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DIFFUSIONAL MASS TRANSFER OF ETHANOL VAPOURS IN PARTICLES OF ACTIVATED CARBONS

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Abstract. *A gravimetric sorption method was employed for the estimation of effective diffusion coefficients of ethanol vapours in particles of activated carbons Supersorbon HS-4, Dezorex FB-4, Silcarbon SIL-15 Extra. The course of the stepwise adsorption of ethanol from a stream of air and the course of the stepwise desorption of ethanol by a stream of air with a lower content of ethanol compared with adsorption, or by a stream of pure air were examined. From experimentally measured data the effective diffusion coefficient* D_e *was calculated for each adsorption and desorption step. The calculated values of* D_e *are ranging from* 4.06×10^{-11} m^2s^{-1} *to* 1.42×10^{-9} m^2s^{-1} *and the dependences of* D_e *on adsorbate concentration were found for all activated carbons. The transport of ethanol vapours in pores of activated carbons proceeds via a combination of Knudsen diffusion and surface diffusion.*

Key words*: diffusion, mass transfer, ethanol, activated carbon*

Introduction

The diffusional mass transfer of substances in solid porous bodies is described in details in the monographs of Barrer [1], Jost [2], Aris [3], Cunnigham [4], and Kärger and Ruthven [5]. The solutions of the equation of unsteady diffusion for the basic forms of a porous material and chosen initial and boundary conditions are given in the work of Crank [6]. They can also obtained by the solution of unsteady heat transfer in a solid material [7]. A lot of attention is devoted to mass transfer in solid porous sorbents in the monographs of Timofeev [8], Ruthven [9], Keltsev [10], Kast [11], Suzuki [12], Satterfield [13] and other authors.

In the study of a cyclic pressure swing adsorption and desorption Sundram and Yang [14] described diffusion mass transfer in the solid phase. These authors suggested that the values of the effective diffusion coefficients do not vary with the adsorbate concentration and pressure over the given range of parameters. Al-Duri and Mc Kay [15] investigated parallel diffusion and adsorption of high molecular coloured organic substances in the particles of activated carbon in a batch system. The authors drew the following conclusion: The values of the effective diffusion coefficients depend on the adsorptive concentration in the batch exponentially. In studying the drying of solid particles Levy et al. [16] described the transport of vapours in the pores of a solid phase. Models for the diffusion in the pores of solid catalysts are presented in the papers of Haugaard and Livbjerg [17]. The dependence of the surface diffusion on the concentration of adsorbate and the porous structure of an adsorbent was reported by Do and Do [18]. Chen and Yang [19] investigated the diffusion in the adsorbed phase during the multilayered adsorption. Mass transfer in the absence of an inert in the pores of a certain size was described by Mac Elroy and Suh [20]. Cracknell et al. [21] studied the diffusion of methane in micropores of graphite having a slot form. Pore diffusion of substances within crystals of zeolites was investigated in the works [22] - [25]. In studying sorption Park and Do [26] used for the description of mass transfer unsteady diffusion within adsorbent particles with a bidisperse structure. The influence of the shape of adsorption isotherms on the diffusion in activated carbon particles was investigated by Linders et al. [27]. Simultaneous diffusion and adsorption of hydrocarbons in activated carbon particles was studied by Do and Do [28]. Sundaram and Yang [29] used multicomponent diffusion in solving the kinetics of pressure swing adsorption in separating oxygen and nitrogen from air by molecular sieve carbon. In the investigation of adsorption of NaJ on granulated activated carbon Drazer et al. [30] found a concentration dependence of the effective diffusion coefficient. According to authors [31] the effective diffusion coefficients of benzene and methyl ethyl ketone in the presence of nitrogen are within the range 1.2×10^{-8} to 1.1×10^{-10} m^2 s^{-1}. With increasing concentration of adsorptive the values of the effective diffusion coefficient increase. Diffusion of hydrogen sulphide and methyl mercaptane from air onto microporous alkaline activated carbon is reported by Chiang et al. [32]. In measurements spent activated carbon, regenerated activated carbon, fresh activated carbon, impregnated – regenerated activated carbon and impregnated-fresh activated carbon were used. The estimated values of the effective diffusion coefficients are ranging from 2.1×10^{-12} to 6.5×10^{-10} m^2 s^{-1}. Lordgooei et al. [33] modelled the effective diffusion coefficients of volatile organic compounds in activated carbon fibres. Chen et al. [34] investigated dyestuffs adsorption on pith. From film-pore diffusion modelling effective diffusivity ranging from 5.27×10^{-11} m^2s^{-1} to 8.6×10^{-10} m^2s^{-1} was found. The branched pore diffusion model was applied to the single component adsorption of reactive dyes on activated carbon in a batch stirred vessel [35]. The calculated surface diffusivity of dyes is ranging from 1.15×10^{-10} to 4.0×10^{-10} cm^2s^{-1} what is an about three orders lower value than the effective diffusivity published in [34]. In spite of numerous works dealing with the problem of solution of transport of component in solid phase pores this problem has not been solved yet. Obviously it is due to a complicated pore structure of the solid phase and the complexity of transport phenomena taking place in the adsorbent pores.

