DIFFUSION OF 1,2-DICHLOROETHANE IN PARTICLES OF ACTIVATED CARBON

Daniel BOBOK and Eva BESEDOVA[1]

Department of Chemical Engineering, Slovak University of Technology, Faculty of Chemical Technology, 812 37 Bratislava, Slovak Republic; e-mail: [1] besedova@cvt.stuba.sk

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Simultaneous diffusion and adsorption of 1,2-dichloroethane from air into activated carbon particles was studied at ambient temperature. The measurements were carried out in adsorbers with a bed height equal to the diameter of activated carbon particles. On the basis of the assumption of diffusion and adsorption in a quasihomogenous porous medium, effective diffusion coefficients were calculated. Their values are linearly dependent on the concentration of adsorptive in the inlet gas. For the evaluation of errors, mass transfer resistances in the fluid and solid phases were calculated. The maximum value of the former did not exceed 12.5% of the overall resistance.

Key words: Adsorption; Diffusion; Activated carbon; 1,2-Dichloroethane.

Here we report a study of diffusion in solid porous media, aimed at obtaining velocity parameters required for the design of commercial separation and catalytic processes as well as for the identification and description of particular process steps participating in the mass transfer within solid phase pores. Numerous works have been devoted to the investigation of mass transfer within a precisely defined porous zeolite structure[1–4], various measuring methods being used for these investigations. Differences between values of diffusion coefficients of substances in zeolite crystals measured under the same conditions by NMR, gravimetric of chromatographic techniques cover several orders of magnitude[5]. Some of the causes of the differences are known; however, up to the present time, no procedure has been reported for the employment of these data in describing mass transfer necessary for the design of adsorbers. An approach is adopted to designing adsorbers which uses the rate data obtained under the same or similar assumptions concerning mass transfer as they are used in the design. In the present contribution, we assume that diffusion with sorption proceeds in a quasihomogeneous medium, which is also considered in the design of sorption equipments.

THEORETICAL

Mass Transfer in a Quasihomogeneous Medium

Let is consider a solid porous medium with pores filled with a fluid phase, which is isotropic from the standpoint of mass transfer. If adsorption of one component takes place in the pores and there exists a concentration gradient of this component in the fluid phase, then the unsteady mass transfer in porous media can be described by the following relationship:

$$\beta \frac{\partial c_\mathrm{A}}{\partial \tau} + \frac{\partial q_\mathrm{A}}{\partial \tau} = D' \, \Delta c_\mathrm{A} \ . \qquad (1)$$

Diffusion coefficient D' of substance A in a porous medium characterizes the mass transfer in solid phase pores by molecular, Knudsen or surface diffusion and/or their combination. If one assumes an infinitely rapid trapping of the adsorptive from the close vicinity on the adsorption surface and the validity of a linear isotherm in the form of

$$q_\mathrm{A} = K c_\mathrm{A} \ , \qquad (2)$$

then one can rewrite Eq. (*1*) into the following form

$$\frac{\partial c_\mathrm{A}}{\partial \tau} = D_\mathrm{e} \, \Delta c_\mathrm{A} \ , \qquad (3)$$

in which diffusion coefficient D_e is given by the relation

$$D_\mathrm{e} = \frac{D'}{\beta + K} \ . \qquad (4)$$

Equation (*3*) can be solved analytically or numerically for a given form of particle of the porous medium and for chosen initial and boundary conditions. For cylindrical particles and symmetric diffusion, Eq. (*3*) can be rewritten to:

$$\frac{\partial c_\mathrm{A}}{\partial \tau} = D_\mathrm{e} \left(\frac{\partial^2 c_\mathrm{A}}{\partial r^2} + \frac{1}{r} \frac{\partial c_\mathrm{A}}{\partial r} + \frac{\partial^2 c_\mathrm{A}}{\partial z^2} \right) . \qquad (5)$$

If the cylindrical particle of the sorbent having radius R and length L is supposed to be without adsorbate and adsorptive and, from a certain time, a constant concentration of adsorptive c_{A1} is kept on the particle surface, one can define both initial and boundary conditions by

$$c_A(r,z,0) = 0; \quad c_A(R,z,\tau) = c_{A1}; \quad c_A(r,\pm L/2,\tau) = c_{A1}$$

$$\frac{\partial c_A(0,z,\tau)}{\partial r} = 0 \qquad \frac{\partial c_A(r,0,\tau)}{\partial z} = 0 \ . \tag{6}$$

