ADSORPTION OF AMMONIA ON ACTIVATED CARBON

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Adsorption isotherms were measured for ammonia on untreated FB4 activated carbon, FB4 activated carbon impregnated with $ZnCl_2$, and on activated carbon from an anti-ammonia filter (Leipzig, F.R.G.). The potential theory was applied to the measurements. The Dubinin–Radushkevich plot in linearized coordinates for sorbents of the first structural type revealed that the Czechoslovak FB4 activated carbon possesses a bidisperse structure, giving two linear segments in the plot. The sample from the filter, which served as a reference material, exhibited a single straight line in the plot. The measurements were supplemented by the mercury porosimetry determination of the differential distribution curves. The three types of activated carbon were characterized by emission spectral analysis. The characteristic curve enables the equilibrium adsorption to be converted to different pressure and temperature conditions, and thus it is a suitable method for trapping ammonia in freezing stores to protect foods in casé of leak of coolant.

Activated carbons are suitable sorbents for trapping vapours. They are divided into two groups with respect to their adsorption behaviour to vapours at low relative pressures ($h < 0{\cdot}2$). In activated carbon of the first type, micropores with equivalent pore radii $r < 1$ nm predominate. In these pores, the effects of the opposite walls act concurrently, and thus the sorption force field intensity increases. At low pressures, adsorption occurs therefore first in narrow pores. In activated carbon of the second type, micropores with $r > 1$ nm predominate, and the effect of force increase is small if any. With respect to phenomena occurring in them during sorption, pores are classed[1] as micropores ($r < 0{\cdot}6-0{\cdot}7$ nm), supermicropores ($0{\cdot}6-0{\cdot}7$ nm $< r < 1{\cdot}5-1{\cdot}6$ nm), mesopores ($1{\cdot}5-1{\cdot}6$ nm $< r < 100-200$ nm) and macropores ($r > 100$ nm). Common activated carbons possess the so-called tridisperse structure, i.e. micropores, mesopores as well as macropores are present in them. In a particular activated carbon, the radii of the pores lie within rather narrow ranges[2].

The potential theory developed by Polanyi and Berenyi and later elaborated by Dubinin and his collaborators proved to suit well to the description of adsorption on finely porosive adsorbents, in which volume filling of micropores and mesopores takes place. It is based on the concept of the adsorbate concentrating on the adsorbent surface due to attractive forces which only reach a limited distance. The field of these forces is defined by the adsorption potential[3] ε, which is work of this force field spent on transferring one mole of adsorbate from the gaseous state to the adsorbed state. The largest possible space W_0 is bounded by the equipotential surface $\varepsilon = 0$ and the surface of the adsorbate, where $\varepsilon = \varepsilon_{max}$. The adsorption potential is a thermodynamic potential, corresponding to the entire possible work of the adsorption forces; we have

$$-\varepsilon = \Delta H - T\Delta S\,, \qquad (1)$$

where T is temperature and ΔH and ΔS are the enthalpy and entropy changes associated with the transfer of a mole of the adsorbing substance from the liquid bulk to the liquid in the pores. During the adsorption of da moles of the sorbing substance, the Gibbs function changes by $\mathrm{d}G = \varepsilon\,\mathrm{d}a$, where ε is the potential, defined as $\varepsilon = -RT\ln h$. Three general cases of adsorption can occur, viz. (i) T is higher than the critical adsorbate temperature T_k; (ii) T is just below T_k; and (iii) T is well below T_k ($T \leqq 0{\cdot}8T_k$). It is the last case that interests us because in our measurement with ammonia, $T/T_k = T_R = 0{\cdot}67$. In this case all the adsorbate is in the liquid state, and the adsorption volume obeys the equation[4]

$$W = a'V_m = a'M/\varrho\,, \qquad (2)$$

where a' is the adsorbed amount in moles per gramme of adsorbent, V_m is the molar volume of the liquid, M is the molecular mass and ϱ is the density of the adsorbate.

