Mechanism of Ethanol Vapours Diffusion in Particles of Activated Carbons*

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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 lower content of ethanol compared with that used for adsorption, or by a stream of pure air were examined. From measured data the effective diffusion coefficient D_e was calculated for each adsorption and desorption step. The calculated values of D_e were ranging from 4.06×10^{-11} to 1.42×10^{-9} m^2 s^{-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* combination of Knudsen diffusion and surface diffusion.

All methods of the adsorption equipment design based on an adequate physical description of the adsorption process assume that the overall mass transfer resistance can be divided at least into two partial resistances: the resistance in the fluid phase surrounding the adsorbent particles, and that in the adsorbent particle pores. It is obvious that both these resistances can play a significant role in the calculation of the basic dimensions of an adsorber. The partial mass transfer resistance in the flowing fluid phase is relatively well described for various arrangements of the system. The values of individual mass transfer coefficients in the fluid phase can be calculated from available equations with dimension one. The problem of determination of the partial mass transfer resistance in the adsorbent particle pores cannot be considered to be solved, despite the fact that numerous papers devoted to this topic have recently appeared in the literature. This problem originates from the complicated pores structure in the solid phase, their characterization and the description of transport within the pores. In spite of the existence of various mechanisms, mass transfer in the adsorbent particle pores occurs *via* unsteady diffusion which is described by the Fick's second law of diffusion and characterized by the effective diffusion coefficient, D_e. Within the adsorbent pores often different mass transport mechanisms take place simultaneously, whereby the prevailing mechanism and also the determined values of effective diffusion coefficient may change according to experimental conditions.

The diffusion of substances in solid porous bodies is described in detail in the monographs of *Barrer* [1], *Jost* [2], *Aris* [3], *Cunnigham* and *Williams* [4], and *Kärger* and *Ruthven* [5]. The solutions of equation describing the unsteady diffusion for the basic forms of porous materials and chosen initial and boundary conditions are given in the work of *Cranck* [6]. They can be obtained also by solving the 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], *Kel'tsev* [10], *Kast* [11], *Suzuki* [12], *Satterfield* [13], and other authors.

In the study of a cyclic pressure swing adsorption and desorption method *Sundaram* and *Yang* [14] described the diffusion mass transfer in the solid phase. For given range of parameters the authors found that the values of D_e did vary neither with the adsorbate concentration nor with pressure. *Al-Duri* and *McKay* [15] investigated parallel diffusion and adsorption of high-molecular coloured organic substances in the particles of activated carbon in a batch system. They concluded that the values of the effective diffusion coefficients depend on the adsorptive concentration in the batch exponentially. The observations made during the solid particles drying were used by *Levy et al.* [16] to describe the transport of vapours in the pores of solid phase. Models of diffusion in pores of solid catalysts are presented in the paper of *Haugaard* and

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Livbjerg [17]. The influence of adsorbate concentration and the adsorbent porous structure on the surface diffusion 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 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* [14] 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 NaI on granulated activated carbon *Drazer et al.* [29] found a concentration dependence of the effective diffusion coefficient. According to authors [30] the effective diffusion coefficients of benzene and methyl ethyl ketone in the presence of nitrogen are within the range 1.1×10^{-10} to 1.2×10^{-8} $m^2\ s^{-1}$. With increasing concentration of adsorptive the values of the effective diffusion coefficient increase. Diffusion of hydrogen sulfide and methyl mercaptane from air onto microporous alkaline activated carbon is reported by *Chiang et al.* [31]. During their experiments fresh, spent, regenerated, fresh-impregnated, and regenerated-impregnated activated carbons were used. The estimated values of the effective diffusion coefficients were ranging from 2.1×10^{-12} to 6.5×10^{-10} $m^2\ s^{-1}$. *Lordgooei et al.* [32] modelled the effective diffusion coefficients of volatile organic compounds in activated carbon fibres. *Chen et al.* [33] investigated dyestuffs adsorption on pith. From film-pore diffusion modelling effective diffusivity ranging from 5.27×10^{-11} to 8.6×10^{-10} $m^2\ s^{-1}$ 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 [34]. The calculated surface diffusivity of dyes is ranging from 1.15×10^{-10} to 4.0×10^{-10} $cm^2\ s^{-1}$ what is an about three orders lower value than the effective diffusivity published in [33]. 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.