By solving Eq. (*5*) for conditions (*6*), one obtaines the following result[6]:

$$\frac{c_A}{c_{A1}} = 1 - \sum_{n=1}^{\infty}\sum_{m=1}^{\infty} \frac{2}{\mu_n I_1(\mu_n)} (-1)^{m+1} \frac{1}{(2m-1)\pi} I_0(\mu_n, \frac{r}{R}) \ .$$

$$. \cos\frac{(2n-1)\pi z}{L} \exp\left[-\left(\frac{\mu_n^2}{R^2} + \frac{(2n-1)^2}{L^2}\right)^2 D_e \tau\right] \ . \tag{7}$$

Equation (*7*) makes it possible to calculate the concentration of adsorptive in an arbitrary place of the cylindrical adsorbent particle at a chosen time. In determining the values of effective diffusion coefficient, one should know the adsorbed amount or concentration of adsorbate at a chosen time. The required relation derived from Eqs (*2*) and (*7*) is given[6] by:

$$\gamma_\tau = \frac{\Delta m_\tau}{\Delta m_\infty} = \frac{q_{A\tau}}{q_{A\infty}} = 1 - \frac{32}{\pi^2}\sum_{n=1}^{\infty}\sum_{m=1}^{\infty} \frac{1}{\mu_n^2 (2m-1)^2} \exp\left[-\left(\frac{\mu_n^2}{R^2} + \frac{(2m-1)^2 \pi^2}{L^2}\right) D_e \tau\right] \ . \tag{8}$$

EXPERIMENTAL

1,2-Dichloroethane (DCE) contained 99.67 wt.% of DCE, and 0.29 wt.% and 0.04 wt.% of lower- and higher-boiling substances, respectively.

Activated carbon Supersorbon HS-4 in the form of cylinders with a mean diameter of 4.61 mm and a mean length of 6.70 mm.

Apparatus, schematically drawn in Fig. 1, consists of two flows necessary for ensuring the required flow rate of pure air and a required concentration of DCE. The prepared mixture of air and DCE passes the adsorber with an activated carbon bed height equal to the particle diameter and further adsorbers filled with activated carbon, in which the rest of the adsorptive is quantitatively entrapped. In the adsorbers, the activated carbon bed was placed in the centre of the adsorber and both the upper and the lower parts of the equipment were filled with hollow glass cylinders of approximately equal thickness and length as those of the activated carbon particle.

Prior to the measurement, all adsorbents were activated by heating at 150 °C at small flow rates of dried air for about 3 h. After reaching constant values of flow rates and adsorptive concentration (about 30 min), the flow rate of saturated air was switched to one of the adsorbers. The time course of the adsorbed amount was estimated by weighing the adsorbers. In our measurement, at least two adsorbers with a bed height equal to the particle diameter were used. The adsorption was carried out in one of these adsorbers and the other was weighed. The inlet concentration of adsorptive was estimated from the total adsorbed amount and the amount of air.

RESULTS AND DISCUSSION

From the measured set of data ($m_{\tau i}$; τ_i) and using Eq. (*8*), values of effective diffusion coefficients were calculated by the optimization method. As an optimization function, Eq. (*9*) was used:

$$F = \sum_{n=1}^{N} \left[\left(\frac{\Delta m_\tau}{\Delta m_\infty} \right)_{\mathrm{meas}} - \left(\frac{\Delta m_\tau}{\Delta m_\infty} \right)_{\mathrm{calc}} \right]^2 . \qquad (9)$$

The calculated values of effective diffusion coefficients along with measuring conditions are listed in Table I and plotted in Fig. 2.

The utilized measuring method, as it follows from initial and boundary conditions (*6*), necessitates keeping a constant concentration of adsorptive on the outer adsorption surface. It is obvious that the fulfilment of this condition requires a zero resitance to mass transfer in the fluid phase and, relative to the supplied amount of adsorptive, a negligible portion of adsorptive entrapped in the adsorber investigated. The foregoing facts are manifested in the plot D_e *vs* flow rate of gas. Figure 2 reveals that the used flow rate of 18 l min^{-1} is necessary for the adsorber utilized. At a flow rate of 4.8 l min^{-1}, the mass transfer resistance in the fluid phase, especially at higher adsorptive concentra-

