concept of independent co-adsorption and illustrates its possibilities under static conditions for mixtures of benzene and water vapours at 293 K.

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THEORETICAL

Physical adsorption of vapours by active carbons is well described by Dubinin’s theory for the volume filling of micropores (Dubinin 1989; Stoeckli 1993, 1995). Its fundamental expression is the Dubinin–Astakhov equation:

\[ N_a = N_{a_0} \exp[-(A/E)^n] \] (1)

where \( N_a \) represents the amount (in mmol/g of solid) adsorbed at relative pressure \( P/P_0 \) and temperature \( T \), and \( N_{a_0} \) is the limiting amount adsorbed in the micropores. The latter is related to the micropore volume \( W_n = N_{a_0} V_m \), where \( V_m \) is the volume of the liquid-like adsorbate. The quantity \( A = \text{RT} \ln(P_0/P) \), and \( E \) is the so-called characteristic energy of the system under investigation. It has been shown that \( E \) depends on the micropore system and on the adsorbate. The effect of the latter can be expressed by a specific coefficient \( \beta \), called the affinity coefficient, such that \( E = \beta E_{a_0} \). By convention, the reference vapour is benzene, for which \( \beta = 1 \), and consequently \( E(C_6H_6) = E_{a_0} \).

For nitrogen at 77 K, \( \beta = 0.33 \). For activated carbons of low and medium burn-off (up to 35–40%), the exponent \( n \) is equal to 2, which corresponds to the classical equation of Dubinin and Radushkevich.

It can be shown (Stoeckli 1995) that the DA equation leads to an exact relation for \( \Delta h \), the enthalpy of immersion of a microporous carbon into a liquid, whose vapour is adsorbed according to equation (1). One obtains:

\[ \Delta h (J/g) = -E N_{a_0} (1 + \alpha \Gamma) (1 + 1/n) + h S_e \] (2)

where \( \alpha \) is the expansion coefficient of the liquid, \( \Gamma \) is the tabulated ‘Gamma’ function and \( h_i (< 0) \) is the heat of wetting of the external surface area \( S_e \) of the carbon. The last term is only a fraction of \( \Delta h \).

Traditionally, the DA equation (1) has been used in connection with adsorption isotherms of type I or II and water, which corresponds to a type IV isotherm, has been fitted to other models (Dubinin and Serpinski 1981). However, as described more recently (Stoeckli et al. 1994a; Stoeckli 1995, 1997), water adsorption also follows Dubinin’s theory. The main difference is the low value of \( E(H_2O) \), typically between 1 and 3 kJ/mol, as opposed to values of 15 to 30 kJ/mol for benzene.

As the oxygen content of the surface increases, the characteristic energy \( E(H_2O) \) also increases and the inflexion point of the S-shaped isotherm is shifted toward lower values of the relative pressure \( P/P_0 \). Exponent \( n \), on the other hand, reflects the slope of the isotherm at the inflexion point.

In the case of water adsorption, the characteristic energy \( E \) depends essentially on the specific interactions between this molecule and the oxygen content of the surface. This means that there exists no definite affinity coefficient for water.

On the basis of immersion calorimetry, it has been shown recently (Lopez-Ramón et al. 1999) that the dispersive interactions between water and microporous carbons correspond on average to 0.8 kJ/mol of water, against 12.1 kJ/mol for the specific interaction with the oxygen atoms of the surface complexes. It is also found that the water isotherm may present a small initial section of the Langmuir type (Vartepetyan et al. 1982; Stoeckli et al. 1994b; Carrasco-Marín et al. 1997), for which \( E(H_2O) \) is ca. 7 kJ/mol and \( n = 2 \).

Since water also follows the DA equation (1), the MPD theory may be used in the case of vapour mixtures containing water and an organic compound miscible with it in the liquid state. This appears to be the case for the system water + acetone at 293 K, currently under investigation. On the other hand, for a system such as water + benzene, MPD is no longer valid and an alternative approach
must be found. A relatively simple, but plausible description is the model of independent co-adsorption (Stoeckli et al. 1998). It assumes, to a first approximation, that each component is adsorbed according to its specific DA equation (1), but that the corresponding micropore volume is the total volume of the carbon \( W_0 \) reduced by the volume occupied by the other component. For an organic vapour (1) and water (2), one obtains, respectively:

\[
W_1 = N_{11} V_{m1} = (W_0 - W_2) \exp(- (A_1/E_1) \theta_1)
\]

\[
W_2 = N_{22} V_{m2} = (W_0 - W_1) [(1 - \phi) \exp(- (A_2/E_2) \theta_2) + \phi \exp(- (A_2/E_2) \theta_2)]
\]

Indices 21 and 22 refer to the type I and V contributions to the overall isotherm and \( \phi \) is the fraction of water adsorbed as a type V isotherm.

