

Application of the Adsorbate Pore Filling Correction Model to Diffusion of Ethanol Vapours in Activated Carbon

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Abstract

The model of adsorbate pore filling correction was applied to describe ethanol vapour diffusion from a stream of air in particles of activated carbon. The calculated values of pore diffusivity D'_{AB} were ranging from 1.06×10^{-6} to $2.60 \times 10^{-6} \text{ m}^2 \text{ s}^{-1}$. Transport of ethanol vapours in pores of activated carbon Supersorbon HS-4 proceeded via combination of Knudsen and surface diffusion. The values of effective diffusivity D_e calculated from the pore diffusivity D'_{AB} varied from 3.13×10^{-11} to $2.461 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$ and a dependence of D_e on adsorbate concentration was found.

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

Diffusion of substances in solid porous bodies is described in details in several monographs [1—11]. Cranck [12] published solutions of an equation describing the unsteady diffusion for the basic forms of porous material and chosen initial and boundary conditions. In many published papers kinetic adsorption data are treated as unsteady diffusion in adsorbent particles [13, 14]. Such a treatment is based on the assumption of the existence of a linear isotherm of infinitely rapid entrapment of adsorptive on the adsorption surface. The advantage of this procedure is that the mass transfer of adsorptive in particles of adsorbent is characterized by the only one information, i.e. the effective diffusion coefficient.

The aim of this work was to treat the experimental kinetic data from the measurements of stepwise adsorption and desorption of ethanol vapours on activated carbon Supersorbon HS-4 by the adsorbate pore filling correction model of diffusion described in paper [15]. The model is based on the equation describing unsteady diffusion in the spherical particles pores, where the volume of pores is corrected by the volume of adsorbate entrapped. The adsorption equilibrium is described by the Langmuir or Toth isotherms [15]. The model enables to calculate the diffusion coefficient of ethanol in the presence of air in the pores of activated carbon whose volume is not filled with adsorbed ethanol.

Theoretical

The model of adsorptive diffusion with pore filling correction of adsorbate has the following form [15]

$$\frac{\partial C_A}{\partial T} = \frac{\beta_o - X_A / R_A}{(\beta_o - X_A / R_A) + S} \left[\frac{2}{R} \frac{\partial C_A}{\partial R} + \frac{\partial^2 C_A}{\partial R^2} \right] - \frac{S / R_A}{(\beta_o - X_A / R_A) + S} \left(\frac{\partial C_A}{\partial R} \right)^2 \quad (1)$$

whereby the variables have a dimension equal to one and

$$X_A = \frac{X_{Am} B C_A}{1 + B C_A} \quad (2)$$

and

$$S = \frac{\partial X_A}{\partial C_A} = \frac{X_{Am} B}{(1 + B C_A)^2} \quad (3)$$

Initial and boundary conditions for adsorption or desorption steps:

$$\begin{array}{lll} T=0 & 0 \leq R \leq 1 & C_A = C_{A1} \\ T>0 & R=1 & C_A = C_{A2} \\ T>0 & R=0 & \partial C_A / \partial R = 0 \end{array} \quad (4)$$

By substitution of derivations by differences and by modification of eqn (1) one gets

$$C_{i,j+1} = C_{i,j} + \frac{\Delta T}{(\Delta R)^2} \frac{1}{[(\beta_o - X_A / R_A) + S]} \left\{ \frac{\beta_o - X_A / R_A}{i-1} [C_{i+1,j} - C_{i-1,j}] + (\beta_o - X_A / R_A) [C_{i+1,j} - 2C_{i,j} + C_{i-1,j}] - (S/4R_A) [C_{i+1,j} - C_{i-1,j}]^2 \right\} \quad (5)$$

where

$$R = (i-1) \Delta R \quad (6)$$

whereby $i=1$ in the particle centre. Values X_A and S are calculated from eqns (2), and (3) for the value $C_{i,j}$. If the number of dividing sections in the direction of radius is equal to m and time n , one obtains from eqn (5) $m.n$ algebraic equations. The number of points in the direction of the radius will be $m+1$.

