Adsorption of Ethanol on Activated Carbon*

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Adsorption and desorption equilibria of ethanol were measured on two types of activated carbon: Supersorbon HS4 and Dezorex DB1 at temperatures −10 °C, 0 °C, 10 °C, and 20 °C. Experiments were performed within the range of relative pressures from 0 to 1. The analysis of equilibrium data confirmed adsorbed molecules interactions at lower temperatures and higher adsorbate concentrations. Relatively low values of adsorption heats suggest physical adsorption on homogeneous adsorption surfaces. From the modified Dubinin—Astakhov equation was found out the volume of micropores, in which the physical adsorption occurred; for activated carbon Supersorbon HS4 it was 350 cm^3 kg^{-1} and for Dezorex DB1 340 cm^3 kg^{-1}. At higher relative pressures, capillary condensation occurred. During adsorption and desorption of ethanol on activated carbon a not significant hysteresis was manifested. The starting point of this hysteresis, at which capillary condensation of ethanol started, was estimated: $A_{Gr} = 4.6$ kJ mol^{-1}, which corresponds to the values p/P_s from 0.12 to 0.15 at −10 °C to 20 °C for both activated carbons Supersorbon HS4 and Dezorex DB1.

Information on adsorption equilibria is of increasing interest because of its necessity for industrial processes. For the design of an appropriate adsorption equipment adsorption equilibrium data are fundamental. Numerous known equations can be used for characterizing various types of adsorption mechanisms. For the sake of reducing the experimental measurements the effort is aimed at predicting adsorption equilibria.

In paper [1] a new model is proposed for the a priori prediction of single-component adsorption equilibria of different gases and vapours on activated carbon. Emphasis is laid on the Henry region, where the interaction energy between adsorbate molecules and the adsorbent determines adsorption characteristics. Do and Do [2] presented a new adsorption isotherm for a heterogeneous adsorbent. The basis of this isotherm equation is that the degree of heterogeneity is reflected through the variation of the isosteric heat of adsorption with respect to loading. The results of adsorption and desorption of methane on two types of microporous carbon with different chemical surface nature are reported in citation [3]. In this work also calorimetric measurements are enclosed. Yao [4] compares his extended Langmuir model with the Langmuir, Langmuir—Freundlich, and Toth models in their ability to fit experimental data. The theory of volume filling of micropores is applied and treated in papers [5] and [6]. Berezin et al. [5] presented an equation for the internal pressure acting on adsorbate in micropores. This equation was obtained by the Dubinin—Radushkevich equation considering that the chemical potential of an adsorbate in micropores was equal to that in an equilibrium gas phase. The application of the adsorption integral equation to microporous adsorbents is discussed by Eiden and Schlünder [6]. A modified Dubinin—Astakhov equation which takes into account the end of micropore filling is proposed.

The purpose of this study was to investigate the adsorption mechanism using the equilibrium data of ethanol vapours on activated carbons with the following trade names: Supersorbon HS4 and Dezorex DB1.

THEORETICAL

For the description of adsorption equilibria, equations derived from adsorption isotherms under various presumptions can be used. Localized adsorption in a monolayer may be described by the Langmuir equation

$$\frac{a}{a_m} = \frac{Kp}{1 + Kp} \qquad (1)$$

This equation can be used also in a form, in which the

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independent variable p_r is the relative pressure defined as $p_r = p/P_s$.

The BET theory describes adsorption of vapours in several layers. For an adsorbate with an infinite number of layers a relationship in the following form was derived [7]

$$\frac{a}{a_m} = \frac{cp_r}{(1 - p_r)[1 + (c - 1)p_r]} \quad (2)$$

where a_m is related to the adsorbate concentration in a monomolecular layer.