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.

THEORETICAL

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

$$\beta \frac{\partial c_\mathrm{A}}{\partial \tau} - R_\mathrm{A} = \nabla \cdot D'' \nabla c_\mathrm{A} \qquad (1)$$

where c_A is the adsorptive concentration, D'' 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

$$D'' = D' + D_\mathrm{s} \Gamma \qquad (2)$$

where D' 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

$$q_\mathrm{A} = \Gamma c_\mathrm{A} \qquad (3)$$

where q_A is the adsorbate concentration.

If mass transfer is a result of molecular and surface diffusion combination, eqn (*2*) can be rewritten into the following form

$$D'' = D_\mathrm{AB} \frac{\beta}{k^2} + D_\mathrm{s} \Gamma = D_\mathrm{AB} \frac{\beta}{\tau_\mathrm{T}} + D_\mathrm{s} \Gamma \qquad (4)$$

where D_AB is the coefficient of molecular diffusion, k is the coefficient of waving of pores, and τ_T is tortuosity.

Similarly, if combination of Knudsen and surface diffusion is responsible for the mass transfer, eqn (*2*) is modified into the form

$$D'' = D_\mathrm{K} \frac{\beta}{k^2} + D_\mathrm{s} \Gamma = D_\mathrm{K} \frac{\beta}{\tau_\mathrm{T}} + D_\mathrm{s} \Gamma \qquad (5)$$

where D_K is the coefficient of Knudsen diffusion.

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 value does not depend on spatial coordinates, *i.e.* the porous material is isotropic in terms of mass transfer, eqn (*1*) can be written as

$$\beta \frac{\partial c_\mathrm{A}}{\partial \tau} + \frac{\partial q_\mathrm{A}}{\partial \tau} = D'' \nabla^2 c_\mathrm{A} \qquad (6)$$

If one assumes the validity of linear isotherm in the form of eqn (*3*), and an infinitely rapid trapping of the adsorptive from the close vicinity onto the adsorption surface, then eqn (*6*) can be rewritten into the following form

$$\frac{\partial c_\mathrm{A}}{\partial \tau} = D_\mathrm{e} \nabla^2 c_\mathrm{A} \qquad (7)$$

where the effective diffusion coefficient D_e is given by the relation

$$D_e = \frac{D''}{\beta + \Gamma} \tag{8}$$

For symmetrical diffusion in spherical particles eqn (*7*) has the following form

$$\frac{\partial c_A}{\partial \tau} = D_e \left[\frac{\partial^2 c_A}{\partial r^2} + \frac{2}{r} \frac{\partial c_A}{\partial r} \right] \tag{9}$$

where r is the radial coordinate.

For symmetrical diffusion in a cylindrical particle eqn (*7*) is given by

$$\frac{\partial c_A}{\partial \tau} = D_e \left[\frac{\partial^2 c_A}{\partial r^2} + \frac{1}{r} \frac{\partial c_A}{\partial r} + \frac{\partial^2 c_A}{\partial z^2} \right] \tag{10}$$

where z is the axial coordinate. Eqns (*9*) and (*10*) are solved for the required initial and boundary conditions.

If prior the adsorption the adsorbent is supposed to be free of adsorbate and adsorptive and, from a certain time a constant adsorptive concentration c_{Ao} is kept on the particle surface, one can define the initial and boundary conditions by

$$\begin{aligned} c_A &= 0; \quad & 0 \le r \le r_o; \quad & \tau = 0 \\ c_A &= c_{Ao}; \quad & r = r_o; \quad & \tau > 0 \end{aligned} \tag{11}$$

By solving eqn (*9*) for conditions (*11*) 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 eqn (*9*) by transformation for adsorbate concentration at a chosen time. Then, the final form of solution is given by [1, 6, 8]

$$\gamma_\tau = \frac{\Delta q_\tau}{\Delta q_\infty} = \frac{\Delta m_\tau}{\Delta m_\infty} = 1 - \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} \exp\left(-\frac{n^2 \pi^2 D_e \tau}{r_o^2} \right) \tag{12}$$

where Δm_τ, Δq_τ, Δm_∞, Δq_∞ are increments of the amount of sorbate and/or adsorbate concentration at a time τ and the increment of the amount of sorbate and/or the adsorbate concentration at equilibrium, respectively.