From eqn (4) the following equations were derived for initial conditions

$$C_{i,0} = C_{A1} \quad i=1, 2, \dots, m+1 \quad (7)$$

for boundary conditions on the particle surface

$$C_{m+1,j} = C_{A2} \quad j=1, 2, \dots, n \quad (8)$$

and for boundary conditions in the particle centre

$$C_{1,j} = C_{2,j} \quad j=1, 2, \dots, n \quad (9)$$

The solution is done in such a way that the adsorptive and adsorbate concentrations throughout the particle are calculated for the chosen time. At the beginning of calculation the values $C_{i,0}$ given by eqn (7) are used as a starting concentration at each point of the particle. The solution begins from the first time step $j = 1$. For $i = 1$, the values in the particle centre (obtained from eqn (9)) are inserted and for $i = 2, 3, \dots, m+1$, $C_{i,j+1}$ is calculated from eqn (6). Thus, one obtains distribution of the concentrations of adsorptive $C_A(R)$ and adsorbate concentration $X_A(R)$ in the particle at chosen time. This procedure is repeated for further time steps up to $j = n$. Thus, the calculation is performed in two cycles. For the chosen time, distribution of the adsorptive concentration $C_A(R)$ (and also adsorbate concentration $X_A(R)$) in the particle is calculated. For comparison of data obtained from the model with experimental data one needs to calculate the middle adsorbate concentration in the particle at a certain time with dimension equal to one for the n -th adsorption step

$$X_t = \frac{\int_0^1 X_A(R, T) \rho_p r_o^3 4\pi R^2 dR}{4\pi r_o^3 \rho_p / 3} \quad (10)$$

The computation tends towards the determination of the optimal value D_1 for the given point from the experimental kinetic curve. Ten optimal values of D_1 were calculated for each adsorption or desorption step. From all optimal values of D_1 the integral mean of \bar{D} was calculated for adsorption and desorption steps using the relation

$$\bar{D} = \frac{\int_{X_1}^{X_{10}} D_1 dX}{X_{10} - X_1} \quad (11)$$

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 the molecular sieve 3A. The activated carbon Supersorbon HS-4 has the following parameters: sieve fraction 1.25—1.40 mm, surface area 917 m² g⁻¹, $\beta=0.46012$ and particle density $\rho_p=0.709$ g cm⁻³. The method of kinetic data measurement is described elsewhere [14].

Results and Discussion

Results of measurements of stepwise adsorption treated by the pore filling correction model are summarized in Table 1

Table 1. Results of Computation for Stepwise Adsorption of Ethanol Vapours on Supersorbon HS-4

$r_o=0.6615 \times 10^{-3}$ m, $\rho_p=709$ kg m ⁻³ , $\rho_A=789$ kg m ⁻³ , $\beta_o=0.46012$, $m=100$; $\Delta T=0.1$										
A1	$C_{A1}=0$, $C_{A2}=8.415 \times 10^{-7}$, $X_{Am}=0.20875$, $B=489474.6$									
t/s	306	612	918	1224	1530	1836	2142	2448	2754	3060
$X_i \times 10^2$	2.15	3.65	4.63	5.24	5.59	5.78	5.89	5.98	6.05	6.09
$D_1 \times 10^6 / (m^2 s^{-1})$	3.01	4.86	5.98	6.54	6.72	6.65	6.50	6.52	7.78	7.05
$\bar{D}=5.26 \times 10^{-6}$ m ² s ⁻¹										
A2	$C_{A1}=8.415 \times 10^{-7}$, $C_{A2}=4.289 \times 10^{-6}$, $X_{Am}=0.20875$, $B=489474.6$									
t/s	246	492	738	984	1230	1476	1722	1968	2214	2460
$X_i \times 10^2$	10.82	12.84	13.56	13.76	13.85	13.96	14.06	14.08	14.05	16.16
$D_1 \times 10^6 / (m^2 s^{-1})$	3.49	4.45	4.08	3.36	2.81	2.53	2.38	2.17	1.88	2.01
$\bar{D}=3.85 \times 10^{-6}$ m ² s ⁻¹										
A3	$C_{A1}=4.289 \times 10^{-6}$, $C_{A2}=1.131 \times 10^{-5}$, $X_{Am}=0.30345$, $B=203388.4$									
t/s	114	228	342	456	570	684	798	912	1026	1140
$X_i \times 10^2$	17.96	19.74	20.49	20.78	20.91	20.99	21.04	21.08	21.12	21.15
$D_1 \times 10^6 / (m^2 s^{-1})$	2.43	3.54	3.64	3.31	2.94	2.61	2.27	1.90	1.64	1.87
$\bar{D}=3.11 \times 10^{-6}$ m ² s ⁻¹										
A4	$C_{A1}=1.131 \times 10^{-5}$, $C_{A2}=2.082 \times 10^{-5}$, $X_{Am}=0.43369$, $B=84682.76$									
t/s	150	300	450	600	750	900	1050	1200	1350	1500
$X_i \times 10^2$	26.10	26.83	27.08	27.20	27.28	27.33	27.37	27.40	27.42	27.44
$D_1 \times 10^6 / (m^2 s^{-1})$	3.12	2.46	1.94	1.58	1.35	1.17	1.03	0.93	0.84	0.77
$\bar{D}=2.31 \times 10^{-6}$ m ² s ⁻¹										