The theory of volume filling of micropores (TVFM) derived from the potential theory does not accept the presumption that adsorbate is formed in layers. This theory uses the micropore volume as the basic geometrical parameter characterizing a porous adsorbent. According to this theory attractive forces between adsorbate and adsorbent decrease with increasing distance from the surface. Thus, the force field of the adsorbent surface exhibits a gradient of adsorption potential A. If a characteristic curve $A = f(V)$, which is independent of temperature, does exist, the mechanism of the TVFM can be accepted. One of equations derived from this theory is the Dubinin—Astakhov equation (DA) [8]

$$\frac{V}{V_0} = \frac{a}{a_0} = \exp\left[-\left(\frac{A}{E}\right)^n\right] \quad (3)$$

where V_0 is the maximal filled volume of adsorbate corresponding to the micropore volume, A is the adsorption potential, $A = RT\ln(P_s/p)$, E is the characteristic adsorption energy, and n is an integer from the interval 1—6, which characterizes the distribution of the pore width.

Eiden and *Schlünder* [6] modified the Dubinin—Astakhov equation taking into account the limiting potential A_{Gr}

$$\frac{V}{V_s} = \exp\left[-\left(\frac{A - A_{Gr}}{E_0}\right)^n\right] \quad (4)$$

This parameter A_{Gr} is independent of the sorbent but is a function of the adsorbed substance. The advantage of this modification is that for an adsorption potential A near to the limiting adsorption potential A_{Gr}, the filled volume V turns into the limiting micropore volume V_s.

Equations of adsorption isotherms enable to describe only the region of physical adsorption in micropores. Capillary condensation can be formally involved among models of the volume filling of micropores. However, a link to the potential theory does not exist. Condensation of an adsorptive in micropores takes places at relative pressures lower than 1 due to the curvature of the condensate levelling pores of small diameters. The relation between vapour pressure above curved surface and the radius of incurvation of the liquid meniscus in the pore is given by the

Kelvin equation. With the help of the Kelvin equation it is possible to calculate the limiting pore radii r_{Gr} corresponding to A_{Gr} [6]

$$r_{Gr} = \frac{2\sigma v}{A_{Gr}}\cos\Theta + d_{mol} \quad (5)$$

where $d_{mol} = [6M(1 - \Psi)/\pi N_A\rho]^{1/3}$. The Kelvin radius is corrected for the thickness of one preadsorbed layer, which is about one molecule in diameter. The contact angle Θ is assumed to be zero. Eqn (5) offers the possibility to calculate A_{Gr} independently without adsorption experiments.

EXPERIMENTAL

Activated carbon Supersorbon HS4 consisted of cylindrical particles with a diameter of 2—3 mm, a length of 5—6 mm, and a specific surface area of 917 m^2 g^{-1}.

Activated carbon Dezorex DB1 was in form of cylindrical particles with a diameter of 1.4—1.6 mm, a length of 1.9—3 mm, and a specific surface area of 727 m^2 g^{-1}.

The specific surface area of activated carbons was determined from the nitrogen isotherm, which was measured at the boiling point of liquid nitrogen and atmospheric pressure by means of the instrument Sorptomatic 1900 (Erba, Milano) and evaluated by means of the commercial software Milestone 200.

Ethyl alcohol had a purity of 99.99 mass %. Ethanol was obtained by a double rectification of 96 % technical ethanol, which was prior to rectification diluted by demineralized water to a volume ratio 1:1. Water was removed from the azeotropic mixture by burnt lime CaO, which was added in an amount, which was higher than the stoichiometric amount. After centrifuging the mixture ethanol was finally dried by molecular sieve 3A.

Equilibrium data of adsorption of ethanol vapours on activated carbon Supersorbon HS4 and Dezorex DB1 were measured in a glass gravimetric apparatus, which was described in more detail in paper [9]. The basic principle of the measurements involved weighing a sample of adsorbent in a closed space by means of the McBain balance either in vacuum at the activation temperature or in an atmosphere of pure adsorptive at a required temperature. The pressure of the adsorptive was also measured at the same time. By a step increase of pressure up to the pressure of saturated vapours of adsorptive adsorption data were obtained at the temperature of adsorption equilibrium. Then, by removing a part of the adsorptive from the surrounding of the McBain balance the adsorptive pressure changed stepwise. After reaching a stable state equilibrium adsorption data were measured.