Eqn (*12*) is recommended for higher adsorption times when the series rapidly converges. For low values of adsorption time *Cranck* [6] derived the following relation

$$\gamma_\tau = 6 \sqrt{\frac{D_e \tau}{r_o^2}} \left[\frac{1}{\sqrt{\pi}} + 2 \sum_{n=1}^{\infty} \mathrm{ierfc}\left(\frac{n r_o}{\sqrt{D_e \tau}} \right) \right] - 3 \frac{D_e \tau}{r_o^2} \tag{13}$$

For the above-mentioned adsorption conditions in cylindrical particles initial and boundary conditions can be written as follows

$$c_A(r, z, 0) = 0; \; c_A(r_o, z, \tau) = c_{Ao}; \; c_A(r, \pm l/2, \tau) = c_{Ao}$$
$$\frac{\partial c_A(0, z, \tau)}{\partial r} = 0; \quad \frac{\partial c_A(r, 0, \tau)}{\partial z} = 0 \tag{14}$$

Then, the final form of solution suitable for determining D_e is

$$\gamma_\tau = \frac{\Delta q_\tau}{\Delta q_\infty} = \frac{\Delta m_\tau}{\Delta m_\infty} = 1 - \frac{32}{\pi^2} \sum_{n=1}^{\infty} \sum_{m=1}^{\infty} \frac{1}{\mu_n^2 (2m-1)^2} \cdot \cdot \exp\left[-\left(\frac{\mu_n^2}{r_o^2} + \frac{(2m-1)^2 \pi^2}{l^2} \right) D_e \tau \right] \tag{15}$$

where l is the length of the cylindrical particle. D_e can be determined from kinetic measurements and eqns (*12*), (*13*), and (*15*).

EXPERIMENTAL

Ethyl alcohol containing 99.99 mass % 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 [35] were examined. The course of adsorption and desorption was investigated in two adsorbers by weighing, when the same 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. As a result the two sets of data $\{q_{\tau i}; \tau_i\}$ for each adsorption step were obtained. 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 and along with kinetic data in Fig. 1. 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. The data $\{q_{\tau i}; \tau_i\}$ obtained from two parallel measurements at the same adsorption times were only little different. Thus, in further treatment of data average values of two measurements were used.

Table 1. Properties of Activated Carbons

Activated carbon	Particles	Dimensions	S*	V_p** ($r_p > 3.7$ nm)	β**	ρ_p
		mm	$m^2\ g^{-1}$	$cm^3\ g^{-1}$	%	$g\ cm^{-3}$
HS-4	Sieve fraction	1.25—1.40	917	0.2872	24.12	0.709
SIL-15	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 [36].

Table 2. Results of Calculations

Measurement	t	$c_A \cdot 10^3$	q_A	q_{mid}	$D_e \cdot 10^{11}$	$D_e \cdot 10^{11}$
	°C	$mol\ m^{-3}$	$mol\ m^{-3}$	$mol\ m^{-3}$	$m^2\ s^{-1}$	$m^2\ s^{-1}$
Ethanol—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—SIL-15						
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—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 to [36] 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 averaged data $\{\gamma_{\tau i}; \tau_i\}$ the values of effective diffusion coefficients were calculated by the optimization method. For model parameters optimization the following equation was used

$$F = \sum_{i=1}^{N} \left[(\gamma_{\tau i})_{exp} - (\gamma_{\tau i})_{calc} \right]^2 \qquad (16)$$