**EXPERIMENTAL**

The co-adsorption of water and benzene vapours by carbon U-02 has been carried out at 293 K by the Headspace-Gas Chromatography technique described in detail earlier (Lavanchy et al. 1996). More than 150 experiments were performed on samples of ca. 0.6 g of carbon using variable amounts of water (0.001–0.300 ml) and benzene (0.015–0.450 ml). The liquids were not put in direct contact with the solid in the vials in order to avoid hysteresis effects. The adsorption equilibrium was established through the gas phase over a period of 24 h.

Pre-adsorption of \( n \)-nonane and \( n \)-undecane, followed either by immersion into water at 293 K or the determination of nitrogen adsorption isotherms at 77 K, was carried out as described in detail by Stoeckli et al. (1991, 1992).

The main characteristics of the carbons and the adsorbates are listed in Table 1.

<table>
<thead>
<tr>
<th>Adsorbative</th>
<th>C₆H₆ (293 K)</th>
<th>H₂O (293 K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Micro pore volume, ( W_0 ) (m³/kg)</td>
<td>U0-2 0.448 \times 10⁻³ 0.448 \times 10⁻³</td>
<td></td>
</tr>
<tr>
<td>Characteristic energy, ( E ) (kJ/mol)</td>
<td>U0-2 17.00 1.20</td>
<td></td>
</tr>
<tr>
<td>Characteristic energy, ( E ) (kJ/mol)</td>
<td>U0-3 16.95 1.12</td>
<td></td>
</tr>
<tr>
<td>External surface area, ( S_e ) (m²/g)</td>
<td>U0-2 105</td>
<td></td>
</tr>
<tr>
<td>External surface area, ( S_e ) (m²/g)</td>
<td>U0-3 60</td>
<td></td>
</tr>
<tr>
<td>Saturation pressure, ( P_s ) (Pa)</td>
<td>9985 2337</td>
<td></td>
</tr>
<tr>
<td>Thermal expansion coeff., ( \alpha ) (10⁻¹ K⁻¹)</td>
<td>1.132 0.2585</td>
<td></td>
</tr>
<tr>
<td>Molar volume of the liquid, ( V_m ) (m³/mol)</td>
<td>88.97 \times 10⁻⁶ 18.08 \times 10⁻⁶</td>
<td></td>
</tr>
</tbody>
</table>

**RESULTS AND DISCUSSION**

The analysis of the adsorption data for the system benzene + water on carbon U0-2 at 293 K leads to Figures 1 and 2 which depict the calculated and experimental relative pressures of the individual components for the various amounts adsorbed. One observes a good agreement for benzene, but in
Figure 1. Comparison of the calculated and experimental equilibrium relative pressures, $P/P_s$, for benzene adsorbed by carbon U0-2 at 293 K in the presence of variable amounts of water.

Figure 2. Comparison of the calculated and experimental equilibrium relative pressures, $P/P_s$, for water adsorbed by carbon U0-2 at 293 K, in the presence of variable amounts of benzene. It is assumed that $E(H_2O)$ is constant.
the case of water the data show a smooth deviation from the straight line corresponding to an ideal correlation. Since the two components do not mix in the micropores, the discrepancy observed for water cannot be explained in terms of an activity coefficient and another explanation must be found.

It may be assumed that the description of the water isotherm in the presence of another component (benzene) may be oversimplified. Consequently, the individual water isotherms were re-calculated from the mixed adsorption data and compared with the initial isotherm in the absence of benzene. As shown in Figure 3, the water isotherms corresponding to successive amounts of co-adsorbed benzene are not affine with the original isotherm. It appears that they are moved to higher relative pressures and become flat, which indicates a decrease in the characteristic energy \( E(H_2O) \) and in exponent \( n \) of the DA equation (1). The values are given in Table 2.

**TABLE 2.** Characteristic Energies, \( E(H_2O) \), and Exponents, \( n \), for Water Adsorption at 293 K on Carbons U0-2 (Co-adsorption of Benzene) and U0-3 (Pre-adsorption of n-Undecane)

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Carbons studied</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>U0-2</td>
</tr>
<tr>
<td>( \theta(C_6H_6) ) or ( \theta(C_{10}H_{20}) )</td>
<td>0.00 0.14 0.25 0.40 0.74 0.00 0.20 0.35 0.48 0.71 0.90</td>
</tr>
<tr>
<td>( E(H_2O) ) (kJ/mol)</td>
<td>1.20 1.47 0.85 0.88 0.44 1.12 1.00 0.87 0.75 0.35 0.45</td>
</tr>
<tr>
<td>( n )</td>
<td>3.8 2.2 1.6 1.7 1.2 4.0 2.9 1.9 1.8 0.9 0.5</td>
</tr>
</tbody>
</table>