The purpose of this study was to investigate the effective diffusivity of ethanol vapours in different types of activated carbon particles and to judge the transport mechanism of ethanol vapours in the presence of air in the activated carbon particle pores.

Diffusion of adsorptive in porous body

For unsteady mass transfer in solid porous media the following equation can be derived from the balance of substance *A*:

$$\beta \frac{\partial c_A}{\partial \tau} - R_A = \nabla . D''\nabla c_A \tag{1}$$

where c_A is the adsorptive concentration, is the equivalent diffusion coefficient, R_A is the rate of production of component *A* in the balanced volume, β is adsorbent porosity, τ is time. The equivalent diffusion coefficient of the adsorbing component is defined by

$$D'' = D' + D_s \tilde{A} \tag{2}$$

where is the diffusion coefficient of the component in the porous medium, D_s is the coefficient of surface diffusion and Γ is the equilibrium constant given by

$$q_A = \tilde{A} c_A \tag{3}$$

where q_A is the adsorbate concentration.

For simultaneous diffusion and adsorption in a porous medium R_A represents a negative change of the adsorption rate with respect to the volume of the porous medium If the diffusion coefficient is equal in all directions, i. e. the porous material is isotropic in terms of mass transfer, Eq. (1) can be written as:

$$\beta \frac{\partial c_A}{\partial \tau} + \frac{\partial q_A}{\partial \tau} = D''\nabla^2 c_A \tag{4}$$

If one assumes the validity of a linear isotherm in the form of Eq. (3), and an infinitely rapid trapping of the adsorptive from the close vicinity on the adsorption surface, then one can rewrite Eq. (4) into the following form

$$\frac{\partial c_A}{\partial \tau} = D_e \nabla^2 c_A \tag{5}$$

where the effective diffusion coefficient D_e is given by the relation

$$D_e = \frac{D''}{\beta + \tilde{A}} . \tag{6}$$

In the case of performing the study of diffusion within spherical or cylindrical adsorbent particles Eq. (5) can be transformed for spherical or cylindrical coordinates. For symmetrical diffusion in spherical particles Eq. (5) has the following form:

$$\frac{\partial c_A}{\partial \tau} = D_e \left[\frac{\partial^2 c_{\text{Á}}}{\partial r^2} + \frac{2}{r} \frac{\partial c_{\text{Á}}}{\partial r} \right] \tag{7}$$

where *r* is the radial coordinate.

For symmetrical diffusion in a cylindrical particle Eq. (5) is given by

$$\frac{\partial c_A}{\partial \tau} = D_e \left[\frac{\partial^2 c_{\text{Á}}}{\partial r^2} + \frac{1}{r} \frac{\partial c_{\text{Á}}}{\partial r} + \frac{\partial^2 c_{\text{Á}}}{\partial z^2} \right] \tag{8}$$

where *z* is the axial coordinate. Eqs. (7) and (8) are solved for the required initial and boundary conditions.

