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ESTIMATION OF EFFECTIVE DIFFUSION COEFFICIENTS FROM BREAKTHROUGH CURVES

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Abstract

The purpose of this study was to present the possibility of calculation of effective diffusion coefficients from experimentally obtained breakthrough curves. From the course of adsorption of n-heptane from a mixture with methylcyclohexane in a fixed bed of molecular sieve Calsit - 5 at temperatures 120, 210, and 340ºC the heights of the mass transfer zone ranging from 6.3 to 49.2 cm were computed. This height depends upon the temperature, adsorbent particle size and hydrodynamic conditions. For the relative mass ratio of n-heptane in the feed stream 0.12 kg.kg^{-1} the following numbers of transfer units for the overall driving force in the gas phase were calculated: 3.37; 3.45 and 4.88 at the respective temperature of 120ºC, 210ºC, and 340ºC. The calculated values of the overall volume coefficient K_ya ranging from 10 000 to 25 000 kg.m^{-3} .h^{-1}.(mass ratio)$^{-1}$ increase with an increase in the *Re* number to a certain value and then, they remain constant. At 210ºC and in the region, where the mass transfer coefficient does not change, the individual mass transfer resistance in the solid phase accounts for already 98.99 % of the overall mass transfer resistance. The corresponding value of the effective diffusion coefficient of n-heptane in the particles of molecular sieve Calsit - 5 is 3.824.10^{-10} m^2.s^{-1} at 210ºC. The calculated value of the activation energy of diffusion of n-heptane in the particles of molecular sieve Calsit - 5 is 15.777 kJ. mol^{-1}.

Key words: n-heptane, diffusion, effective diffusion coefficient, molecular sieve, breakthrough curve, adsorption

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In designing adsorbers by physically substantiated methods the mass transfer resistance is divided into two individual resistances: the resistance against mass transfer in the fluid phase flowing through the adsorbent bed and the resistance against mass transfer in adsorbent particle pores. Both resistances can be significant and should be taken into account. The mass transfer resistance in the fluid phase is well described in the literature. In the designs this resistance is usually expressed by the individual coefficient of mass transfer, whose values can be calculated by relations available for example in references[1],[2]. The mass transfer in adsorbent particles is described by unsteady diffusion employing the second Fick´s law, in which the effective diffusion coefficient is the only quantity, which takes into account properties of both the porous body and the transported component, at adsorption conditions. The values of the effective diffusion coefficient can be estimated experimentally by various methods. Post reports in his work[3] that the values of effective diffusion coefficients of substances measured on molecular sieves by various methods differ by several orders of magnitude. Therefore, in the choice of data used in designing adsorbers one should use values obtained by methods, which apply the conditions close to the conditions of industrial adsorption.

For the effective diffusion coefficient estimation, experimental data of breakthrough curves are employed.

THEORETICAL

For the differential section of adsorbent bed (in the mass transfer zone) the following rate equation holds:

$$\dot{G}dY_A = K_Y a\left(Y_A - Y_{AS}\right)Sdz = K_y a \frac{Y_A - Y_{AS}}{\left(1+Y_A\right)\left(1+Y_{AS}\right)}Sdz \qquad (1)$$

where $\dot{G}$ is the flowrate of the component not being adsorbed, Y_A is the relative fraction of adsoptive, S is the cross-section of adsorber, z is the axial coordinate, $K_Y a$ and $K_y a$ are overall mass transfer coefficients in expressing the driving force in the gas phase by relative fraction and/or mole fraction. By integrating Eq. (1) one obtaines

$$Z_a = \frac{\dot{G}}{SK_y a}\int_{Y_1}^{Y_2} \frac{Y_A - Y_{AS}}{\left(1+Y_A\right)\left(1+Y_{AS}\right)}dY_A \qquad (2)$$

or

$$Z_a = H_{TOG}.N_{TOG} \qquad (3)$$

where Z_a – height of the mass transfer zone, H_{TOG} – height of transfer unit and N_{TOG} – number of transfer units