For a given adsorbent–adsorbate system, the characteristic curve of dependence of the adsorption potential ε on the adsorption space W is temperature independent. It can be set up based on the experimental isotherm, isobar or isostere. This postulate enables us, based on a single equilibrium isotherm to calculate the adsorption at other temperatures[5] $T \leqq 0{\cdot}8T_k$. The underlying principle is the validity of the relation $a_1/\varrho_1 = a_2/\varrho_2$ at $\varepsilon_1 = \varepsilon_2$. Knowing the amount a_1 adsorbed at temperature T_1 and relative presure h_1, we calculate the relative pressure h_2 at temperature T_2 based on the relation $\varepsilon_1 = \varepsilon_2$, where $\varepsilon_i = -RT_i \ln h_i$; hence, $T_1 \ln h_1 = T_2 \ln h_2$. Based on the theorem of corresponding states, density can be replaced by the expansion factor, which is calculated as[6]

$$\omega_i = 0{\cdot}1745 - 0{\cdot}0838T_{Ri}\,, \qquad (3)$$

where $T_{Ri} = T_i/T_k$. So, the relation $a_1/\omega_1 = a_2/\omega_2$ can be employed for the calculation of the adsorbed amount.

Dubinin and Radushkevich[7] found that on carbon sorbents, silica gels and zeolites, the characteristic curves obey the relation

$$W = W_0 \exp(-K_1 \varepsilon^2) \tag{4}$$

where W is the adsorption space (volume), W_0 is the limiting adsorption space in which the adsorption potential decreases to zero, and K_1 is a constant. The authors refer to substances obeying equation (*4*) as sorbents of the first structural type.

A smaller group of substances was found to obey the equation

$$W = W_0' \exp(-K_2 \varepsilon)\,. \tag{5}$$

This group was referred to as adsorbents of the second structural type (the meaning of symbols in equations (*4*) and (*5*) is analogous).

Expressing the adsorption space as the volume in a gramme of adsorbent (cm^3/g) and the adsorbed amount in grammes per gramme of adsorbent, we have $W = a/\varrho$, $W_0 = a_0/\varrho$, where ϱ is the density of the liquid adsorbate (g/cm^3). By inserting in Eq. (*4*) we obtain the Dubinin–Radushkevich equation in the linear form in the coordinates

$$\log a = C - D \log^2 (1/h) \tag{6}$$

where $C = \log a_0$, $D = 0{\cdot}43B(T/\beta)^2$. Analogously, Eq. (*5*) can be written in the form

$$a = a_0 \exp(AT \log h/\beta) = k_F P^{1/n'} \tag{7}$$

where A and n' are constants and k_F is the constant of the Freundlich isotherm with which this equation is identical.

Dubinin and Izotova found[8] that in the $\log a$ vs $(\log 1/h)^2$ coordinates, active carbon activated to a certain degree gives a linear plot over the region of $h = 10^{-5}$ to $5 \,.\, 10^{-4}$ only; at higher relative pressures, the points depart from the straight line in the direction of higher adsorbed quantities and form a straight line. This can be explained in terms of the existence of two groups of micropores with different size. The authors assume that manifestation of this dual structure is dependent on the inhomogeneity of the starting material during its reaction with activating agents.

The aim of the present work was to measure the adsorption isotherms of ammonia on Czechoslovak activated carbon and to attempt to increase the sorption ability of the latter by impregnation with $ZnCl_2$. The sorbent from a German anti-ammonia filter was used as a reference material (no filter protecting food in freezing stores in case of ammonia coolant leak is manufactured in Czechoslovakia). The adsorption isotherms were correlated by means of Eq. (*4*), which allows the adsorption values to be converted to those at other temperatures and pressures, and also other thermodynamic quantities to be calculated. This equation has also been applied with success to the determination of structure parameters of platinum hydrogenation catalysts and supports[9,10]. Equation (5) has been applied to the correlation of propylamine isotherms on alumina, obtained chromatographically[11].

