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Prediction of Adsorption of Organic Component and Water Vapour Mixture onto Activated Carbon

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A simple isotherm equation is derived for the adsorption of an organic component onto activated carbon in presence of water vapour. The theoretical results are compared with experimental data for toluene-water vapour-activated carbon, which were published by *Ripperger* and *Germerdonk* [10].

(Keywords: Adsorption isotherm; Multicomponent adsorption)

Vorhersage der Adsorption einer organischen Komponente und Wasserdampf an Aktivkohle

Es wird eine einfache Adsorptionsisotherme abgeleitet, welche die gleichzeitige Adsorption eines organischen Stoffes und Wasser an Aktivkohle beschreibt. Die theoretischen Ergebnisse werden mit experimentellen Resultaten von *Ripperger* und *Germerdonk* [10] für Toluol-Wasser-Aktivkohle verglichen.

Symbols

a_i	adsorbate concentration in adsorbent, kg/kg of carbon
a_{0i}	monolayer capacity, kg/kg of carbon
b_i	kinetic parameter of the *Langmuir* equation
E_j	adsorption energy in the j-th layer
i	i-th component ($1-$water vapour, $2-$organic compound)
j	j-th layer
m	number of layers
n	number of adsorbed components
p	partial pressure, Pa
p^*	saturation partial pressure, Pa
p_C	water vapour partial pressure at begining of capillary condensation, Pa
θ	surface coverage

Introduction

Activated carbons are widely used for solvent vapours recovery from exhaust gases. The adsorption of dry single or multicomponent organic vapours on a dry activated carbon has been the subject of many papers. A number of methods have been proposed for prediction of an adsorption equilibrium of mixtures from the isotherms of individual components [1–3].

The purified gases contain usually water vapour besides organic solvents. It changes the adsorption capacity of activated carbons especially at low solvent concentrations in a gas phase [4–12]. Adsorption isotherms of water vapour onto carbon adsorbents have a different shape compared to organic components. *Dubinin* and co-workers [13–14] have presented a number of water vapour isotherms on various types of activated carbons. All isotherms have belonged to types III or V of the *Brunauer* classification, while organic compound isotherms belong to types I or II. For this reason earlier proposed methods of prediction of mixture adsorption are not suitable for the systems containing water vapour. *Manes* [15] has presented to our knowledge, the only method of estimation the effect of humidity on the adsorption of organic vapours onto activated carbons. The method, which is based on the *Polanyi* theory, assumes two-phase filling of adsorbent pores. Thus the *Manes* model is restricted only to water immiscible solvents.

We are presenting a new simple method to estimate the organic component adsorption from a moist gas onto activated carbon.

Theory

Let us assume that water vapour forms a multilayer adsorbed phase. Following *Langmuir* assumptions, adsorption equilibrium in the first layer is given by:

$$b_1 p(1 - \theta_1) = \theta_1 \tag{1}$$

in the second layer:

$$b_2 p(\theta_1 - \theta_2) = \theta_2 \tag{2}$$

and in *m*-th layer:

$$b_m p(\theta_{m-1} - \theta_m) = \theta_m \tag{3}$$

Experimental studies of water vapour adsorption onto activated carbon have revealed that the differential heat of adsorption is almost independent of the amount of adsorbed water vapour [14]. Therefore we make additional assumption that:

$$E_1 = E_2 = \ldots = E_m \tag{4}$$

From condition (4) the following equalities arise:

$$b_1 = b_2 = \ldots = b_m = b \tag{5}$$

When the condition (5) is submitted into Eqs. (1)–(3) we obtain:

$$\theta_1 = \frac{bp}{1 + bp} \tag{6}$$

$$\theta_2 = \left(\frac{bp}{1 + bp}\right)^2 \tag{7}$$

$$\theta_m = \left(\frac{bp}{1 + bp}\right)^m \tag{8}$$

The total adsorption of water vapour is given by:

$$\theta = \sum_{j=1}^{m} \theta_j = \sum_{j=1}^{m} \left(\frac{bp}{1 + bp}\right)^j \tag{9}$$

If the number of layers is increasing to infinity, Eq. (9) is reduced to:

$$\theta = bp \tag{10}$$

which describes a linear relationship between the water vapour concentrations in the adsorbent and in the gas phase. Activated carbons practically used are characterized by a highly developed porous structure, where besides "pure" adsorption of water vapour a capillary condensation occurs especially at higher relative humidities. According to the *Kelvin* equation there is a straight relationship between the beginning of the capillary condensation and the size of the adsorbent pores. The amount of condensed water can be calculated from the modified *Dubinin-Radushkevich* aquation:

$$a_c = a_M \exp\left[-B \ln^2\left(\frac{p - p_c}{p^* - p_c}\right)\right] \tag{11}$$

Parameters a_M, B, and p_c are associated with the porous structure of the adsorbent and can be evaluated from the experimental water vapour isotherm.

