

ADSORPTION EQUILIBRIA OF ETHANOL VAPOURS ON ACTIVE CARBON

A. ZUKAL and O. KADLEC

*Institute of Physical Chemistry,
Czechoslovak Academy of Sciences, Prague 2*

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Experimental results obtained during a study of adsorption equilibria of ethanol vapours on active carbon in the region of temperatures from -30°C to 80°C proved deviations from the validity of basic relations of the theory of volume filling of micropores. The deviations were explained by different degree of association of ethanol in the adsorbed and liquid phases. Based on this idea, an equation was proposed describing the adsorption isotherms of ethanol vapours on active carbon in a wide range of equilibrium pressures and temperatures.

During studies of adsorption equilibria of gases and vapours on different types of active carbon, the theory of the volume filling of micropores¹ has proved very valuable. This theory is a modern improvement of the potential theory of adsorption equilibria on microporous adsorbents. In the case of adsorbates with molecules associating in the liquid phase exceptions concerning the validity of the theory of the volume filling of micropores were found. Water may be considered as an example of adsorbate exhibiting intermolecular associations by way of hydrogen bonds. From the S-shaped form of the adsorption isotherm of water vapours on active carbon it is obvious that the mutual interaction of adsorbed molecules of water, which constitutes the grounds for their association, is stronger than their interaction with the adsorbent². The system methanol-active carbon exhibits a similar behaviour; S-shaped adsorption isotherms were found also here³.

Adsorption isotherms in the studied system ethanol-active carbon are of the usual Langmuir type. As ethanol molecules are associated in the liquid state by hydrogen bonds, it is necessary to assume that this association occurs also in the adsorbed phase and that it affects the adsorption equilibria. The degree of association of adsorbed molecules is determined first of all by their concentration in the adsorbent force field; this concentration is of course changing during the adsorption process. It is therefore apparent that when applying the theory on the adsorption equilibria of ethanol it is necessary to consider the dependence of the mutual interaction of adsorbed ethanol molecules on the parameters of the adsorption equilibria.

EXPERIMENTAL

A Desorex active carbon is manufactured from carbonized wooden material by a steam activation and it is a heterogeneous mixture of differently activated particles. It was airsorted⁴ into several homogeneous fractions; for the study of the adsorption equilibria, the medium activated

fraction was used which was being extracted in a Soxhlet extractor by distilled water for 300 hours before the measurements.

The temperature dependence of the adsorption equilibria was measured in a volume apparatus with a microburette⁵. The studied sample of active carbon was firstly evacuated for 20 hours at a temperature of 400°C until a vacuum of 10^{-6} Torr was reached. Known amounts of ethanol vapours were subsequently added to the evacuated sample; after each addition, the dependence of the equilibrium pressure of the adsorbate vapours on the adsorbent temperature was measured. Taking into account that the dead space volume in the apparatus (*i.e.* the volume of the vessel with the sample, manometers and connecting pipes) was very small, almost all ethanol was present in the adsorbed phase and the obtained dependences approached adsorption isosters. The dead space volume was determined by a calibration by helium and deviations from isosteric conditions were considered in all calculations. The measurements were performed in the pressure range 0.005–50.0 Torr and temperature range from –30 to 80°C. Adsorption equilibria at higher temperatures were not studied, as above 150°C the adsorbed ethanol decomposed slowly yielding most probably ethylene and water. For this reason a special attention was paid to checking on the adsorbate contamination during the process. With the same sample of active carbon and by the same method, the temperature dependence of adsorption of the benzene vapours serving as a standard adsorbate⁶ was measured. In view of the fact that the thermal decomposition of adsorbed benzene did not occur, the measurements were performed in the temperature range from 60 to 350°C.

RESULTS AND DISCUSSION

All adsorption measurements were performed in the region of low relative pressures at which only adsorbent micropores are volume-filled by the adsorbate and at which the capillary condensation in mesopores does not proceed yet. In Fig. 1, the dependences are given of the ethanol equilibrium vapour pressures as measured at a constant amount of added ethanol. These dependences cannot be distinguished in the figure from the adsorption isosters as the amount adsorbed changes only negligibly in all dependences. Each dependence was measured during both increasing and decreasing temperature. Points obtained in both directions of the temperature changes lie always on the same line, which confirms that the data are really equilibrium ones. In Fig. 2, adsorption isotherms of ethanol vapours are given as obtained by interpolating the experimental dependences for entire values of the temperature. These adsorption isotherms served as starting data for further processing. Adsorption isotherms of benzene vapours were obtained in the same manner, *i.e.* by interpolating the experimental temperature dependences of the equilibrium pressure.