The used weight of the activated carbon sample and the sensitivity of quartz springs enabled to determine the adsorbate concentration with a maximum

Table 1. Results of Equilibrium Measurements of Ethanol on Activated Carbons

p/Pa	$a_1/(g/100\ g)$	$a_2/(g/100\ g)$	p/Pa	$a_1/(g/100\ g)$	$a_2/(g/100\ g)$
	Adsorption at 20 °C			Desorption at 20 °C	
0	0	0	5861	33.857	43.014
1.3	0.019	0.154	1650	29.709	29.138
3.8	0.164	0.240	861	27.001	27.034
3.0	0.420	0.560	408	22.519	24.058
3.2	0.618	0.924	254	19.417	21.675
9.0	0.911	1.394	118	14.664	17.505
33	2.251	3.230	42	9.571	12.041
41	4.505	5.749			
94	7.569	10.005			
176	12.213	15.826			
285	16.346	20.087			
579	22.925	24.778			
1501	29.007	28.822			
3060	31.016	32.017			
4292	31.708	34.109			
5103	32.214	36.436			
5654	32.888	40.586			
5861	33.857	43.014			
	Adsorption at 10 °C			Desorption at 10 °C	
0	0	0	3135	39.344	49.803
3.7	0.147	0.172	3104	38.828	49.140
5.5	0.368	0.363	2653	33.926	41.236
12	0.744	0.952	1423	32.365	32.635
28	2.451	3.021	898	31.212	30.392
45	4.49	6.063	464	28.908	28.233
76	8.319	10.939	263	26.008	26.238
116	12.889	16.310	172	23.639	24.567
361	25.29	26.320	69	18.632	20.895
1047	30.885	30.88	56	14.628	17.499
1874	32.414	33.466			
2601	33.178	36.397			
3038	34.046	41.031			
3135	35.822	45.284			
3135	39.344	49.803			
	Adsorption at 0 °C			Desorption at 0 °C	
0	0	0	1568	34.396	41.284
3.7	0.221	0.320	973	32.661	35.307
5.4	0.657	0.893	436	31.093	30.929
9.3	2.552	3.941	281	29.855	29.476
12	6.467	9.324	200	28.669	28.520
32	11.745	16.021	98	24.596	25.917
101	20.402	24.374	46	20.774	23.050
252	28.665	28.643			
740	31.897	32.657			
1335	33.126	36.617			
1568	34.396	41.284			
	Adsorption at −10 °C			Desorption at −10 °C	
0	0	0	726	36.188	46.413
15	5.746	7.924	669	34.232	42.885
40	17.428	21.603	566	33.583	38.925
103	27.711	28.397	361	32.743	35.523
596	33.145	36.974	323	32.462	33.686
714	35.972	45.713	204	31.615	31.535
720	36.034	45.951	159	30.820	30.422
726	36.188	46.413	108	29.851	29.396
			71	28.221	27.990
			47	25.902	26.579

Index 1 represents Supersorbon HS4; index 2 represents Dezorex DB1.

error of $\pm 4 \times 10^{-3}$ g/100 g. The adsorptive pressure was measured within the range 0—1 Pa with a maximal error ± 0.02 Pa, within the range 1—10 Pa with a maximal error ± 0.25 Pa, and above 10 Pa with a maximal error ± 2 Pa. The maximal temperature change during measurements was $\pm 0.2\,°C$.

Experimental equilibrium data obtained by adsorption and desorption measurements of ethanol on activated carbon Supersorbon HS4 and Dezorex DB1 at $-10\,°C$, $0\,°C$, $10\,°C$, and $20\,°C$ are presented in Table 1.

Saturated vapours pressures of ethanol for working temperatures were calculated according to the Wagner equation

$$\ln(p/P_c) = (AF + BF^{1.5} + CF^{2.5} + DF^6)/T_r \quad (6)$$

where $F = 1 - T_r$ and $T_r = T/T_c$. Following values of parameters were used

$T_c = 513.920$ K $\quad A = -8.68587 \quad C = -4.8762$
$P_c = 6.132$ MPa $\quad B = 1.1783 \quad D = 1.5880$

This equation is valid in the temperature range of 159—513 K and the pressure range of 0—6132 kPa.