If at the beginning of adsorption the adsorbent is supposed to be without adsorbate and adsorptive and, from a certain time a constant adsorptive concentration c_{Ao} is kept on the particle surface, one can define both initial and boundary conditions by

$$\begin{aligned} &c_A = 0 ; \qquad && 0 \le r \le r_o ; \qquad && \tau = 0 \\ &c_A = c_{Ao} ; && r = r_o ; && \tau > 0 \end{aligned} \tag{9}$$

By solving Eq. (7) for conditions (9) one obtains the dependence $c_A = f(r;\tau)$, which makes it possible to calculate the adsorptive concentration in an arbitrary place of the spherical adsorbent particle at an arbitrary time. The relation required for the purpose of determining D_e is derived from the solution of Eq. (7) by transformation for adsorbate concentration at a chosen time. Then, the final form of solution is given by [1, 6, 8]:

$$\gamma_\tau = \frac{\Delta q_\tau}{\Delta q_\infty} = \frac{\Delta m_\tau}{\Delta m_\infty} = 1 - \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} \exp\left(- \frac{n^2 \pi^2 D_e \tau}{r_o^2} \right) \tag{10}$$

where $\Delta m\tau$, $\Delta q\tau$, $\Delta m\infty$, $\Delta q\infty$ are increments of the amount of sorbate and/or adsorbate concentration at time τ and the increment of the amount of sorbate and/or the adsorbate concentration at equilibrium, respectively.

Eq. (10) is recommended for higher adsorption times when the series rapidly converges. For low values of adsorption time Crank [6] derived the following relation

$$\gamma_\tau = 6 \sqrt{\frac{D_e \tau}{r_o^2}} \left[\frac{1}{\sqrt{\pi}} + 2 \sum_{n=1}^{\infty} \operatorname{ierfc}\left(\frac{n r_o}{\sqrt{D_e \tau}} \right) \right] - 3 \frac{D_e \tau}{r_o^2} \tag{11}$$

For equal adsorption conditions in cylindrical particles initial and boundary conditions can be written by:

$$\begin{aligned} &c_A(r,z,0) = 0 ; \qquad && c_A(r_o,z,\tau) = c_{A_o} ; \\ &c_A(r,\pm l/2,\tau) = c_{A_o} && \\ &\frac{\partial c_A(0,z,\tau)}{\partial r} = 0 ; && \frac{\partial c_A(r,0,\tau)}{\partial z} = 0 \end{aligned} \tag{12}$$

Then, the final form of solution suitable for determining D_e has the following form:

$$\gamma_\tau = \frac{\Delta q_\tau}{\Delta q_\infty} = \frac{\Delta m_\tau}{\Delta m_\infty} = 1 - \frac{32}{\pi^2} \sum_{n=1}^{\infty} \sum_{m=1}^{\infty} \frac{1}{\mu_n^2 (2m-1)^2} \exp\left[- \left(\frac{\mu_n^2}{r_o^2} + \frac{(2m-1)^2 \pi^2}{l^2} \right) D_e \tau \right] \tag{13}$$

where *l* is the length of the cylindrical particle. D_e can be determined from kinetic measurements and Eqs. (10), (11) and (13).

Experimental

Materials employed:

Ethyl alcohol containing 99.99 wt. % of ethanol was prepared from technical grade 96 vol.% ethanol by rectification in a packed column and by subsequent drying using CaO and molecular sieve 3A.

The physical properties of activated carbons are listed in Table 1.

Both the course of adsorption of ethanol from a stream of air and the course of desorption of ethanol by a stream of mixture of air and ethanol or pure air in an adsorber with a bed height equal to the diameter of a single adsorbent particle were examined in an apparatus described in paper [36]. The course of adsorption and desorption was investigated in two adsorbers by weighing, when equal adsorption times elapsed. The required concentration of adsorptive in air during the adsorption process was obtained by evaporating the adsorptive from a free surface in tempered saturators. This concentration value was estimated from the overall adsorbed amount of ethanol in differential adsorbers and adsorbers incorporated in the stream before the outlet, through which air was directed into the atmosphere, and from the overall volume of air passing through the adsorber. The results of these measurements represent two sets of data $\{q_{\tau i}; \tau_i\}$ for each adsorption step. Both the concentration of ethanol vapours in air during adsorption c_A and the concentration of adsorbate at the end of adsorption q_A for each step are listed in Table 2. After the completion of adsorption, desorption of ethanol followed. It was done by a stream of mixture of air and ethanol or by a stream of pure air, whereby the mass was determined by weighing. Again a set of measured data $\{q_{\tau i}; \tau_i\}$ was obtained for each desorption step.