The height of the mass transfer zone can be calculated from the data of breakthrough curves using the following relationship:

$$\frac{Z_a}{Z} = \frac{\tau_a}{\tau_N - \tau_F} = \frac{G_a}{G_N - G_F} \qquad (4)$$

where Z is the overall height of the adsorbent bed, $\tau_a = \tau_N - \tau_P$, in which τ_N and τ_P correspond to the time of saturation and breakthrough on the experimental curve $Y/Y_o=f(\tau)$, as can be seen in Fig. 1, Y_o is the relative fraction of adsorptive in the feed stream, τ_F is the time necessary for formation of the mass transfer zone in the adsorbent bed, $G_a = G_N - G_P$, in which G_N and G_P are the respective amounts of the passing inert in the saturation point and breakthrough point on the curve Y/Y_o =f(G).

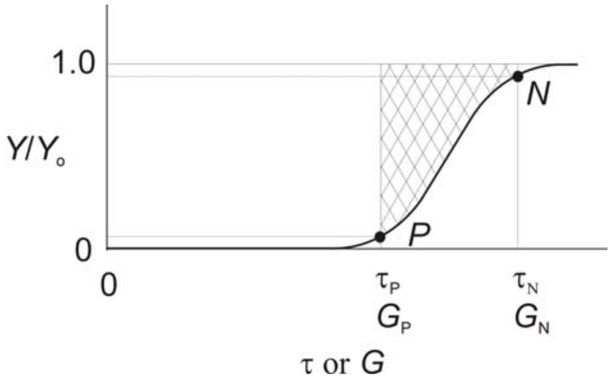


Fig. 1. Dependence Y /Yo=f(τ) or Y /Yo =f(G). P-breakthrough point, N-saturation point.

The quantities τ_F and G_F are defined as follows

$$\tau_F = \left(1-f\right)\tau_a = \left(1-f\right)\left(\tau_N - \tau_P\right) \qquad (5)$$

$$G_F = \left(1-f\right)G_a = \left(1-f\right)\left(G_N - G_P\right) \qquad (6)$$

where the adsorption ability of the adsorbent in the mass transfer zone is given by

$$f=\frac{\int_{G_P}^{G_N}(Y_o-Y)dG}{GY_o}=\frac{\int_{G_P}^{G_N}(1-Y/Y_o)dG}{G} \qquad (7)$$

From the data of the breakthrough curve and by using relations (4) - (7) one may get values Z_a. The number of transfer units may be obtained from equilibrium data and the operating line. The value of the overall mass transfer coefficient may be then calculated from Eq. (2).

It is obvious that the total mass transfer resistance includes the resistance to mass transfer in the fluid phase and solid adsorbent pores. Hence,

$$\frac{1}{K_y a}=\frac{1}{k_y a}+\frac{m''}{k_x a} \qquad (8)$$

or

$$R=R_G+R_S \qquad (9)$$

where $k_y a,\ k_x a$ are the individual volumetric mass transfer coefficients in the gas and solid phases, R, R_G and R_S are the total resistance to mass transfer, and individual resistances to mass transfer in the gas and solid phases, respectively. The quantity m'' is defined by the expression

$$m''=\frac{y_{Ai}-y_{AS}}{x_{Ai}-x_A} \qquad (10)$$

At known total mass transfer resistance and individual resistance in the fluid phase, one can calculate from Eq. (9) the individual resistance to mass transfer in the solid phase. This enables to calculate the effective diffusion coefficient by using equation[4].

$$k_q a_p=\frac{60D_e}{d_p^2} \qquad (11)$$

in which k_q is the individual mass transfer coefficient in the solid phase, whereas the adsorbate concentration is related to the volume of particles, a_p is the volumetric surface of adsorbent particle and D_e is the effective diffusion coefficient.