**Figure 3.** Isotherms of water adsorbed at 293 K by carbon U0-2 in the presence of various amounts of benzene. The fraction of the total micropore volume filled by benzene \( \theta(C_6H_6) = 0.00 \) (▲), \( \theta(C_{10}H_{20}) = 0.25 \) (■), \( \theta(C_{10}H_{20}) = 0.74 \) (●).
These results were compared with a new examination of data obtained some years ago for the static adsorption of water at 293 K on carbon U0-3, following the pre-adsorption of variable amounts of n-nonane and n-undecane. The enthalpies of immersion into water, as a function of the degree of prefilling, have also been determined at 293 K. As seen in Figure 4, the water isotherms follow a pattern similar to that observed for carbon U0-2 (Figure 3). The corresponding values of $E(H_2O)$ and of $n$ are also given in Table 2. There is less dispersion in the case of water on carbon U0-3 due to the fact that these isotherms were determined directly. The data for carbons U0-2 and U0-3 can be fitted, to a first and good approximation, to the simple linear relations

$$E(H_2O)_n = (1 - \theta)E'(H_2O)$$  \hspace{1cm} (5)$$

and

$$n(\theta) = (1 - \theta)n'$$  \hspace{1cm} (6)$$

where $E'(H_2O)$ and $n'$ correspond to the adsorption of water alone on these carbons.

The variation of exponent $n$ and of $E(H_2O)$ with the degree of pre-adsorption $\theta$ of the organic component, for example $\theta(C_{11}H_{22})$ on carbon U0-3, is confirmed by the agreement obtained between enthalpy of immersion into water $\Delta h(H_2O)$, calculated on the basis of variable parameters $E$ and $n$, and the experimental enthalpy (see Figure 5).

In the case of carbon U0-3, nitrogen isotherms were also measured at 77 K following the pre-adsorption of n-nonane (Stoeckli et al. 1992), and analysed with equation (1) in the DR form ($n = 2$). As shown in Table 3, $E_n$, decreased from 17.2 kJ/mol to 11 kJ/mol as $\theta$ increased from 0 to 0.77. This indicates that, under equilibrium conditions, n-nonane occupies preferentially the smaller micropores. Consequently, with increasing pre-adsorption (or co-adsorption), only the wider micropores become available to the second component.

Another reason for the decrease of $E(H_2O)$ in the case of pre-adsorption or co-adsorption is the
Figure 5. Enthalpy of immersion of carbon U0-3 into water at 293 K following the pre-adsorption of variable amounts of n-nonane \( C_{9}H_{18} (\Delta) \) and of n-undecane \( C_{11}H_{24} (\bullet) \). The curve corresponds to the calculated enthalpy, assuming variable energies \( E(H_{2}O) \) (see Table 2).

### TABLE 3. Characteristic Energy, \( E_{v} \), Calculated from the \( N_{2} \) (77 K) Isotherms on Carbon U0-3 Following Variable Degrees of Pre-adsorption, \( \theta \), of n-Nonane

<table>
<thead>
<tr>
<th>( \theta(C_{9}H_{18}) )</th>
<th>0.00</th>
<th>0.09</th>
<th>0.18</th>
<th>0.37</th>
<th>0.63</th>
<th>0.77</th>
</tr>
</thead>
<tbody>
<tr>
<td>( E_{v} ) (kJ/mol)</td>
<td>17.2</td>
<td>16.9</td>
<td>16.4</td>
<td>15.3</td>
<td>13.1</td>
<td>11.0</td>
</tr>
</tbody>
</table>

location of the oxygen complexes within the solid and, at this stage, it is difficult to assess its importance. (This question is currently under investigation and will be reported in due course.)

As illustrated by Figure 6, taking the variation of parameters \( E(H_{2}O) \) and \( n \) into account leads to a much better correlation between the calculated and experimental data for the independent co-adsorption of water by carbon U0-2 in the presence of benzene. The variation of parameter \( E \) and of exponent \( n \) improves the model corresponding to equations (3) and (4). It may therefore be suggested that, to a first and probably good approximation, a linear decrease of \( E \) and \( n \) with the degree of micropore filling occurs, as suggested by equations (5) and (6). However, as shown by equation (2), parameter \( n \) has only a small influence on the adsorption energies.

The adsorption of water and benzene mixtures by active carbon U0-3, at 298.2 K and under dynamic conditions, has recently been examined by Lavanchy and Stoeckli (1999) on the basis of equations (3) and (4) and a computer simulation model (Ladugie \textit{et al.} 1992). The calculated breakthrough times are in good agreement with the experimental values, in spite of the fact that \( E(H_{2}O) \) and \( n \) were not modified. A possible explanation is the fact that under dynamic conditions, as opposed to static conditions, benzene occupies the micropore system more randomly, which means that \( E(H_{2}O) \) is closer to the value for the adsorption of pure water.
In conclusion, the present study shows that it is now possible to predict the adsorption of vapour mixtures corresponding to miscible and immiscible liquids, the first corresponding to the MPD approach and the second to the model of independent co-adsorption, with the improvement regarding the variation of the characteristic energy E(H,O) and of exponent n. The intermediate case, combining both theories, corresponds to the adsorption of water in the presence of two organic compounds, immiscible with water in the liquid state. This will be investigated and the results will be presented in due course.

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REFERENCES