Table 1. Properties of Activated Carbons

Activated carbon	Particles	Dimensions/ mm	S*/ ($m^2\ g^{-1}$)	V_P** (r_P>3.7nm)/ ($cm^3\ g^{-1}$)	β**/ %	ρ_P/ ($g\ cm^{-3}$)
HS-4	Sieve fraction	1.25-1.40	917	0.2872	24.12	0.709
SIL15	cylinders	d=1.95 l=4.70	1136	0.4924	34.96	0.529
FB-4	cylinders	d=3.86 l=6.21	554	0.6481	39.27	0.958
HS-4***	cylinders	d=4.81 l=5.24	916	0.3221	25.77	0.709

* Data from Sorptomatic 1900
** Data from porosimeter 2000,
*** Activated carbon used in [37]

Table 2. Results of Calculations

Measurement	Temperature °C	$c_A.10^3$ mol m^{-3}	q_A mol m^{-3}	q_{mid} mol m^{-3}	D_ex10^{11} m^2s^{-1}	D_ex10^{11} m^2s^{-1}
Ethanol – Supersorbon HS-4, fraction 1.25 – 1.4 mm						
A1	21.5	25.90	937.67	468.84	4.06	16.03 a)
A2	21.5	132.01	2176.09	1556.88	9.95	20.17 a)
A3	22.2	348.17	3255.48	2715.78	19.34	33.34 a)
A4	22.4	640.83	4263.6	3759.54	21.22	49.34 a)
D1	22.3	348.17	3240.65	3752.13	24.39	42.48 b)
D2	22.3	132.01	2128.29	2684.47	13.85	27.24 b)
D3	23.7	25.90	978.46	1553.38	7.76	14.89 b)
D4	24.1	0	244.31	611.38	3.55	7.57 b)
Ethanol – Silcarbon SIL-15 Extra, cylindrical particles, d = 1.95 mm, l = 4.70 mm						
A1	22.0	9.82	773.80	336.90	4.46	
A2	21.9	37.98	1915.98	1344.89	6.41	
A3	23.6	195.58	3209.22	2562.60	39.10	
A4	24.1	338.38	3530.11	3369.66	74.12	
D1	22.9	195.58	3291.28	3410.70	70.58	
D2	22.1	37.98	1947.12	2619.20	15.20	
D3	22.3	9.82	851.52	1399.32	6.65	
D4	24.0	0	146.96	499.24	4.17	
Ethanol – Dezorex FB-4						
A1	20.8	11.01	994.11	497.06	24.84	
A2	21.9	38.62	2417.17	1705.64	14.53	
A3	22.4	184.17	3447.65	2932.41	52.01	
A4	22.7	329.24	3772.45	3610.05	113.80	
D1	23.0	184.17	3552.84	3662.64	142.60	
D2	21.9	38.62	2957.54	3255.19	57.10	
D3	22.0	11.01	2362.80	2660.17	18.70	
D4	22.3	0	1618.13	1990.46	12.30	

a) Calculated according [37] for cylindrical particles d = 4.81 mm, l = 5.24 mm
b) Unpublished data for the same cylindrical particles

Results and Discussion

From the sets of data $\{ \gamma_{\tau i}, \tau_i \}$ the values of effective diffusion coefficients were calculated by the optimization method. As optimization function Eq. (14) was used:

$$F = \sum_{i=1}^{N} \left[(\gamma_{\tau i})_{exp} - (\gamma_{\tau i})_{calc} \right]^2 \qquad (14)$$

The values $(\gamma_{\tau i})_{calc}$ were calculated for the respective experimental adsorption or desorption time in spherical or cylindrical particles using Eq. (10) and Eq. (13), respectively. In calculating D_e from desorption kinetic data the same procedure was used. However, the values of γ_τ were defined by following relation:

$$\gamma_\tau = 1 - \frac{\Delta q_\tau}{\Delta q_\infty} = 1 - \frac{\Delta m_\tau}{\Delta m_\infty} \qquad (15)$$

The calculated values of the effective diffusion coefficients for particular adsorption and desorption steps are presented in Table 2. The values of D_e for activated carbon Supersorbon HS-4 acquired from measurements on cylindrical particles of activated carbon [37] are given in the last column of this table.

The calculated effective diffusion coefficients obtained from adsorption measurements increase with an increase in the adsorbate concentration. A similar dependence is also manifested in the case of the values of effective diffusion coefficients determined from desorption measurements. However, these coefficients exhibit a certain deviation as can be seen in Figure 1.