EXPERIMENTAL

Materials used:

n-heptane, chromatographic composition: 99.7mol % n-heptane and 0.3 mol.% methylhexane, density 0.6838 g.cm^{-3}, boiling point 98.3ºC. Methycyclohexane, chromatographic composition: 0.09 % n-hexane, 0.55 % 2-methylhexane, 0.09 % 3-methylhexane, 0.96 % n-heptane, 98.31 % methylcyclohexane. Molecular sieve Calsit – 5, produced in Slovnaft VÚRUP, sieve fraction 0.8-0.9 mm, mineral density 2.858g.cm^{-3}, volume of intracrystalline cavities 0.215 cm^3.g^{-1}, bulk density 0.800 g.cm^{-3}, particle density 1.120 g.cm^{-3}.

The measuring method used:

In measurements an apparatus schematically drawn in Fig. 2 was employed. An n-heptane-methylcyclohexane mixture of required concentration is fed by a plunger pump 2 into a glass evaporator 4. The feed vapours are directed through adsorber 5 filled with a molecular sieve and glass beads. The residue, which has not been adsorbed, is directed through a cooler, where it condenses and cools down. The cooled residue is quantitatively entrapped, whereas the concentration of n-heptane is examined by a refractometer. The temperature of the evaporator was chosen to be by 20 – 100ºC higher than the boiling point of the feed.

Prior to measurements, the molecular sieve was heated in an oven to a temperature of 400 ºC for 2 hours at a low flow-rate of pure nitrogen, in which oxygen was removed by absoption in pyrogalol, and water by molecular sieves.

RESULTS AND DISCUSSION

The courses of adsorption of the model mixture of n-heptane-methylcyclohexane were measured experimentally at chosen flow-rates of the feed stream and temperatures of 120, 210, and 340ºC. From the measured dependences by using Eqs. (4) - (7) the heights of mass transfer zones were calculated. The obtained values are depicted in Fig. 3 against the modified Reynolds number, which is defined as:

$$\mathrm{Re} = \frac{d_p w \rho}{\mu} \qquad (12)$$

where d_p is the mean diameter of adsorbent particle, w is the superficial velocity of inert, ρ is the density of inert and μ is the viscosity of inert at adsorption temperature.

By using equilibrium data of the coordination system $\overline{Y} - \overline{X}$ (mass relative fractions) the following numbers of transfer units N_{TOG} were calculated for the used relative mass fraction of n-heptane in methylcyclohexane in the feed $\overline{Y}_0 = 0.12$ kg.kg^{-1} and for the overall driving force in the gas phase:

3.37 at a temperature of 120ºC,
3.45 at a temperature of 210ºC and
4.88 at a temperature of 340ºC.

Then, the overall volume mass transfer coefficients were calculated by using Eq. (2). The dependence of these coefficients upon the modified Reynolds number is depicted in Fig. 4.

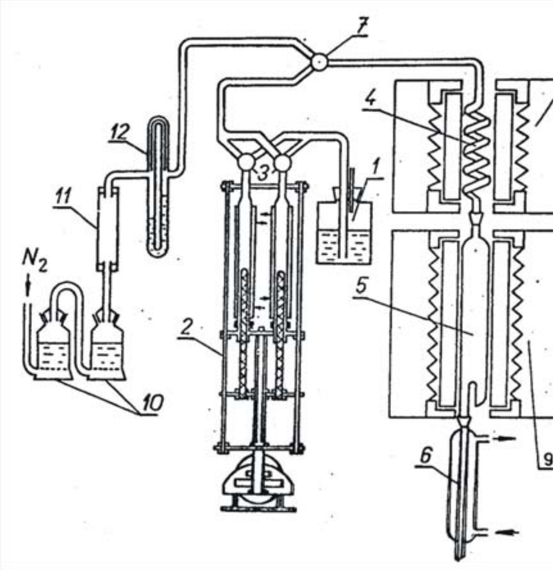


Fig. 2. Schematic diagram of apparatus employed: 1-feed tank, 2-plunger pump, 3-distribution valves, 4-evaporator, 5-adsorber, 6-cooler, 7, 8, 9-ovens, 10-washing bottle, 11-adsorber filled with molecular sieve, 12-flowmeter