The theory of the volume filling of micropores is based on two postulates whose validity has been proved by relatively abundant experimental data. The postulates make it possible to calculate from the knowledge of one adsorption isotherm not only adsorption isotherms at different temperatures but also adsorption isotherms of a whole series of other substances. The first postulate is the assumption of independence of the characteristic curve $A = f(W)$ on the temperature

$$(\partial A / \partial T)_W = 0, \quad (I)$$

where $A = RT \ln (f_s/f)$ is the differential molar work of adsorption and $W = aV$ is the volume

of the adsorbed phase. The symbol f stands for the fugacity of the equilibrium gaseous phase over the adsorbent, f_s for the fugacity of the saturated adsorbate vapours at a temperature T , a for the adsorbed amount in mol/g (adsorbent) and V^* for the molar volume of the substance in the adsorbed phase. According to the second postulate, the characteristic curves of different substances adsorbed by the same adsorbent are not mutually independent because the ratio of the differential molar works A of the given adsorbate and A_0 of a standard adsorbate is constant at the given degree of filling W of the adsorption space, *i.e.*

$$(A/A_0)_W = \beta = \text{constant} . \quad (2)$$

Constant β , the so called affinity coefficient, depends neither on the volume of the adsorbed phase nor on the temperature. The value of the affinity coefficient may be determined with the help of the characteristic curves of both substances; Dubinin and coworkers have proven that in the case of adsorption on active carbon, the relation holds⁶

$$\beta = V/V_0 , \quad (3)$$

where V and V_0 are the molar volumes of the given and standard liquid substances.

For calculations of volume W of adsorbed ethanol and benzene it is necessary to know the molar volume of these substances in the adsorbed phase. The molar volume of an adsorbed substance at temperatures lower than its normal boiling point may be approximated by its molar volume in the liquid phase, at higher temperatures it is inevitable to use the values determined by a special procedure⁷. As the adsorption equilibria of ethanol were measured only below 80°C, it was possible to determine the volume of adsorbed ethanol immediately; for the calculations of the volume of

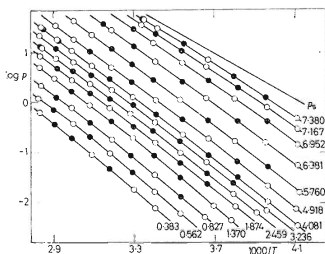


FIG. 1

Adsorption Isosters of Ethanol Vapours (p , Torr; T , °K)

Each isoster is labelled by the adsorbed amount in mmol/g. ● Temperature increasing, ○ temperature decreasing.

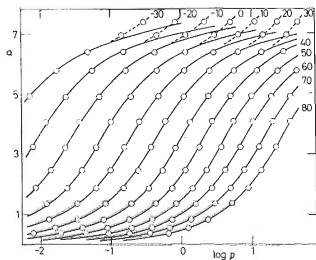


FIG. 2

Adsorption Isotherms of Ethanol Vapours (p , Torr; a , mmol(g))

Each isotherm is labelled by the temperature in °C. — Calculated according to Eq. (9), - - - experimental isotherms.

adsorbed benzene, the values of the molar volume V^* from a previous work⁸ were used. At temperatures higher than the normal boiling point of the adsorbate it is necessary to consider the real state behaviour of saturated adsorbate vapours in the calculations of the differential molar work of adsorption A , *i.e.* it is not possible to replace the fugacity by pressure. As the adsorption equilibria of benzene were measured up to temperatures considerably above the boiling point of this substance, the fugacity of the saturated benzene vapours was determined with the aid of the generalized fugacity diagram. The characteristic curves of ethanol and benzene are given in Fig. 3 in coordinates $\log W$ vs A^2 of the linearized Dubinin equation for adsorbents of the first structural type¹:

$$\Theta = a/a_0 = W/W_0 = \exp - (A/\beta E_0)^2. \quad (4)$$

The symbols W_0 and a_0 denote the limiting adsorption volume and the limiting adsorbed amount and E_0 is the characteristic energy which is related to the dimensions of micropores. From Fig. 3 it is obvious that Postulate (I) of the temperature independence of the characteristic curve is not fulfilled in the case of ethanol, whereas it holds well in the case of benzene. The values of constants W_0 and E_0 are $0.406 \text{ cm}^3/\text{g}$ and 5.49 kcal/mol as determined from the characteristic curve of benzene. It is not possible to describe the shape of the characteristic curves of ethanol by Eq. (4),

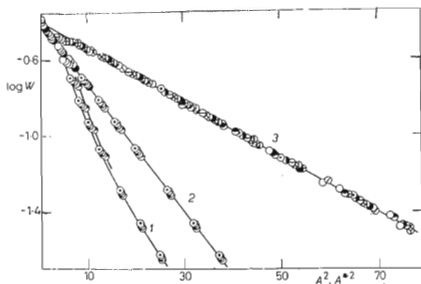


FIG. 3

Characteristic Curves of Ethanol 1, 2 and Benzene 3 (W , cm^3/g ; A , kcal/mol)

Points obtained at different temperatures differ by shape. The dependence 1 is the ethanol characteristic curve in coordinates $\log W$ vs A^2 ; at low values of A it joins the curve 2. The dependence 2 is the ethanol characteristic curve in coordinates $\log W$ vs A^2 ; the straight line passing through the single points of this dependence has been calculated according to Eqs (3) and (4).

not even on the assumption that the constants of this equation are temperature-dependent.

A theoretical characteristic curve of ethanol may be determined with the help of Eqs (3) and (4) and from the known characteristic curve of benzene. This characteristic curve cannot naturally coincide with the experimental characteristic curves of ethanol. The difference between the shapes of the theoretical and experimental characteristic curves of ethanol may be explained by a lower degree of association of ethanol in the adsorbed phase in comparison with that in the liquid phase. Therefore the value of the fugacity f_s of the saturated ethanol vapours which was used in the calculation of the differential molar work of adsorption A does not characterize correctly the standard state of ethanol.

Instead of using the fugacity f_s in the formula for the differential molar work of adsorption A , the effect of association of the adsorbed ethanol molecules on the adsorption equilibria may be expressed by employing such a fugacity f_s^* of the saturated vapours which would be exhibited by ethanol if it were associated in the liquid phase to the same degree as in the adsorbed phase⁹. Because the degree of association of an adsorbed substance depends on the degree of adsorption, the fugacity f_s^* must depend both on the temperature and on the adsorbed amount. If we denote $A^* = RT \ln(f_s^*/f)$, then the ethanol characteristic curve constructed in the coordinates W vs A^* (or $\log W$ vs A^{*2}) should be temperature-independent and identical with the theoretical characteristic curve.

The theoretical characteristic curve of ethanol calculated according to Eq. (4) with constants $W_0 = 0.406 \text{ cm}^3/\text{g}$ and $E_0 = 5.49 \text{ kcal/mol}$ is given in Fig. 3. The affinity coefficient of ethanol was determined from formula (3); as its value according to this formula depends weakly on temperature, a value of $\beta = 0.657$ was used calculated for a temperature of 25°C , *i.e.* for the mean value from the temperature interval studied. By comparing the theoretical characteristic curve with the experimental ones we can now simply find an empirical relation between the differential molar work of adsorption A and the differential molar work A^* . The difference between the two works may be expressed in the whole studied range of the degree of adsorption by the first three terms of the expansion in powers of $(1 - \Theta)$, *i.e.*

$$A^* - A = k_1(1 - \Theta) + k_2(1 - \Theta)^2 + k_3(1 - \Theta)^3. \quad (5)$$

The values of the constants at 20°C are as follows: $k_1 = -1.63 \text{ kcal/mol}$, $k_2 = 6.10 \text{ kcal/mol}$, $k_3 = -3.30 \text{ kcal/mol}$. These constants depend linearly on the temperature and their temperature coefficients are: $dk_1/dT = 0.0237 \text{ kcal/mol deg}$, $dk_2/dT = -0.0512 \text{ kcal/mol deg}$, $dk_3/dT = 0.0275 \text{ kcal/mol deg}$. A relation between the fugacities f_s and f_s^* follows directly from formula (5). If we put:

$$f_s^* = \nu f_s, \quad (6)$$

$$\text{then: } \nu = \exp \{ [k_1(1 - \Theta) + k_2(1 - \Theta)^2 + k_3(1 - \Theta)^3] / RT \}. \quad (7)$$