The densities of ethanol were computed according to the Martin equation

$$\rho = \sum \left[A_i \left(1 - T/T_c \right)^{i/3} \right] \quad i = 0—7 \quad (7)$$

where $T_c = 513.88$ K. Following values of parameters were used

$A_0 = 0.2760000 \quad A_1 = -0.2739686 \quad A_2 = 10.49591$
$A_3 = -49.98835 \quad A_4 = 123.0696 \quad A_5 = -162.4311$
$A_6 = 108.7218 \quad A_7 = -28.799903$

This equation is valid in the temperature range of 160—480 K with an error of 0.1 %.

The temperature dependences of calculated and used properties of ethanol are listed in Table 2.

Table 2. Used Values of Ethanol Properties

$t/°C$	-10	0	10	20
P_s/Pa	764	1592	3135	5861
$\rho/(\text{kg m}^{-3})$	815	806	798	789
$r/(\text{kJ mol}^{-1})$	46.4	45.7	44.9	44.1

RESULTS AND DISCUSSION

Experimental equilibrium data cover practically the whole interval of values of the relative pressure p_r ranging from 0 to 1 and exhibit a not significant

Table 3. Values of Adsorption Heats of Ethanol on Activated Carbons Supersorbon HS4 and Dezorex DB1 Calculated from Eqn (6)

$t/°C$	-10	0	10	20
		Supersorbon HS4		
$q/(\text{kJ mol}^{-1})$	52.4	52.1	51.7	51.3
		Dezorex DB1		
$q/(\text{kJ mol}^{-1})$	49.0	48.4	47.7	47.0

hysteresis. In an effort to judge the influence of adsorption surface heterogeneity and the interaction of adsorbed molecules by means of the Graham function [7] the values of parameters a_m and c of eqn (2) were calculated from equilibrium data (for which $p_r < 0.3$) by nonlinear regression.

For the system ethanol—Supersorbon HS4 and the investigated temperature interval the dependence a_m vs. temperature may be expressed by the relationship $a_m = 6.933 - 0.0167t$. The values of the parameter c can be determined from the relation $\ln c = 5.07537 - 612.87/T$. The values of the adsorption heat for the investigated temperatures were calculated from the following expression [7]

$$q = RT \ln c + r \quad (8)$$

and assembled in Table 3. The values of the adsorption heat differ only little from the heat of evaporation, which suggests the existence of physical adsorption of ethanol on activated carbon Supersorbon HS4. By employing the determined values of a_m and experimental measurements the values of the Graham function were calculated as follows

$$K = \frac{\theta}{(1 - \theta)p} \quad (9)$$

These values are plotted in Fig. 1. The course of the Graham function manifests that during adsorption of ethanol on activated carbon Supersorbon HS4 the adsorption surface heterogeneity can be neglected. However, at temperatures, which are lower than $10\,°C$ and at higher adsorption coverage, interactions of adsorbed molecules play a role.