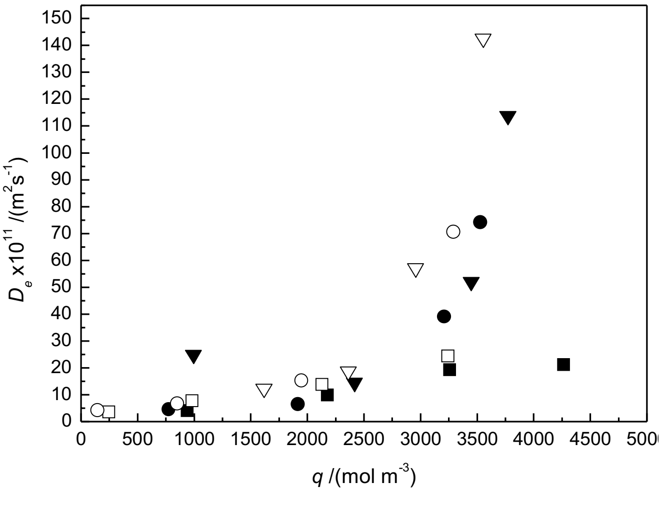

Figure 1. The dependence of effective diffusivities on adsorbate concentration: ■ Adsorption AC HS-4, □ Desorption AC HS-4, ● Adsorption AC SIL-15, ○ Desorption AC SIL-15, ▼ Adsorption AC FB-4, ▽ Desorption AC FB-4

A comparison of the values of D_e of alcohol in particles of Supersorbon HS-4 with values of D_e determined for Silcarbon SIL-15 Extra reveals higher differences at higher concentration of ethanol. This effect may be connected with a higher mobility of ethanol on the adsorption surface of Silcarbon SIL-15 Extra. More significant differences can be observed by comparison of D_e obtained for activated carbons Supersorbon HS-4 and Silcarbon SIL-15 Extra with values of D_e determined on activated carbon Dezorex FB-4. Higher values of D_e of ethanol on activated carbon Dezorex FB-4 are probably linked with a higher portion of transporting pores in comparison with activated carbon Supersorbon HS-4 and Silcarbon SIL-15 Extra. This is partly supported by the differences in values of the specific volume of transport pores with a radius higher than 3.7 nm as shown in Table 1.

In Table 2 are also given values of the effective diffusion coefficient of ethanol determined on cylindrical particles of activated carbon Supersorbon HS-4 (d = 4.81 mm, l = 5.24 mm) [37]. The obtained values of D_e are significantly higher than those obtained for the sieve fraction 1.25 to 1.4 mm of the above mentioned active carbon. The fact that the values of effective diffusion coefficients obtained from measurements on larger particles of activated carbon Supersobon HS-4 are significantly higher than the corresponding values acquired from measurements on smaller particles can be associated with the mode of preparation of smaller particles. Smaller particles were obtained by cutting larger cylindrical particles. It seems that during the cutting process particles were broken through the largest pores. Thus, smaller particles with a smaller portion of the largest pores were obtained. A relative larger portion of smaller transport pores in smaller particles could cause an increase of the resistance against mass transfer. Hence, also the values of D_e were reduced in the case of smaller particles. Tab. 1 reveals that the total volume of pores with a diameter higher than 3.7 nm was decreased from 0.3221, to 0.2872 cm^{3}g^{-1} during the cutting process. The dependence of the cumulative volume of pores measured by mercury porosimetry for both samples of activated carbon Supersorbon HS-4 is drawn in Figurfe 2.

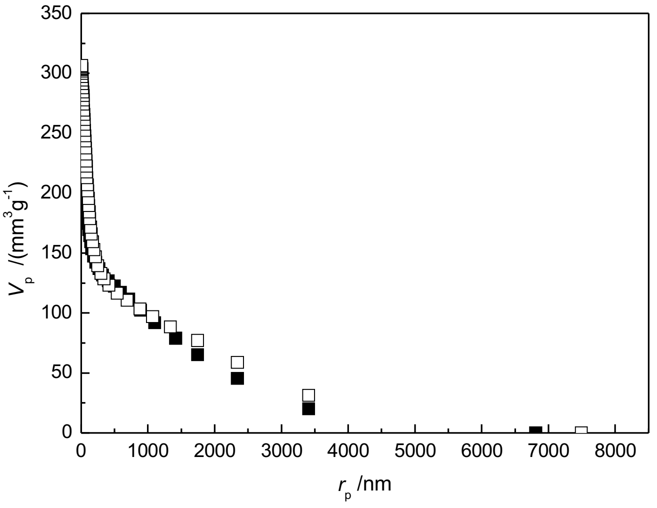

Figure 2. The dependence of cumulative specific pore volume from pore radius of activated carbons Supersorbon HS-4: ■ fraction 1.25 – 1.4 mm, □ original sample