The values $(\gamma_{\tau i})_{calc}$ were calculated for the respective experimental adsorption or desorption time in spherical or cylindrical particles using eqns (*12*) and (*15*), respectively. During D_e calculation from desorption kinetic data the same procedure was used. However, the values of γ_τ were defined by the following relation

$$\gamma_\tau = 1 - \frac{\Delta q_\tau}{\Delta q_\infty} = 1 - \frac{\Delta m_\tau}{\Delta m_\infty} \qquad (17)$$

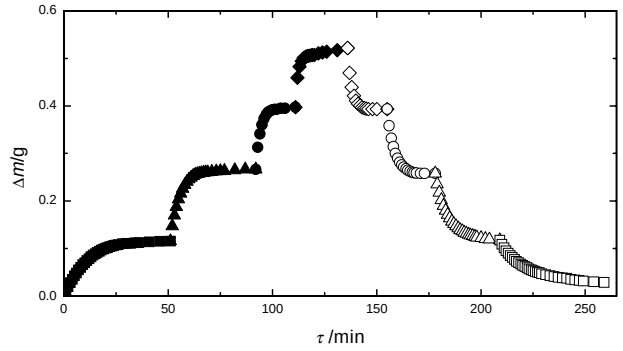

Fig. 1. The dependence of ethanol concentration on activated carbon on time for consecutive adsorption and desorption steps: A1: ■, A2: ▲, A3: ●, A4: ◆, D1: ◇, D2: ○, D3: △, D4: □.

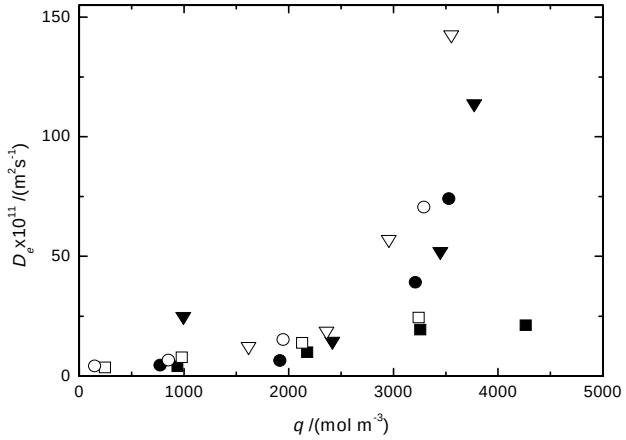

Fig. 2. The dependence of effective diffusivities on adsorbate concentration measured for HS-4 (squares), SIL-15 (circles), and FB-4 (triangles) activated carbons. Data obtained for adsorption (full symbols) and desorption (opened symbols).

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 [36] are given in the last column of this table.

The calculated effective diffusion coefficients obtained from adsorption measurements increase with an increase of 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 Fig. 2.

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

In Table 2 also values of the effective diffusion coefficient of ethanol determined for cylindrical particles of activated carbon Supersorbon HS-4 ($d = 4.81$ mm, $l = 5.24$ mm) [36] are given. The obtained values of D_e are significantly higher than those obtained for the sieve fraction 1.25 to 1.4 mm of the same active carbon. This discrepancy can be associated with the mode of preparation of smaller particles of activated carbon HS-4. 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 the mass transfer. Hence, also the values of D_e were reduced in the case of smaller particles. Table 1 reveals that the total specific volume of pores with a diameter higher than 3.7 nm was decreased from 0.322 to 0.287 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 HS-4 is shown in Fig. 3.