The total water amount in activated carbon is equal to the sum of the adsorbed and condensed water:

$$a_T = a + a_c \tag{12}$$

The second term of the last equation is equal to zero below the capillary condensation point and becomes significant with growing relative partial pressures of water vapour. Now we consider a simultaneous adsorption of water vapour and organic compound in a low humidity range (beyond the capillary condensation point). The following assumptions are made in our model:

- homogeneous surface of activated carbon
- ideally localized adsorption
- monolayer adsorption of organic compound on the bare surface
- multilayer adsorption of water vapour everywhere except the part of the surface covered by organic compound.

On the base of the above assumptions, a kinetic equation of water vapour adsorption in presence of organic compound will take the form:

$$b_1 p_1 (1 - \theta_2) = \theta_1 \tag{13}$$

The kinetic equation of solvent adsorption is as follows:

$$b_2 p_2 (1 - \theta_1 - \theta_2) = \theta_2 \tag{14}$$

Simple transformation of Eqs. (13) and (14) lead to:

$$\theta_1 = \frac{b_1 p_1}{1 + b_2 p_2 (1 - b_1 p_1)} \tag{15}$$

$$\theta_2 = \frac{b_2 p_2 (1 - b_1 p_1)}{1 + b_2 p_2 (1 - b_1 p_1)} \tag{16}$$

Equations (15) and (16) can be extended for the adsorption of organic solvent mixtures in presence of water vapour.

The appropriate equations are:

$$\theta_1 = \frac{b_1 p_1}{1 + \sum_{i=2}^{n} b_i p_i (1 - b_1 p_1)} \tag{17}$$

$$\theta_i = \frac{b_i p_i (1 - b_1 p_1)}{1 + \sum_{i=2}^{n} b_i p_i (1 - b_1 p_1)} \tag{18}$$

$$i = 2, 3, \ldots, n$$

At high relative partial pressures of water vapour we should take into account the capillary condensation. Since the organic component is preferentially adsorbed by activated carbon, the amount of condensed water will be significantly reduced. Similar to the 4-th assumption we assume that capillary condensation will occur everywhere except on the part of the surface covered by organic adsorbate. Comparing with Eq. (12) the total water amount on activated carbon can be calculated from:

$$a_{1T} = a_1 + (1 - \theta_2) a_{1c} \tag{19}$$

When Eq. (15) and (16) are substituted into the last equation we obtain:

$$a_{1T} = \frac{a_{01}\, b_1 p_1 + a_{1M} \exp\left[- B\left(\ln \frac{p_1{}^* - p_c}{p_1 - p_c} \right)^2 \right]}{1 + b_2 p_2 (1 - b_1 p_1)} \tag{20}$$

Equation (20) is a straightforward extension of the Eq. (15) in which the term of capillary condensation is added in a numerator. Although it contains six coefficients, they may be estimated from the individual organic compounds or water vapour isotherms.

Results and Discussion

The most published adsorption data for the system water vapour—organic compound—activated carbon are usually restricted to few points of the equilibrium curves [4–9, 12, 16]. Hence they are inadequate to verify our model. An exception to the mentioned papers is the work of *Ripperger* and *Germerdonk* [10], who have extensively studied the adsorption of toluene and water vapour on active carbon in a range of concentrations important for practical purposes. The individual toluene isotherm is shown in Fig. 1 together with the *Langmuir* equation. Although the experimental points are not very well approximated by the *Langmuir* model, it is acceptable in this range of toluene concentration. The experimental water vapour isotherms shown in Fig. 2 belong to type V of the *Brunauer* classification and can be approximated by a straight line only at a relative humidity below 0.55.