According to the model the diffusion coefficient of component A in a porous medium can be calculated by

$$D'_{AB} = \frac{D_{AB}\beta}{k^2} = \beta \bar{D} \quad (12)$$

If the mass transfer takes place only by molecular diffusion $\bar{D}=D_{AB}/k^2$. If only Knudsen diffusion is responsible for the mass transfer $\bar{D}=D_K/k^2$. During the transport of adsorbing component in the solid phase pores also surface diffusion takes place. At simultaneous molecular and surface diffusion

$$D'_{AB} = \frac{D_{AB}\beta}{k^2} + \frac{\beta D_s}{\beta} f'(c) = \beta \bar{D} = \beta \left[\frac{D_{AB}}{k^2} + \frac{D_s}{\beta} f'(c) \right] \quad (13)$$

For simultaneously proceeding Knudsen and surface diffusion holds

$$D'_{AB} = \frac{D_K\beta}{k^2} + \frac{\beta D_s}{\beta} f'(c) = \beta \bar{D} = \beta \left[\frac{D_K}{k^2} + \frac{D_s}{\beta} f'(c) \right] \quad (14)$$

where $f(c)$ describes the formula of the adsorption isotherm

$$q = f(c) \quad (15)$$

and $f'(c)$ is the derivative of $f(c)$ with respect to c .

From eqns (13) and (14) follows that if surface diffusion takes place, then the term including the contribution of surface diffusion can be significant what influences the transport mechanism of ethanol vapours in the activated carbon particle.

Both the coefficient of molecular diffusion of ethanol in air $D_{AB}=1.220 \times 10^{-5} \text{ m}^2 \text{ s}^{-1}$ and the coefficient of Knudsen diffusion of ethanol in the activated carbon particle $D_K=3.476 \times 10^{-7} \text{ m}^2 \text{ s}^{-1}$ were calculated for measuring conditions. Taking into account the fact that the tortuosity value for chosen activated carbon is higher than 1.5 and the contribution of surface diffusion is significant one can conclude that the transport of ethanol in the presence of air in pores of activated carbon Supersorbon HS-4 is a combination of Knudsen and surface diffusion.

For the effective diffusion coefficient calculation one can derive the relation

$$D_e = \bar{D} \frac{\beta}{\beta + K'} \quad (16)$$

where the equilibrium constant for stepwise adsorption and desorption is defined by

$$q_A = K'c_A + e \quad (17)$$

Table 2. summarizes the values of the effective diffusion coefficient calculated from eqn (16) and from the assumption of unsteady diffusion in spherical particles [14]. The values calculated for both models exhibit the same trend and their difference is negligible.

Table 2. Calculated Diffusivity Values

Measurement	q_{mid} (mol m ⁻³)	K'	$\beta \bar{D} \times 10^6$ (m ² s ⁻¹)	$D_e \times 10^{10}$ / (m ² s ⁻¹)	
				eqn (16)	II. Fick's law
A1	468.84	72 402	2.42	0.3343	0.4065
A2	1556.88	23 341	1.77	0.7589	0.9949
A3	2715.78	9 987	1.43	1.4360	1.9345
A4	3 759.54	6 890	1.06	1.5430	2.1229
D1	3 752.13	6 991	1.72	2.4610	2.4390
D2	2 684.47	10 292	1.78	1.7350	1.3853
D3	1 553.38	21 672	2.60	1.2000	0.7758
D4	611.38	56 687	2.47	0.4375	0.3550