Table 2 and Fig. 2 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

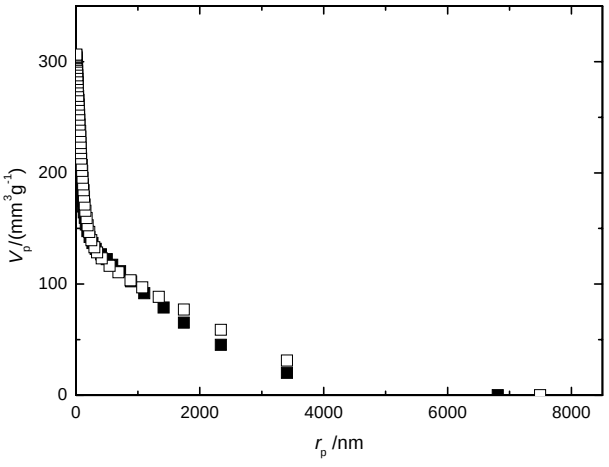

Fig. 3. The dependence of cumulative specific pore volume on pore radius of activated carbon Supersorbon HS-4: ■ fraction 1.25—1.4 mm and □ cylindrical pellets.

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

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

use eqn (*8*) defining the effective diffusion coefficient. By combination of eqns (*8*) and (*4*) one obtains the following relation

$$D_e = \frac{D_{AB}\beta/k^2 + D_s\Gamma}{\beta + \Gamma} \qquad (18)$$

expressing the effective diffusion coefficient of the combined molecular and surface diffusion of ethanol. When the adsorptive transport is done *via* Knudsen and surface diffusion the effective diffusion coefficient is given by

$$D_e = \frac{D_K\beta/k^2 + D_s\Gamma}{\beta + \Gamma} \qquad (19)$$

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

$$D_s = D_{so}\frac{\theta}{2-\theta} \qquad (20)$$

which corresponds to the following limiting conditions.

At $\theta = 0$ $D_e = 0$. Thus, the contribution of surface diffusion to the transport of component in pores is equal to zero. At $\theta = 1$ $D_s = D_{so}$ and the contribution of surface diffusion to the transport of component in the pores reaches maximum. 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 eqn (*18*) or (*19*) using also eqn (*20*). For the determination of the degree of surface coverage parameters of the Lagmuir equation were calculated

$$\theta = \frac{q_A}{q_m} = \frac{bc_A}{1 + bc_A} \qquad (21)$$

from values q_A, c_A given in Table 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 [37]

$$D_{AB} = \frac{101.325T^{7/4}}{P\left[\left(\sum v_A\right)^{1/3} + \left(\sum v_B\right)^{1/3}\right]^2}\sqrt{\frac{1}{M_A} + \frac{1}{M_B}} =$$

$$= \frac{101.325\,(273.15+22)^{7/4}}{100656\left[50.36^{1/3} + 20.1^{1/3}\right]^2}\sqrt{\frac{1}{46.07} + \frac{1}{29}}\,\mathrm{cm^2\ s^{-1}} =$$

$$= 1.216 \times 10^{-5}\ \mathrm{m^2\ s^{-1}}$$

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

$$D_K = \frac{8\beta}{3S_p\rho_p}\sqrt{\frac{2RT}{\pi M_A}} =$$

$$= \frac{8 \times 0.2412}{3 \times 917 \times 0.709 \times 10^6}\sqrt{\frac{2 \times 8.314 \times 295.15}{\pi \cdot 0.04607}}\ \mathrm{m^2\ s^{-1}} =$$

$$= 1.822 \times 10^{-7}\ \mathrm{m^2\ s^{-1}}$$

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 eqn (*18*) and its combination with eqn (*20*) and modification one obtains

$$\frac{D_e\Gamma}{D_{AB}} = \frac{\beta}{k^2} + \frac{D_{so}}{D_{AB}}\frac{\Gamma\theta}{2-\theta} \qquad (22)$$

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

$$\frac{D_e\Gamma}{D_K} = \frac{\beta}{k^2} + \frac{D_{so}}{D_K}\frac{\Gamma\theta}{2-\theta} \qquad (23)$$

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

$$\Gamma = \frac{\partial q_A}{\partial c_A} = \frac{q_m b}{(1 + bc_A)^2} \qquad (24)$$

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 eqn (*18*) 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, the surface diffusion should not proceed, what is in contradiction with the reality as during the transport of adsorbing components also transport in the