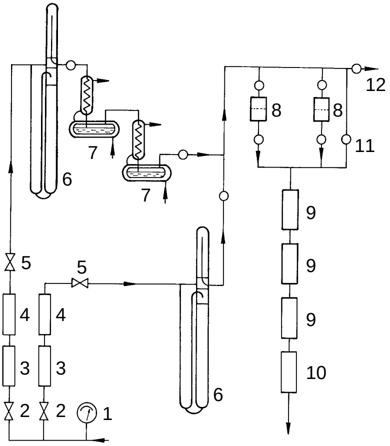

FIG. 1
Diagram of the experimental apparatus: 1 manometer, 2 distribution valve, 3 adsorber filled with activated carbon, 4 adsorber filled with silica gel, 5 needle valve, 6 flow-meter, 7 saturator, 8 adsorber with a differential bed of adsorbent, 9 adsorber filled with activated carbon, 10 adsorber filled with silica gel, 11 cock, 12 outlet of gas into the fume chamber

tions, cannot be neglected. The mass transfer resistance in the fluid phase affects the accuracy in determining D_e by the given method under conditions for which the determined value of D_e practically does not change with an increase in the flow rate. For the conditions of measurements, the mass transfer resistance in the flowing gaseous and solid phases was calculated using the following relations

TABLE I
Effective diffusion coefficients of 1,2-dichloroethane in particles of activated carbon Supersorbon HS-4

Measurement No.	Temperature °C	Air flow l min^{-1}	Superficial velocity of air m s^{-1}	Adsorptive concentration c_{A1} g m^{-3}	Effective diffusion coefficient D_e . 10^{10} $\mathrm{m^2\ s^{-1}}$
1	24.3	4.8	0.0349	1.0	0.35
2	26.0	4.8	0.0349	13.3	2.17
3	27.6	14.0	0.1019	12.5	4.13
4	26.4	18.0	0.1301	0.9	0.75
5	27.0	18.0	0.1301	5.8	2.01
6	27.1	18.0	0.1301	9.2	3.55
7	27.0	18.0	0.1301	12.0	4.34
8	27.6	18.0	0.1301	13.5	5.24

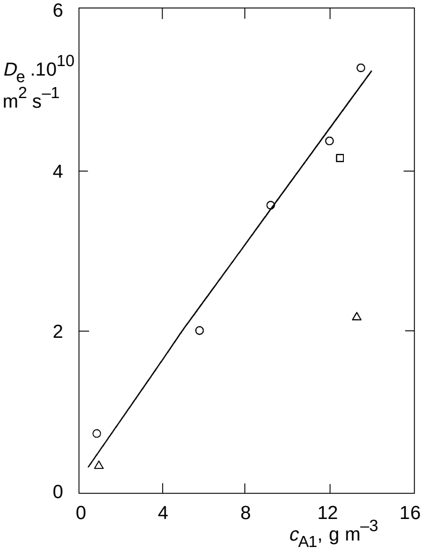

FIG. 2
Dependence of the effective diffusion coefficient (D_e) on the concentration of adsorptive (c_{A1}) in the flowing inert gas at various flow rates: Δ 4.8 l min^{-1}, ❐ 14.0 l min^{-1}, ❍ 18.0 l min^{-1}

$$\boldsymbol{n}_{\mathrm{A}} = K_{\mathrm{c}}(c_{\mathrm{A}} - c_{\mathrm{As}}) = k_{\mathrm{gc}}(c_{\mathrm{A}} - c_{\mathrm{Ai}}) = k_{\mathrm{sq}}(q_{\mathrm{Ai}} - q_{\mathrm{A}}) \qquad (10)$$

$$\frac{1}{K_{\mathrm{c}}} = \frac{1}{k_{\mathrm{gc}}} + \frac{1}{K k_{\mathrm{sq}}} \ . \qquad (11)$$

The value of k_{gc} was calculated from the dimensionless relation for the flow of gases through a fixed bed of solid particles[7]. Values of k_{sq} were calculated from the relation[8]:

$$k_{\mathrm{sq}} = \frac{10 D_{\mathrm{e}}}{d_{\mathrm{p}}} \ . \qquad (12)$$

The resistance of the fluid phase calculated from Eq. (*11*) did not exceed 12.5% of the total resistance. The relation used for the calculation of the mass transfer coefficient in the fluid phase is valid for adsorbers with a fixed bed of adsorbent. The used adsorber had the activated carbon bed with a height equal to the diameter of particles surrounded from both sides by inactive glass particles. Hence, the concentration field of adsorptive in the neighbourhood of adsorbent particles was more suitable than in the case of the adsorber filled only with activated carbon particles. The computed values of Sh number and k_{gc} are, therefore, lower than the real ones. Thus, the estimated mass transfer resistance of the fluid phase is the maximum value. The fact that the greatest possible value of this resistance is 12.5% suggests that the value of the mass transfer resistance in the