For the system ethanol—Dezorex DB1 the values of the parameter a_m can be calculated from the relation $a_m = 6.500 - 0.0100t$ and the values of parameter c from the relationship $\ln c = 3.24701 + 27.762/T$. The calculated values of the adsorption heat of ethanol on Dezorex DB1, listed in Table 3, differ only little from the evaporation heat. This fact suggests the existence of physical adsorption. Graham function plotted in Fig. 2 suggests the interactions of adsorbed molecules, which are more manifested at lower temperatures and higher adsorption coverage. Adsorption surface heterogeneity was not manifested during adsorption of
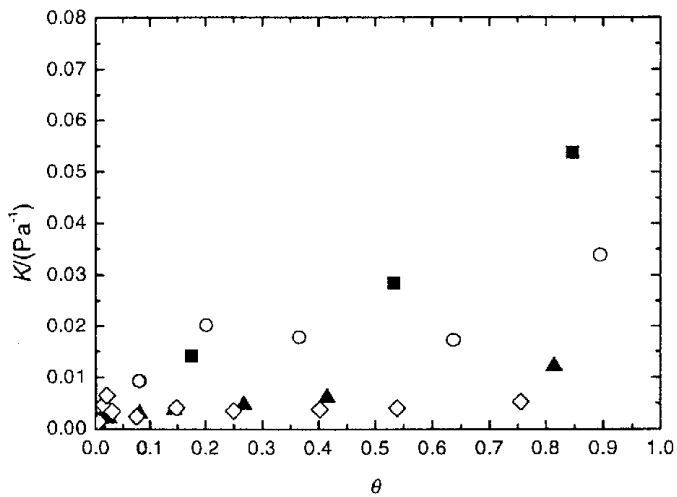
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Fig. 1. Dependence of the Graham function on surface coverage degree of activated carbon Supersorbon HS4. ■ At −10 °C; o at 0 °C; ▲ at 10 °C; ◊ at 20 °C.
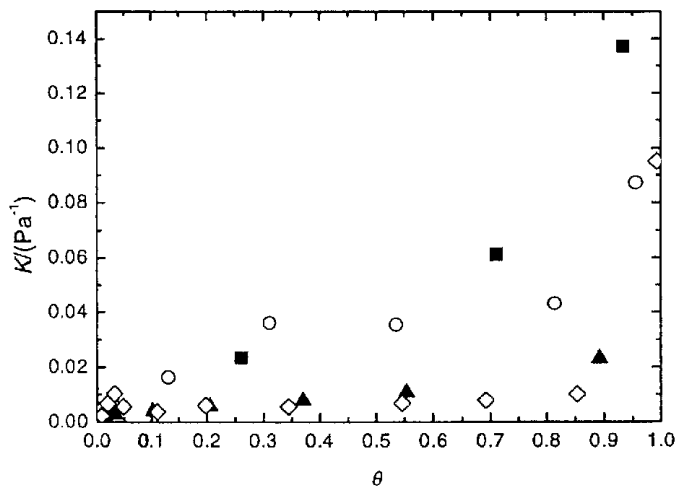

Fig. 2. Dependence of the Graham function on surface coverage degree of activated carbon Dezorex DB1. ■ At −10 °C; o at 0 °C; ▲ at 10 °C; ◊ at 20 °C.
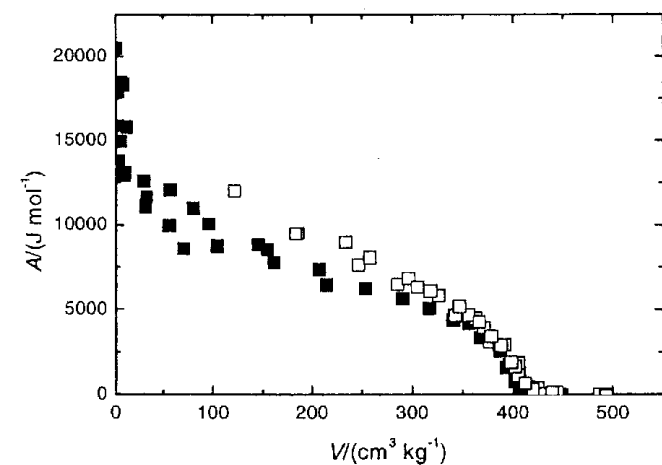

Fig. 3. The characteristic curves of ethanol on Supersorbon HS4. ■ Adsorption, □ desorption.
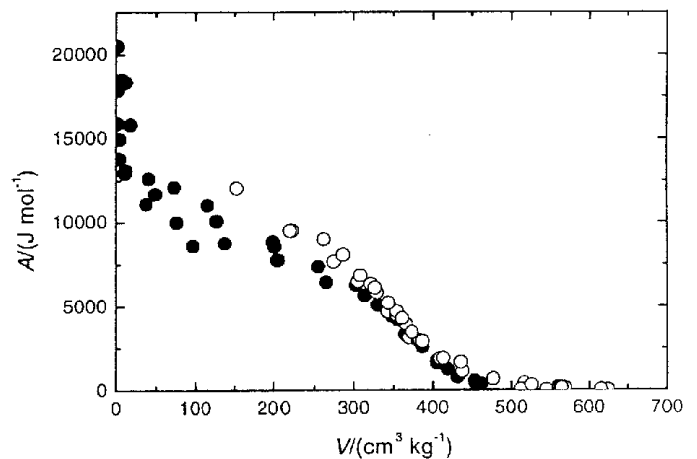