EXPERIMENTAL

FB4 activated carbon (Slovenské lučobné závody, Hnúšťa), specific surface area at least 600 m^2/g. Sorbent from a filter for trapping ammonia (MLW Medizintechnik Leipzig, F.R.G.). Zinc chloride purum (Lachema, Brno). Synthetic ammonia (Synthesia, Pardubice) quality A (Czechoslovak Standard ČSN 651311), purity 99·85% (chromatographically determined), the rest was mainly water. Stored in a pressure cylinder, it was condensed in a glass freezer in a bath of solid CO_2 and alcohol. The required amount of ammonia was gasified in a vacuum apparatus, and water was removed simultaneously.

The samples were labelled as follows: 1 sorbent from anti-ammonia filter; 2 FB4 activated carbon; 3 FB4 activated carbon impregnated with $ZnCl_2$. The three samples were degassed and activated in a lubricant-free apparatus at 300°C and 0·013 Pa for 10 h. The samples were weighed with a precision of 0·1 mg. Changes in their weight were determined with a quartz coil balance. The coil elongation was measured with a precision of 0·01 mm, the mass change Δg (in grammes) obeying the relation $\Delta g = 0{\cdot}10795 \pm 0{\cdot}00005) \Delta l$, where Δl is the elongation in cm. The elongation was remeasured after degassing and 3 h after admitting ammonia, when the equilibrium was reached. The adsorbate pressure in the apparatus was then measured as well. The isotherms were measured at 0°C. The lubricant-free apparatus[12] was equipped with Teflon bellows-type valves[13].

Spectral analyses were performed on a Q 24 spectrograph using an ABR 3 generator; the current was 8 A, exposure 90 s. Porometric measurements were carried out on a Carlo Erba 2000 porometer having a pressure region of 0·1 to 200 MPa; pores from 3·7 to 7 500 nm could be determined with it. The measurements were accomplished at the Chemical Works Research Institute in Litvínov.

RESULTS AND DISCUSSION

The adsorption isotherms of ammonia measured at 273 K, when $T_R = 0{\cdot}67$, are shown in Fig. 1. The adsorption increased in order untreated FB4 carbon < impregnated FB4 carbon < sorbent from filter (sample No. 2 < sample No. 3 < sample No. 1). Figure 2 shows the adsorption isotherms in the linear coordinates of the Dubinin–Radushkevich equation (Eq. (6)). Although, as revealed by emission spectral analysis (Table I), the zinc contents of samples No. 1 and 3 are commensurable, Fig. 2 demonstrates that sample No. 1 is homogeneous (a single straight line), whereas sample No. 3 is bidisperse, exhibiting two linear segments. Sample No. 2 is bidisperse too. The limiting pore volumes of the BF4 carbons are at the same level (Fig. 2) irrespective of whether or not the sample was impregnated to improve its sorption ability[14]. This is also documented by Fig. 3, showing the dependence of the adsorption potential on the adsorbed amount of ammonia with respect to the expansion factor.

TABLE I

Results of emission spectral analysis of sample No. 1 (carbon from filter), No. 2 (untreated FB4 carbon) and No. 3 (impregnated FB4 carbon). The numbers are orders of concentration in per cent values

Element	Sample No.			Element	Sample No.		
	1	2	3		1	2	3
Fe	−1	0	0	Mn	−3	−2	−2
Si	−1	1	1	Al	−3	0 to 1	0 to 1
Cu	−1	−2	−1	Zn	1	0 to 1	1
B	—	−2	−2	Ca	—	0 to 1	0
Pb	—	—	−2	Ba	—	−1 to 0	0
Sn	—	−2	−2	Ni	—	−2 to −1	−1
Mo	—	−3	—	Ti	—	−2 to −1	−2 to −1
Cr	—	−1	−1	Mg	−3 to −2	−1	−1