Table 4. Calculated Values of D_{so}

Activated carbon	Adsorption		Desorption	
	k^2	$D_{so} \cdot 10^{10}$ / m^2 s^{-1}	k^2	$D_{so} \cdot 10^{10}$ / m^2 s^{-1}
Simultaneous molecular and surface diffusion				
HS-4	2.412	< 0	2.412	0.498
	7.094	1.56	7.094	2.41
SIL-15	1.165	< 0	1.165	0.359
	3.496	1.62	3.496	2.43
	6.992	3.23	6.942	2.95
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				
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
SIL-15	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
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

adsorbed phase occurs. As a result, the transport of ethanol vapours in the pores of activated carbon particles may not proceed as the combination of molecular and surface diffusion. Therefore, the transport due to the combination of Knudsen and surface diffusion should be expected.

The results of calculations according to the model assuming simultaneous transport of ethanol in activated carbon pores by Knudsen and surface diffusion show only small changes of D_{so} with tortuosity. Supposing that tortuosity of activated carbons varies from 2 to 7, the differences between the obtained values of D_{so} are negligible. On the other hand, the contribution of surface diffusion to the overall transport of ethanol in activated carbon pores is significant. The values of D_{so} acquired from adsorption data were higher than those obtained from desorption data for all activated carbons used. The biggest differences were observed 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 between the values of D_{so} obtained for adsorption and desorption are linked with the different mechanism of adsorbed component transport during adsorption and desorption. During adsorption the transport of ethanol vapours in the adsorbed phase takes place in transport pores and micropores. The relatively lower values of D_{so} obtained from the adsorption data for HS-4 and SIL-15 activated carbons are connected with smaller portion of transport pores in comparison with activated carbon FB-4. During desorption surface diffusion takes place mainly in micropores. Therefore, also differences in D_{so} for particular activated carbons are relatively low. Desorption represented by an interruption of adsorbate—adsorbent bond is connected with energy consumption. The amount of energy consumed depends on the properties of adsorbed molecules and adsorption surface. The obtained values of D_{so} indicate insignificant differences in the properties of the adsorption surface of activated carbons investigated.

According to the potential theory, at experimental conditions the adsorbed ethanol phase behaved as liquid. Then, the value of D_{so} in accordance with eqn (*20*) should not be higher than the value of the diffusion coefficient of ethanol in ethanol at adsorption conditions. According to *Wilke* and *Chang* [38] 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.

On the other hand, the obtained values of the coefficients of surface diffusion D_s are tenfold higher than those reported by *Prasetyo et al.* [39] for adsorption of strongly adsorbing vapours on porous carbon. However, the authors were accounting for combination of Knudsen and surface diffusion even in conditions when molecular diffusion was primarily responsible for the adsorbate transport within the carbon pores.

They used a method based on experimentally obtained values D_e, from which D_s was determined by eqn (*19*). The value of the equilibrium constant was estimated by derivation of the equilibrium line. For adsorbate concentrations 0—12 kmol m^{-3} and a temperature of 303 K the obtained values of D_s varied within the range of 1.84×10^{-12} to 7.09×10^{-11} m^2 s^{-1}, whereby the experimentally obtained value of D_e was 1.99×10^{-9} m^2 s^{-1}. Thus, their value of D_e is higher than the highest value for Dezorex FB-4 calculated in this study. On the other hand, the calculated values of D_s are by one to two orders lower than those obtained from D_{so} data listed in Table 4. In [39] an experimentally obtained value of tortuosity (4.9) of activated carbon was used. The coefficient of Knudsen diffusion was calculated for the transport pores of activated carbon with a diameter $r_p = 0.8$ μm from the following relation

$$D_K = 9700 r_p \left(\frac{T}{M_A}\right)^{1/2} =$$

$$= 9700 \times 0.8 \times 10^{-4} \left(\frac{295.15}{46.07}\right)^{1/2} \text{cm}^2\ \text{s}^{-1} =$$

$$= 1.964 \times 10^{-4}\ \text{m}^2\ \text{s}^{-1}$$

The calculated value is by one order of magnitude higher than the coefficient of molecular diffusion at experimental conditions. Therefore, we must judge whether at considered conditions Knudsen diffusion takes places in transport pores. The mean free path of molecules can be calculated by

$$\lambda = \frac{kT}{\pi\sigma^2 P\sqrt{2}} = \\ = \frac{1.380\times10^{-23}\times 295.15}{\pi\,(4.1205\times10^{-10})\times 101325\sqrt{2}}\ \mathrm{m} = \\ = 1.293\times10^{-8}\ \mathrm{m}$$