The characteristic curve of ethanol as calculated from the experimental data with the fugacities f_s^* given by formula (6)–(7) is given in Fig. 3; it coincides with the theoretical characteristic curve and is independent of temperature.

At the degree of filling of the adsorption space $\Theta < 0.8$, the coefficient ν decreases rapidly with increasing the adsorbed amount approaching unity at $\Theta > 0.8$. This dependence of the coefficient ν on the degree of adsorption agrees with the conception of the effect of association on adsorption equilibria. Considering that the ethanol molecules during the gradual filling of the micropores are first adsorbed relatively independently in most active places of the adsorption space, the degree of their association is low at the beginning, but it increases as the adsorption proceeds; to this corresponds the mentioned decrease of the coefficient ν in the region of $\Theta < 0.8$. This region then coincides with that of validity of Eq. (4). It is obvious from the shape of the benzene characteristic curve (Fig. 3) that when the volume W of the adsorbed phase approaches the limiting adsorption volume W_0 , Eq. (4) ceases to hold any longer. At a given value of Θ , the coefficient ν always decreases with increasing temperature indicating thus that the degree of association of ethanol decreases more rapidly in the liquid phase than in the adsorbed phase.

The fugacity $f_{s,0}^*$ calculated for $\Theta = 0$ depends simply on temperature. It may be easily verified that on using the Clausius–Clapeyron equation, Eq. (7) and an approximation $f_s = p_s$ we find

$$\ln f_{s,0}^* = \ln (\nu_0 p_s) = - (L - 1.17) / RT + C, \quad (8)$$

where p_s is the saturated vapour pressure of ethanol, L its heat of vaporization, C a constant of the Clausius–Clapeyron equation and ν_0 the value of the coefficient ν at $\Theta = 0$. It follows from the last equation and the Clausius–Clapeyron equation that the fugacity $f_{s,0}^*$ is considerably higher than the saturated vapour pressure of ethanol. If we assume an ideal behaviour of the ethanol vapours, then the difference $L - 1.17$ (kcal/mol) is the heat of vaporization of ethanol with the lowered degree of association. The magnitude of the coefficient ν_0 does not depend on temperature as the sum of the temperature coefficients of constants k_1 , k_2 and k_3 in Eq. (7) is equal to zero. The value, by which the heat of vaporization of ethanol L will be lower, does not depend on temperature from the same reason. By combining relations (4), (6) and (7) it is possible to find an equation of the adsorption isotherm of the ethanol vapours. If we express it in the form in which the variables f and Θ are separated, we obtain

$$h_f = \exp [-\beta E_0 \ln^{1/2} (1/\Theta) / RT] \cdot \exp \{ [k_1(1 - \Theta) + k_2(1 - \Theta)^2 + k_3(1 - \Theta)^3] / RT \}, \quad (9)$$

where $h_r = f/f_s$. The second term in the product on the right hand side of the equation expresses the effect of the mutual interaction of the adsorbed molecules. In the case of $k_1 = k_2 = k_3 = 0$, the equation goes over into the Dubinin equation. In Fig. 2, experimental adsorption isotherms of the ethanol vapours are compared with those calculated according to Eq. (9) with the above mentioned values of the constants. It is possible to say that Eq. (9) expresses satisfactorily the experimental adsorption isotherms. Deviations are observed at adsorbed amounts greater than those corresponding to the volume filling of micropores, *i.e.* in the region where capillary condensation of the adsorbate vapours in mesopores occurs. Results obtained during the study of adsorption equilibria of vapours of methanol and several other hydrogen-bonded substances indicate that the validity of the proposed equation for the adsorption isotherms is not limited to the adsorption equilibria of the ethanol vapours only.

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