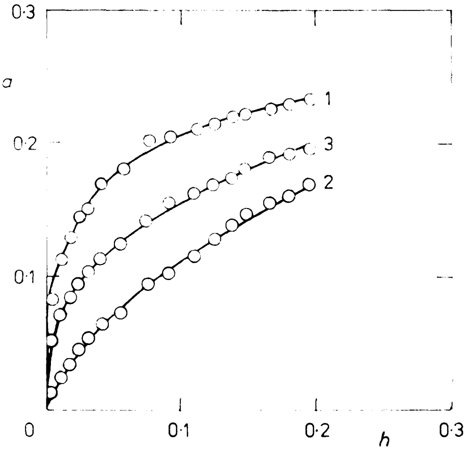


FIG. 1

Adsorption isotherms of ammonia at 273 K and relative pressure *h*. Adsorbent: 1 carbon from anti-ammonia filter; 2 FB4 activated carbon; 3 FB4 activated carbon impregnated with $ZnCl_2$. *a* is adsorbed amount of ammonia (g per g of adsorbent)

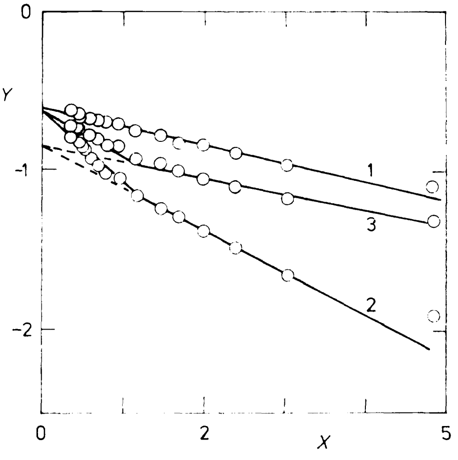


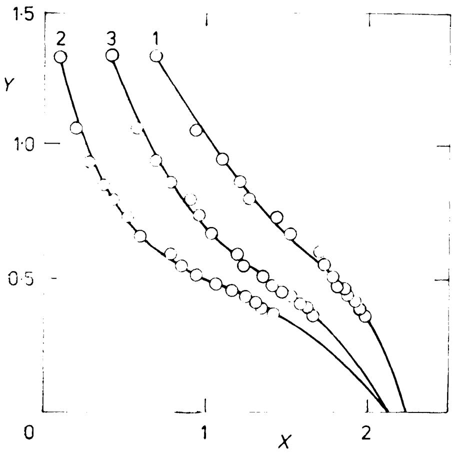
FIG. 2

Adsorption isotherms of ammonia in linearized coordinates of the Dubinin–Radushkevich equation for sorbents of the first structural type I ($Y = \log a$, $X = 1 \, . \, 10^{-5} (-T \log h)^2$). Adsorbent: 1 carbon from anti-ammonia filter; 2 untreated FB4 activated carbon; 3 FB4 activated carbon impregnated with $ZnCl_2$

TABLE II

Maxima on the differential distribution curves obtained by mercury porometry

Carbon from filter		Untreated FB4 carbon		Impregnated FB4 carbon	
Y	*r* nm	*Y*	*r* nm	*Y*	*r* nm
		Principal maxima			
0·667	6·31	0·558	100	0·936	63·1
0·638	79·5	0·459	398	0·932	79·5
		Side maxima			
0·435	50·2	0·410	50	0·466	25·1
0·388	158	0·459	398	0·396	158