Fig. 4. The characteristic curves of ethanol on Dezorex DB1. ● Adsorption, o desorption.
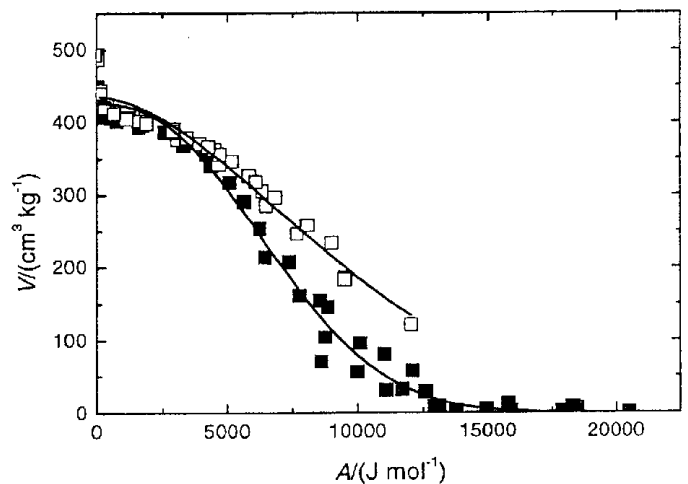

Fig. 5. Measured equilibrium points: ■ for adsorption, □ for desorption, and the course of correlation of ethanol adsorption and desorption on Supersorbon HS4 according to the Dubinin—Astakhov equation.

ethanol on activated carbon Dezorex DB1. The determined values of adsorption heats of ethanol on the used activated carbons agree with calculated values of isosteric heats, which were presented in paper [10].

In order to determine the adsorption mechanism for ethanol on activated carbon, the measured data were transformed into coordinates $A = f(V)$, whereby the whole set of data measured at all temperatures was depicted. The function given in Figs. 3 and 4 is the characteristic curve, the existence of which confirms the validity of Polanyi's potential theory.

For the correlation of measured data the DA equation was applied. In order to obtain more precise results the integer n was substituted by a real number. The calculated values of parameters are given in Table 4 and Figs. 5 and 6.

The values of the parameter V_0 represent the volume of micropores of the given adsorbent. The difference in the values calculated for the micropore sat-

Table 4. Evaluated Parameters of the Dubinin—Astakhov Equation

	Supersorbon HS4		Dezorex DB1	
	Adsorption	Desorption	Adsorption	Desorption
$V_0/(cm^3\ kg^{-1})$	426 ± 6	435 ± 5	508 ± 11	526 ± 10
$E/(kJ\ mol^{-1})$	8 ± 0.1	11 ± 0.4	7.8 ± 0.3	10 ± 0.5
n	2.4 ± 0.1	1.8 ± 0.1	1.6 ± 0.1	1.2

Table 5. Evaluated Parameters of the Modified Dubinin—Astakhov Equation

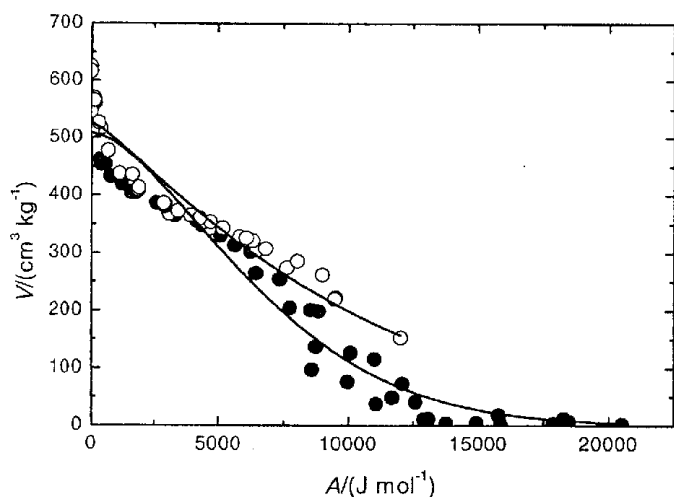|	Supersorbon HS4		Dezorex DB1	
	Adsorption	Desorption	Adsorption	Desorption
$V_s/(cm^3\ kg^{-1})$	350	350	340	340
$A_{Gr}\ /(kJ\ mol^{-1})$	4.6	4.6	4.6	4.6
$E_0/(kJ\ mol^{-1})$	3.9 ± 0.1	7.1 ± 0.03	4.9 ± 0.1	8.4 ± 0.3
n	1.28 ± 0.09	1.4 ± 0.1	1.7 ± 0.1	1.7 ± 0.1