Table 2 and Fig. 1 reveal that the obtained values of the effective diffusion coefficient increase with increasing adsorbate concentration. This increase is probably associated with a rise of the portion of surface diffusion in the transport of ethanol in activated carbon pores. For the judgment of this fact one must use Eq. (6) defining the effective diffusion coefficient. In the combined transport mechanism by molecular diffusion and surface diffusion one can obtain:

$$D_e = \frac{D_{AB}\beta / k^2 + D_s \tilde{A}}{\beta + \tilde{A}} \qquad (16)$$

In the transport of adsorptive by Knudsen diffusion and surface diffusion the effective diffusion coefficient is given by

$$\mathrm{D_e} = \frac{\mathrm{D_K}\beta\ /\mathrm{k}^2 + \mathrm{D_s}\tilde{\mathrm{A}}}{\beta + \tilde{\mathrm{A}}} \tag{17}$$

For the dependence of the coefficient of surface diffusion upon θ the following relationship was used

$$\mathrm{D_s} = \mathrm{D_{so}}\frac{\theta}{2-\theta} \tag{18}$$

which corresponds to the following limiting conditions:

At $\theta = 0$ is $D_s = 0$. Thus, the increment of surface diffusion to the transport of component in pores is equal to zero. At $\theta = 1$ is $D_s = D_{so}$ and the increment of surface diffusion to the transport of component in the pores is maximal. Therefore, D_{so} characterizes the diffusion coefficients at a total surface coverage by adsorbate.

Trying to judge the transport mechanism of ethanol vapours in the presence of air in the activated carbon particle pores the values of D_e were correlated according to Eqs. (16) or (17) using also Eq. (18). For the determination of the degree of surface coverage parameters of the Lagmuir equation were calculated

$$\theta = \frac{\mathrm{q_A}}{\mathrm{q_m}} = \frac{\mathrm{b\,c_A}}{1+\mathrm{b\,c_A}} \tag{19}$$

from values q_A, c_A given in Tab.2 supplemented by point (0;0). For the desorption data the point corresponding to D4 was omitted. The results of calculations are listed in Table 3.

The diffusion coefficient for molecular diffusion was calculated according to the following relation [38]:

$$\mathrm{D_{AB}} = \frac{101.325\mathrm{T}^{7/4}}{\mathrm{P}\left[\left(\sum \mathrm{v_A}\right)^{1/3} + \left(\sum \mathrm{v_B}\right)^{1/3}\right]^2}\sqrt{\frac{1}{\mathrm{M_A}} + \frac{1}{\mathrm{M_B}}} = \frac{101.325(273.15+22)^{7/4}}{100656\left[50.36^{1/3} + 20.1^{1/3}\right]^2}\sqrt{\frac{1}{46.07} + \frac{1}{29}} =$$
$$0.1216\ \mathrm{cm^2s^{-1}} = 1.216\mathrm{x}10^{-5}\mathrm{m^2s^{-1}}$$

The diffusion coefficients of Knudsen diffusion of ethanol in activated carbon particles were calculated from relation

$$\mathrm{D_K} = \frac{8\beta}{3\mathrm{S_p}\rho_\mathrm{p}}\sqrt{\frac{2\mathrm{RT}}{\pi \mathrm{M_A}}} = \frac{8\cdot 0.2412}{3\cdot 917\cdot 0.709\cdot 10^6}\sqrt{\frac{2\cdot 8.314\cdot 295.15}{\pi \cdot 0.04607}} = 1.822\mathrm{x}10^{-7}\mathrm{m^2s^{-1}}$$

The calculated values of D_K for activated carbons used are given in the last column of Table 3.