Then

$$\frac{\lambda}{r_\mathrm{p}} = \frac{1.293\times10^{-8}}{0.8\times10^{-6}} = 0.0162 \ll 1$$

We can conclude that in transport pores molecular diffusion and not Knudsen diffusion takes place in contradiction to paper [39]. It is obvious that if these authors had used instead of the coefficient of Knudsen diffusion the one order lower coefficient of molecular diffusion, the calculated values of the coefficients of surface diffusion would be approximately by one order higher. Then, these values would approach our results.

SYMBOLS

b	parameter of Langmuir isotherm	$\mathrm{m^3\ mol^{-1}}$
c_A	concentration of component A in the gas phase	$\mathrm{mol\ m^{-3}}$
d	diameter of particles	m
D'	diffusion coefficient in porous medium	$\mathrm{m^2\ s^{-1}}$
D''	equivalent diffusion coefficient	$\mathrm{m^2\ s^{-1}}$
D_AB	molecular diffusion coefficient	$\mathrm{m^2\ s^{-1}}$
D_e	effective diffusion coefficient	$\mathrm{m^2\ s^{-1}}$
D_K	diffusion coefficient of Knudsen diffusion	$\mathrm{m^2\ s^{-1}}$
D_s	coefficient of surface diffusion	$\mathrm{m^2\ s^{-1}}$
D_so	coefficient of surface diffusion, defined in eqn (*20*)	$\mathrm{m^2\ s^{-1}}$
F	function defined by eqn (*16*)	1
k	coefficient of wave of pores in eqn (*4*)	1
k_B	Boltzmann constant	$\mathrm{J\ K^{-1}}$
l	length of particles	m
Δm_τ	increment of the adsorbed amount at time τ	kg
Δm_∞	increment of the adsorbed amount in equilibrium	kg
M_A	molecular mass of component A	$\mathrm{kg\ kmol^{-1}}$
M_B	molecular mass of component B	$\mathrm{kg\ kmol^{-1}}$
P	pressure	Pa
q_A	adsorbate concentration	$\mathrm{mol\ m^{-3}}$
q_m	adsorbate concentration at monomolecular coverage	$\mathrm{mol\ m^{-3}}$
q_mid	middle concentration of adsorbate in adsorption or desorption steps	$\mathrm{mol\ m^{-3}}$
Δq_τ	increment of the adsorbate concentration in time τ	$\mathrm{mol\ m^{-3}}$
Δq_∞	increment of the adsorbate concentration in equilibrium	$\mathrm{mol\ m^{-3}}$
r	radial coordinate	m
r_p	mean pore radius	m
r_o	the particle radius	m
R	gas constant	$\mathrm{J\ mol^{-1}\ K^{-1}}$
R_A	rate of production of component A in the volume of a porous body	$\mathrm{mol\ m^{-3}\ s^{-1}}$
S	surface area	$\mathrm{m^2\ g^{-1}}$
S_p	specific surface	$\mathrm{m^2\ kg^{-1}}$
T	temperature	K
t	temperature	℃
V_p	specific pore volume	$\mathrm{cm^3\ g^{-1}}$
Σv_A, Σv_B	diffusion molar volume	$\mathrm{cm^3\ mol^{-1}}$
z	coordinate	m
β	porosity	$\mathrm{m^3\ m^{-3}}$
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
λ	mean free path	m
μ_n	roots of the Bessel function first kind of order zero	1
ρ_p	particle density	$\mathrm{kg\ m^{-3}}$
σ	collision diameter	m
τ	time	s
τ_T	tortuosity	1

Subscripts

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

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