Fig. 6. Measured equilibrium points: ● for adsorption, ○ for desorption, and the course of correlation of ethanol adsorption and desorption on Dezorex DB1 according to the Dubinin—Astakhov equation.

uration value V_0 is about 2 % for adsorption and desorption on Supersorbon HS4. If the value $n = 2$ was used, the value of the micropore saturation volume was the same for adsorption and desorption, i.e. $V_0 = 433$ cm^3 kg^{-1}. For Dezorex DB1 the difference in the calculated values of the micropore saturation volume for adsorption and desorption was higher. However, for Dezorex DB1 we cannot even use the same value of n for adsorption and desorption, because the correlation would not correspond to the measured points. From these results one could conclude that Dezorex DB1 contains more micropores than Supersorbon HS4. However, Figs. 5 and 6 reveal that the application of the DA equation for the whole region of measured data is not convenient, because capillary condensation occurs. Moreover, obviously volume V_0

might include a part of the adsorbate volume from capillary condensation. At low values of the adsorption potential $(A \to 0)$ the calculated curve does not correspond to the measured points.

Parameter E represents the characteristic adsorption energy, which physically corresponds to attractive forces between adsorbent and adsorbate. The characteristic energy for desorption is higher than for adsorption. The reason is a different mechanism of filling and emptying of pores, i.e. adsorption hysteresis. The difference in the values of this parameter is minimal for both adsorbents.

The value of n was calculated as a real number. For Supersorbon HS4 it could be rounded off to the value 2 for adsorption and desorption. However, on Dezorex DB1 the value of n for adsorption and desorption cannot be the same. In order to be able to use the DA equation, a fixed value was used for desorption.

The course of characteristic curves shows the possibility of acceptance of the volume-filling-of-micropores mechanism. The shape of the calculated curve, which correlates with the measured data, is sufficient, but it is insufficient for the value of adsorption potential close to 0, when all the pores might be completely filled. It is clear that the TVFM cannot be used for the filling of wider pores, in which capillary condensation occurs.

Trying to find the beginning of the capillary condensation, the corresponding values V and A at the beginning of the hysteresis loop were taken from characteristic curves. These were inserted into the modified DA equation as V_s and A_{Gr}. Then the values of characteristic energy were calculated. The results obtained are together with errors of fitted parameters given in Table 5.

With regard to the results given in Table 5 it is suitable to consider parameter n as constant for the
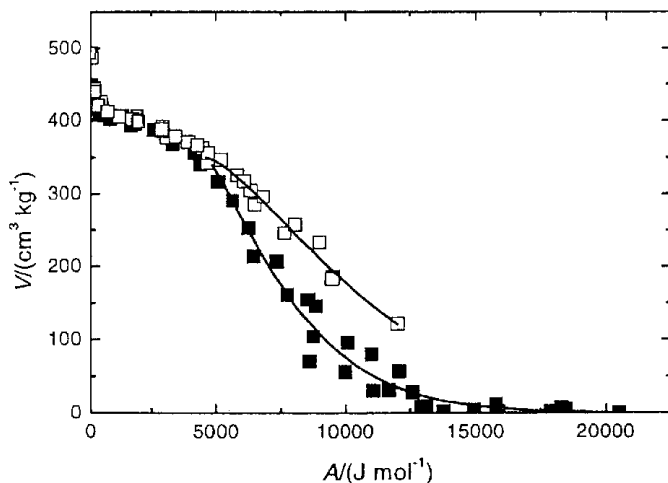
Fig. 7. Measured equilibrium points: ■ for adsorption, □ for desorption, and the course of correlation of ethanol adsorption and desorption on Supersorbon HS4 according to the modified Dubinin—Astakhov equation.
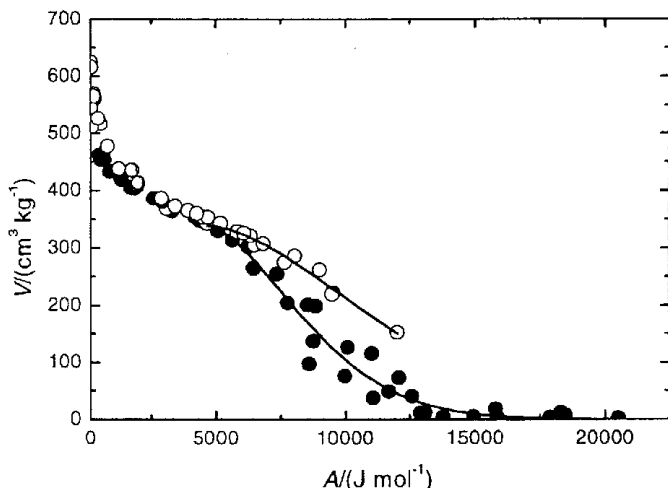