By omitting β in the denominator of Eq. (16) and its combination with Eq. (18) and modification one obtains

$$\frac{\mathrm{D_e}\tilde{\mathrm{A}}}{\mathrm{D_{AB}}} = \frac{\beta}{\mathrm{k}^2} + \frac{\mathrm{D_{so}}}{\mathrm{D_{AB}}}\frac{\tilde{\mathrm{A}}\theta}{2-\theta} \tag{20}$$

which is an equation of straight line with the slope D_{so}/D_{AB} and an y-intercept β/k^2. An analogical equation for the transport by combination of Knudsen diffusion and surface diffusion has the following form

$$\frac{\mathrm{D_e}\tilde{\mathrm{A}}}{\mathrm{D_K}} = \frac{\beta}{\mathrm{k}^2} + \frac{\mathrm{D_{so}}}{\mathrm{D_K}}\frac{\tilde{\mathrm{A}}\theta}{2-\theta} \tag{21}$$

For chosen values k^2 the values D_{so} given in Table 4 were calculated by using Eqs. (22) and (23). The values Γ were computed from the following expression

Table 3. Parameters of Langmuir Isotherm and Diffusion Coefficients of Knudsen Diffusion

Active carbon	Adsorption		Desorption		$D_K.10^7$
	$b/(\mathrm{m^3\ mol^{-1}})$	$q_m\ /(\mathrm{m^3\ mol^{-1}})$	$b/(\mathrm{m^3\ mol^{-1}})$	$q_m\ /(\mathrm{m^3\ mol^{-1}})$	$\mathrm{m^2\ s^{-1}}$
Supersorbon HS-4	5.48	5281	9.38	4137	1.82
Silcarbon SIL-15 Extra	25.0	3912	26.9	3908	2.86
Dezorex FB-4	33.6	4084	163	3585	3.64

Table 4. Calculated Values of D_{so}

Active carbon	Adsorption		Desorption	
	k^2	$D_{so}.10^{10}\ /(\mathrm{m^2s^{-1}})$	k^2	$D_{so}.10^{10}\ /(\mathrm{m^2s^{-1}})$
Simultaneous molecular and surface diffusion				
Supersorbon HS-4	2.412	<0	2.412	0.498
	7.094	1.56	7.094	2.41
Silcarbon SIL-15 Extra	1.165	<0	1.165	0.359
	3.496	1.62	3.496	2.43
	6.992	3.23	6.942	2.95
Dezorex FB-4	1.007	6.80	1.007	2.96
	3.927	13.6	3.927	3.14
	7.012	14.6	7.012	3.17
Simultaneous Knudsen and surface diffusion				
Supersorbon HS-4	1.005	5.50	1.005	3.24
	2.412	5.83	2.412	3.33
	7.094	5.97	8.040	3.38
Silcarbon SIL-15 Extra	1.002	4.57	1.002	3.37
	1.165	4.63	1.165	3.40
	3.496	4.77	3.496	3.43
	6.992	4.80	6.992	3.46
Dezorex FB-4	1.007	15.6	1.007	3.20
	3.927	15.8	3.927	3.20
	7.012	15.8	7.012	3.20

$$\tilde{A} = \frac{\partial q_A}{\partial c_A} = \frac{q_m b}{(1 + bc_A)^2} \qquad (22)$$

The assumption of a simultaneous course of molecular diffusion and surface diffusion of ethanol led in the case of adsorption to a significant dependence of D_{so} upon k^2. This is obviously connected with a relatively high value of D_{AB} in the first term of the numerator in Eq. (16) in comparison with the value of the second term in the numerator. At small values of tortuosity this fact even leads to negative values of D_{so}. Thus, surface diffusion does not proceed, what is in contradiction with the reality in which during the transport of adsorbing components also transport in the adsorbed phase occurs. Thus, the transport of ethanol vapours in the pores of activated carbon particles does not take place by combination of molecular diffusion and surface diffusion. Therefore, we can suppose, that the transport proceeds via combination of Knudsen diffusion and surface diffusion.

The results of calculations according to the model assuming simultaneous transport of ethanol in activated carbon pores by Knudsen diffusion and surface diffusion manifest only small changes of D_{so} with tortuosity. If we suppose that tortuosity of activated carbons varies from 2 to 7, the differences between the obtained values of D_{so} are negligible. This fact is associated with a significant portion of surface diffusion in the transport of ethanol in activated carbon pores. The values of D_{so} acquired from adsorption data are higher than those obtained from desorption data for all three activated carbons. The greatest differences are for the activated carbon Dezorex FB-4, which has the smallest adsorption surface and the highest portion of transport pores among active carbons investigated.