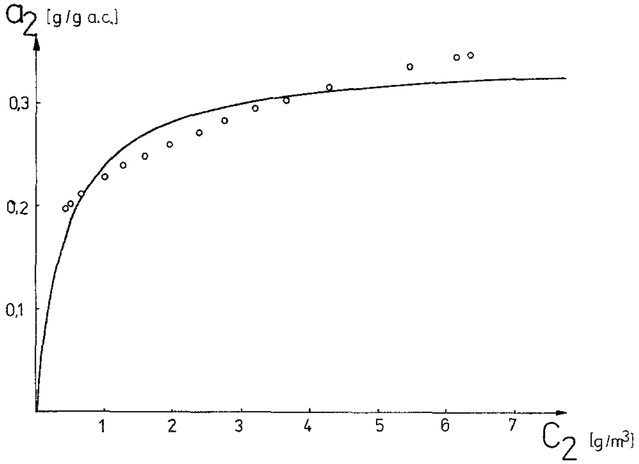

Fig. 1. Adsorption isotherm of toluene at 303K; ——— *Langmuir* equation

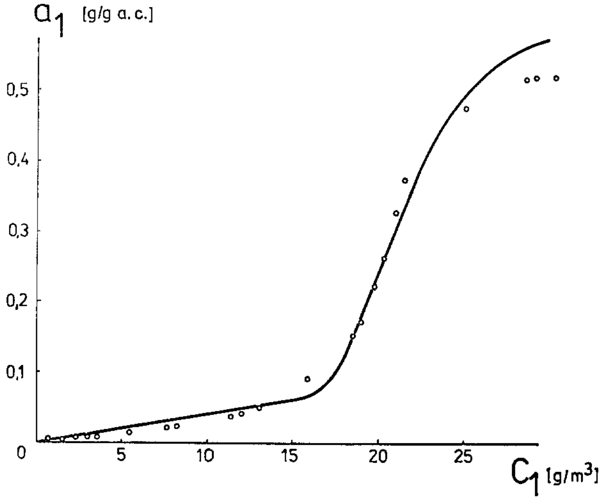

Fig. 2. Adsorption isotherm of water vapour at 303K; ——— theoretical curve

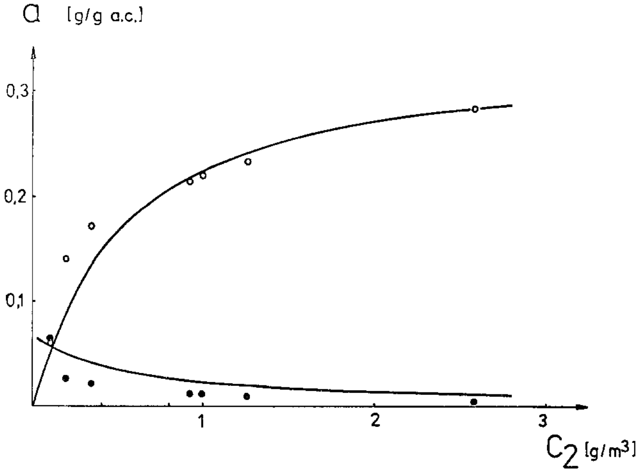

Fig. 3. Binary adsorption of toluene (○) and water vapour (●) at 303K and constant water vapour concentration $c_1 = 16.67 g/m^3$; ——— theoretical curves

In order to use our model we ought to determine coefficients a_{0i} and b_i. Both coefficients a_{02} and b_2 are known for toluene from the *Langmuir* equation. For water vapour we have assumed that a_{01} is equal to the toluene monolayer capacity expressed in a volume unit of the liquid adsorbate. After calculation of a_{01} we determine b_1 from the slope of the

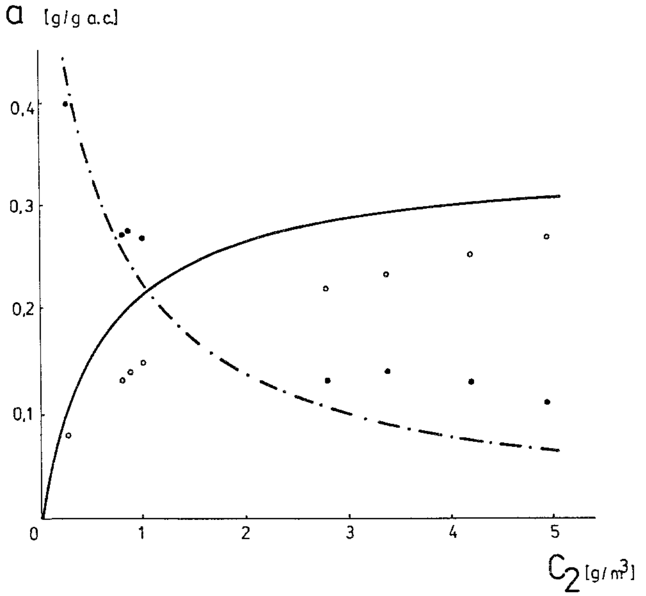

Fig. 4. Binary adsorption of toluene (○) and water vapour (●) at 303 K and constant water vapour concentration $c_1 = 27.29 \mathrm{g/cm^3}$; ═══ theoretical curves

water vapour linear isotherm. The parameters of Eq. (11) which were taken from the paper of *Ripperger* and *Germerdonk* [10] are as follow: $B = 0.8$, $a_{1M} = 0.5$, $p_c = 0.5 p_1^*$. The calculated water vapour isotherm shown in Fig. 2 approximates well the experimental points both at low as well as at high humidities. The mixture adsorption was studied in [10] at a constant relative pressure of water vapour. Figure 3 presents the experimental and theoretical results of the mixture adsorption at 0.55 relative humidity. The predicted toluene adsorption calculated from Eq. (16) agrees well with the experimental points. The theoretic water vapour adsorption curve is above the experimental data, but the differences are not significant. The results of the mixture adsorption at 0.9 relative water vapour pressure, that is in a region of capillary condensation, is shown in Fig. 4. The theoretic toluene adsorption calculated from Eq. (16) is considerably higher than the experimental points. However, the theoretic water vapour curve is below the measured adsorption points. The observed differences can be explain by a specific interaction of water vapour with carbon ash. The activated carbon used by *Ripperger* and *Germerdonk* [10] contains 5% of ash. Contrary to the hydrophobic nature of activated carbon, the ash should adsorb water molecules better. On the other hand, the toluene adsorption from the mixture on activated carbon is reduced in presence of ash. Nevertheless, despite the observed differences between the theoretical and experimental results, the proposed model enables a simple calculation of organic component and water vapour adsorption on activated carbons in the whole range of relative humidities.

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