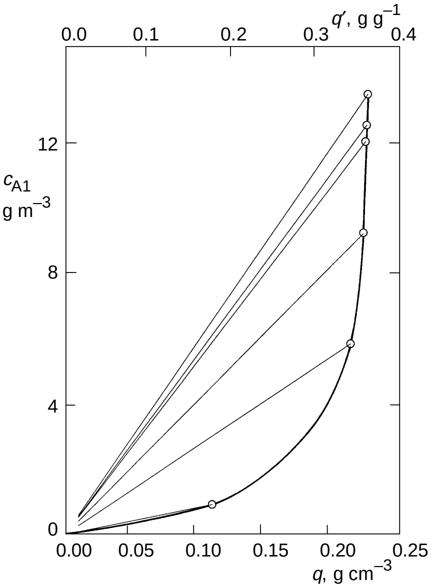

FIG. 3
Adsorption isotherm of 1,2-dichloroethane on activated carbon Supersorbon HS-4

solid phase, R_s, is loaded with a maximum error of 12.5%. By substituting the definition of k_{sq} from Eq. (*12*) into the expression for R_s, one obtains

$$D_e = \frac{d_p}{10KR_s} \ . \qquad (13)$$

From the last equation follows that the relative error of D_e is given by the sum of relative errors of d_p, K and R_s. For low values of K, provided that the adsorption isotherm of 1,2-dichloroethane on activated carbon could be approximated by a straight line, the relative error of D_e does not exceed 20%.

A linear isotherm is assumed in the model used. Figure 3 shows that this condition is only fulfilled for the investigated system at low concentrations. From the viewpoint of the magnitude of the driving force during adsorption, the real nonlinear course of the equilibrium curve is more favourable than the linear course used in the model.

In the literature, values of effective diffusion coefficients of DCE in activated carbon particles are not available. There is no discrepancy between the determined values and data published for other systems. From Fig. 2, a linear relation between the effective difffusion coefficient and the adsorptive concentration, ranging from 1 to 14 g m^{-3}, is apparent. Then, the relation obtained by the least-squares method has the following form:

$$D_e = 3.53 \ . \ 10^{-11} c_{A1} + 2.52 \ . \ 10^{-11} \ . \qquad (14)$$

Measurement No. 6 was carried out in such a manner that, prior to measurement, the adsorber was saturated with water vapour at its partial pressure 124 Pa. The same partial pressure of water vapour was also in the air used in the measurement of D_e. As can be seen in Fig. 2, the moisture content in the investigated range does not significantly influence the value of the effective diffusion coefficient. The moisture content in air has an influence on the equilibrium-adsorbed amount which, due to moisture, decreased by about 3 g/100 g activated carbon.

SYMBOLS

c_A	adsorptive concentration, kg m^{-3}
c_{Ai}	interfacial concentration of adsorptive in air, kg m^{-3}
c_{As}	fictitious concentration of adsorptive in equilibrium with q_A, kg m^{-3}
c_{A1}	adsorptive concentration in air at the adsorber inlet, kg m^{-3}
d_p	diameter of spherical particle, m
D_e	effective diffusion coefficient, m^2 s^{-1}
D'	diffusion coefficient in porous media, m^2 s^{-1}
I_0	Bessel function of the first kind and zero order

I_1	Bessel function of the first kind and first order
k_{gc}	individual mass transfer coefficient in fluid phase (defined by Eq. (*10*)), m s^{-1}
k_{sq}	individual mass transfer coefficient in solid phase (defined by Eq. (*10*)), m s^{-1}
K	equilibrium constant (defined by Eq. (*2*))
K_c	overal mass transfer coefficient (defined by Eq. (*10*), m s^{-1}
L	length of the adsorbent cylinder, m
Δm_τ	increment of the adsorbed amount per time τ, kg
Δm_∞	increment of the equilibrium adsorbed amount, kg
$\boldsymbol{n}_{Az}$	mass flux of component A in z direction relative to stationary coordinates, kg m^{-2} s^{-1}
q_A	adsorbate concentration, kg m^{-3}
q_{Ai}	interfacial concentration of adsorbate, kg m^{-3}
$q_{A\tau}$	increment of adsorbate concentration per time τ, kg m^{-3}
$q_{A\infty}$	equilibrium adsorbate concentration, kg m^{-3}
r	radial coordinate, m
R	radius of adsorbent particle, m
R_s	mass transfer resistance in the solid phase, s m^{-1}
z	axial coordinate, m
β	porosity of solid medium
μ_n	roots of Bessel function of the first kind and zero order
τ	time, s

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