Fig. 8. Measured equilibrium points: ● for adsorption, ○ for desorption, and the course of correlation of ethanol adsorption and desorption on Dezorex DB1 according to the modified Dubinin—Astakhov equation.

given adsorption system, i.e. $n = 1.3$ and 1.7 for Supersorbon HS4 and Dezorex DB1, respectively. The values of parameters V_s and E_0 are lower by using the modified DA equation. As Figs. 7 and 8 reveal, the modified DA equation correlates only data corresponding to physical adsorption. Therefore, the values of the micropore saturation volumes are closer to reality than the values calculated by the aid of the classical DA equation. Thus, the volume of micropores is for both types of activated carbon similar.

We can conclude that capillary condensation starts under conditions given in Table 5, which correspond to values of p/P_s from 0.12 to 0.15 (at $-10\,°C$ to $20\,°C$). In this region about 80 % of adsorption capacity is filled.

For the sake of comparison the limiting pore radius

was calculated as $r_{Gr} = 1.1$ nm using eqn (5). The result is acceptable because the pore diameter 2.2 corresponds to the accepted boundary for the micropore region. For d_{mol} the value of 5.1 nm was inserted. This value was calculated according to the method given by Eiden and Schlünder [6].

SYMBOLS

a	adsorbate concentration	mol kg^{-1}
a_m	maximal adsorbate concentration in monolayer	mol kg^{-1}
a_0	limiting adsorbate concentration	mol kg^{-1}
A	adsorption potential	J mol^{-1}
A_{Gr}	limiting adsorption potential	J mol^{-1}
A, B, C, D	coefficients in eqn (6)	
c	parameter of the BET equation	
d_{mol}	molecule diameter	m
E, E_0	characteristic energy of adsorption	J mol^{-1}
K	parameter of eqn (1), Graham function	Pa^{-1}
M	molar mass	kg mol^{-1}
n	parameters of DA and modified DA equations	
N_A	the Avogadro constant	mol^{-1}
p	equilibrium pressure	Pa
p_r	relative pressure	
P_c	critical pressure	Pa
P_s	vapour pressure of adsorptive	Pa
q	adsorption heat	J mol^{-1}
r	heat of condensation	J mol^{-1}
r_{Gr}	limiting pore radius	m
R	gas constant	J mol^{-1} K^{-1}
t	temperature	°C
T	temperature	K
T_c	critical temperature	K
T_r	reduced temperature	
v	molar volume	cm^3 mol^{-1}
V	adsorbed volume	cm^3 kg^{-1}
V_0	micropore saturation volume from the DA equation	cm^3 kg^{-1}
V_s	micropore saturation volume from the modified DA equation	cm^3 kg^{-1}

Greek Letters

$\theta = a/a_m$	relative adsorbate concentration	
Θ	contact angle in capillary	rad
π	the Ludolph number	
ρ	density	
σ	surface tension	N m^{-1}
Ψ	parameter representing hexagonal packing of spheres ($\Psi = 0.26$)	

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