Differences in the values of D_{so} in adsorption and desorption are linked with differences in the transport mechanism of a component during adsorption and desorption. During adsorption the transport of a component in the adsorbed phase takes places in transport pores and micropores. Thus, the value of D_{so} is given by diffusion in the transport pores and micropores. The relatively lower values of D_{so} obtained from adsorption data for activated carbons Supersorbon HS-4 and Silcarbon SIL-15 Extra are connected with a small portion of transport pores in comparison with activated carbon Dezorex FB-4. In desorption surface diffusion takes place mainly in micropores. Therefore, also differences in D_{so} for particular activated carbons are relatively low. By desorption an interruption of the bond adsorbate – adsorbent takes place, what is connected with a consumption of energy. The amount of this energy is given by the properties of the adsorbed molecules and character of the adsorption surface. The obtained values of D_{so} indicate insignificant differences in the properties of the adsorption surface of activated carbons investigated.

In accordance with the potential theory the adsorbed phase of ethanol behaves like a liquid at considered conditions. Then, the value of D_{so} in accordance to Eq. (18) should not be higher than the value of the diffusion coefficient of ethanol in liquid ethanol at adsorption conditions. According to Wilke and Chang [39] the value of the diffusion coefficient of ethanol in liquid ethanol at experimental conditions is 1.69×10^{-9} m^{2}s^{-1}. This value is close to the value $D_{so} = 1.58 \times 10^{-9}$ m^{2}s^{-1} obtained from adsorption data of ethanol on activated carbon Dezorex FB-4, where diffusion in transport pores prevails.

Symbols

Figure captions

b	parameter of Langmuir isotherm	m^3 mol^{-1}
c_A	concentration of component A in the gas phase	mol m^{-3}
d	diameter of particles	m
D'	diffusion coefficient in porous medium	m^2 s^{-1}
D''	equivalent diffusion coefficient	m^2 s^{-1}
D_{AB}	molecular diffusion coefficient	m^2 s^{-1}
D_e	effective diffusion coefficient	m^2 s^{-1}
D_K	diffusion coefficient of Knudsen diffusion	m^2 s^{-1}
D_s	coefficient of surface diffusion	m^2 s^{-1}
D_{so}	coefficient of surface diffusion, defined in eqn (*20*)	m^2 s^{-1}
F	function defined by Eqn (*16*)	1
k	coefficient of wave of pores in eqn (*8*)	1
l	length of particles	m
Δm_δ	increment of the adsorbed amount at time τ	kg
Δm_8	increment of the adsorbed amount in equilibrium	kg
M_A	molecular weight of component A	kg kmol^{-1}
M_B	molecular weight of component B	kg kmol^{-1}
P	pressure	Pa
q_A	adsorbate concentration	mol m^{-3}
q_m	adsorbate concentration at monomolecular coverage	mol m^{-3}
q_{md}	middle concentration of adsorbate in adsorption or desorption steps	mol m^{-3}
Δq_τ	increment of the adsorbate concentration in time τ	mol m^{-3}
Δq_8	increment of the adsorbate concentration in equilibrium	mol m^{-3}
r	radial coordinate	m
r_p	mean pore radius	m
r_o	the particle radius	m
R	gas constant	J mol^{-1}K^{-1}
R_A	rate of production of component A in the volume of a porous body	mol m^{-3} s^{-1}
S_p	specific surface	m^2 kg^{-1}
V_p	specific pore volume	cm^3 g^{-1}
Σv_A, Σv_B	diffusion molar volume	cm^3 mol^{-1}
z	z coordinate	m
β	porosity	m^3 m^{-3}
γ_τ	dimensionless concentration defined by eqns (*12*), (*13*), or (*15*)	1
Γ	equilibrium constant defined by eqn (*3*)	1
θ	fraction of surface coverage	1
μ_n	roots of the Bessel function first kind of order zero	1
ρ_p	particle density	kg m^{-3}
τ	time	s

Subscripts

calc	calculated
exp	experimental
i	number of measurements in adsorption or desorption step
m	index of series in equation (*15*)
n	index of series in eqns. (*12*), (*13*) and (*15*)

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