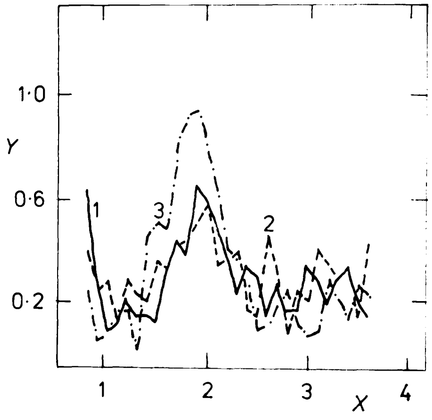


FIG. 3

Dependence of the adsorption potential on adsorbed amount, expressed with respect to the expansion factor ($X = a/\omega$, $Y = \varepsilon . 10^{-4}$). Adsorbent: 1 carbon from anti-ammonia filter; 2 untreated FB4 activated carbon; 3 FB4 activated carbon impregnated with $ZnCl_2$

FIG. 4

Differential distribution curves of pore distribution in dependence on the logarithm of pore radius obtained by mercury porosimetry ($X = \log r$ for r in nm, Y is the differential pore volume relative to the total pore volume). Adsorbent: 1 carbon from anti-ammonia filter; 2 untreated FB4 activated carbon; 3 FB4 activated carbon impregnated with $ZnCl_2$

Although the micropore volume is not affected by impregnation and is highest for sample No. 1 (Figs 2 and 3), Table II demonstrates that in comparison with the untreated FB4 carbon (No. 2), the impregnated FB4 carbon (No. 3) exhibits lower pore radii at the main and side maxima, due to the impregnation.

Thus, the adsorption is primarily determined by the volume of micropores and supermicropores. The pore radius in sample No. 1 is 6·3 nm, which is an order of magnitude less than in samples No. 2 and 3. The limiting adsorption, at which the adsorption potential is zero, is 0·242 g/g for samples No. 2 and 3 and 0·261 g/g for sample No. 1; the ratio of the limiting volumes is 0·927.

As compared to samples No. 2 and 3, sample No. 1 exhibits a higher number of pores with radii smaller than 10 nm. The side maxima lie within the regions of 50 – 158, 50 – 398 and 25 – 158 nm for samples No. 1, 2 and 3, respectively. Impregnation of FB4 carbon with $ZnCl_2$ results in the transformation of a fraction of macropores and of mesopores to lower-radius pores. This can be observed also for the main maxima. Sample No. 1 contains mesopores only, and thus is homogeneous from the distribution point of view, which is consistent with the linear plot in Fig. 2. This indicates that the sorption of ammonia is primarily controlled by the sorbent structure, i.e. by the pore distribution and the limiting pore volume (Figs 3 and 4).

It can be concluded that the potential theory of volume pore filling is applicable to the description of the activated carbon–ammonia system. In terms of the Dubinin–Radushkevich equation in the linearized coordinates (*6*), the homogeneity or bidispersity of the sorbent can be evaluated. Thermodynamic quantities such as isosteric heat[15], enthalpy, or entropy can also be calculated.

SYMBOLS

A	constant, K^{-1}
a	adsorbed amount in grammes per gramme of adsorbent, g/g
a'	adsorbed amount in moles per gramme of adsorbent, mol/g
a_0	adsorbed amount at relative pressure equal to unity, g/g
B	constant, K^{-2}
C, D	constants in Eq. (*6*)
G	Gibbs function, J
ΔH	enthalpy change, J/mol
h	relative pressure
k_F	constant of the Freundlich isotherm, $Pa^{-1/n}$
K_1	constant, $(mol/J)^2$
K_2	constant, mol/J
M	molar mass, g/mol
R	gas constant, J/(mol K)
ΔS	entropy change, J/(mol K)
T	temperature of isotherm, K
T_k	critical temperature, K
T_R	reduced temperature

T_i	chosen temperature of isotherm (i = 1, 2, ...), K
W_0, W_0'	limiting volume of adsorption space, cm^3/g
W	volume of adsorption space on a gramme of adsorbent, cm^3/g
β	affinity coefficient
ε	adsorption potential, J/mol
ϱ	adsorbate density, g/cm^3
ω	expansion factor, mol/m^3

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