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Symbols

b	parameter of the Langmuir isotherm	m ³ kmol ⁻¹
B=b/ρ_p	parameter of the Langmuir isotherm, eqn (2)	1
C_A	concentration of adsorptive	kmol m ⁻³
C_{A1}	concentration of adsorptive before stepwise adsorption or desorption	kmol m ⁻³
C_{A2}	concentration of adsorptive during stepwise adsorption or desorption	kmol m ⁻³
$C_A = c_A / (\rho_p x_A^0)$	concentration of adsorptive	1
C_{A1}, C_{A2}	adsorptive concentrations	1
$C_{i,j}$	adsorptive concentration of a particle in place <i>i</i> at time <i>j</i>	1
$D_1 = D_{AB} / k^2$	diffusion coefficient	m ² s ⁻¹
D_{AB}	diffusion coefficient of molecular diffusion	m ² s ⁻¹
\bar{D}_{AB}	diffusion coefficient in porous body defined by eqn (13) or (14)	m ² s ⁻¹
D_e	effective diffusion coefficient defined by eq(16)	m ² s ⁻¹
\bar{D}	diffusion coefficient defined by eqn (11)	m ² s ⁻¹
<i>e</i>	parameter in eqn (17)	kmol m ⁻³
k^2	tortuosity	1
K'	parameter in eqn (17)	1
<i>q</i>	adsorbate concentration	mol m ⁻³
q_{mid}	middle concentration of adsorbate in adsorption or desorption steps	mol m ⁻³
<i>r</i>	radial coordinate	m
r_0	adsorbent particle radius	m
R=r/r₀	radial coordinate	1
$R_A = \rho_A / \rho_p$	parameter	1
$R_p = \rho_p / \rho_p = 1$	parameter	1
<i>S</i>	quantity defined by eqn (3)	1
<i>t</i>	time	s
T=tD₁/r₀²	time	1
x_A	adsorbate concentration	kmol kg ⁻¹
x_{Am}	adsorbate concentration corresponding to the monomolecular layer	kmol kg ⁻¹

$X_A = x_A / x_A^o$	adsorbate concentration	1
$x_A^o = 1 \text{ kmol kg}^{-1}$	relative unit of adsorbate concentration	kmol kg^{-1}
$X_{Am} = x_{Am} / x_A^o$	monomolecular layer adsorbate concentration	1
X_t	middle adsorbate concentration in the particle at a certain time	1
β	porosity of adsorbent particle	1
β_o	porosity of activated adsorbent particle	1
ρ_A	adsorbate density at temperature of adsorption	kg m^{-3}
ρ_p	density of adsorbent particle	kg m^{-3}

Subscripts

i	spatial coordinate
j	temporal coordinate

References

- [1] Barrer, R. M., Diffusion in and through Solids, University Press, Cambridge, 1951.
- [2] Jost, W., Diffusion in Solids, Liquids and Gases, Academic Press, New York, 1960.
- [3] Timofejev, D. P., Kinetika adsorbicii, Izdatel'stvo Akademii Nauk SSSR, Moskva, 1962.
- [4] Satterfield, C. N., Mass Transfer in Heterogeneous Catalysis, M.I.T. Press, London 1970.
- [5] Aris, R., The Mathematical Theory of Diffusion and Reaction in Permeable Catalysts, Clarendon Press, Oxford, 1975.
- [6] Cunningham, R. E. and Williams, R. J. J., Diffusion in Gases and Porous Media, Plenum Press, New York, 1980.
- [7] Ruthven, D. M., Principles of Adsorption Processes, Wiley, New York, 1984.
- [8] Keľcev, N. V., Osnovy Adsorbcionnoj Techniki, Izdatel'stvo Chimija, Moskva, 1984.
- [9] Kast, W., Adsorption aus der Gasphase, VCH Verlagsgesellschaft GmbH, Weinheim, 1988.
- [10] Suzuki, M., Adsorption Engineering, Elsevier, 1990.
- [11] Kärger, J. and Ruthven, D. M., Diffusion in Zeolites and other Microporous Solids, Wiley, New York, (1992).
- [12] Cranck, J., Mathematics of Diffusion, 2nd Ed., Oxford University Press, London, 1975.
- [13] Bobok, D. and Besedová, E., Chem. Pap. 2003, 57(1), 39
- [14] Bobok, D. and Besedová, E., Chem. Pap. 2004, 58(1), 55
- [15] Bobok, D., Besedová, E., and Bodnár Z., Proceedings of the 31st Int. Conf. SSChE, Tatranské Matliare, Slovakia, 2004.