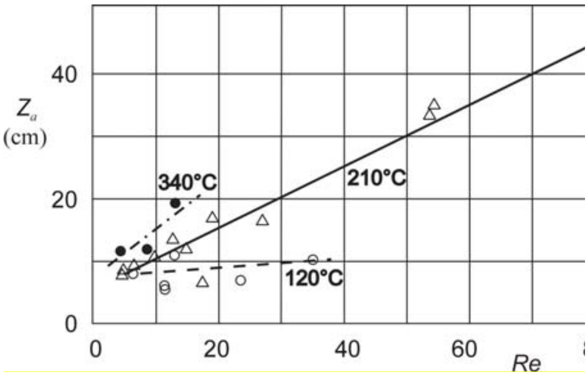


Fig. 3. Dependence of the height of the mass transfer zone upon the modified *Re* number at temperatures of 120ºC, 210ºC, and 340ºC

In this picture we can see that the height of the mass transfer zone increases with *Re*, whereas this growth increases with temperature.

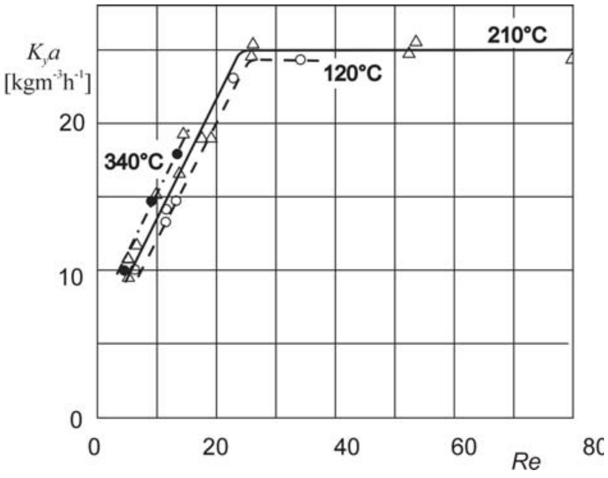
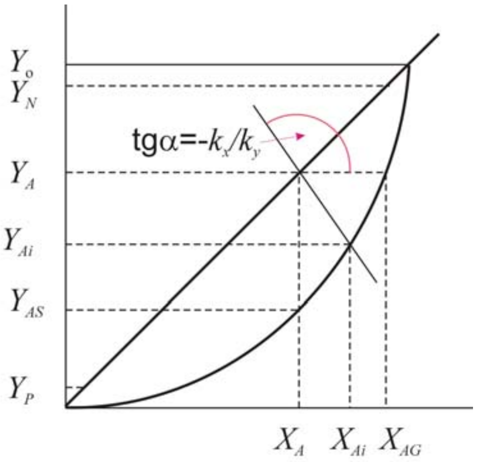


Fig. 4. Dependence of K_ya upon the modified *Re* number at temperatures of 120 ºC, 210 ºC, and 340ºC



$$m'' = \frac{Y_{Ai}-Y_{AS}}{X_{Ai}-X_A} \qquad m = \frac{Y_A-Y_{AS}}{X_{AG}-X_A}$$

Fig. 5. Illustration of driving forces

Fig. 4 (Dependence of K_ya upon the modified *Re* number) documents that in the regions of low *Re* number the mass transfer resistance in the flowing fluid phase decreases with increasing *Re*. After reaching a certain minimum resistance to mass transfer in the flowing phase corresponding to the minimum thickness of the diffusion film surrounding the adsorbent particle the resistance in the fluid phase does not vary. Hence, also the overall volumetric coefficient of mass transfer does not change, because the resistance to mass transfer in the solid porous body does not depend upon the flow-rate of the stream directed through the fixed bed. At a temperature of 210ºC these conditions are fulfilled at *Re* = 30, when the overall volumetric coefficient of mass transfer is 25 000 kg.m^{-3}.h^{-1}(mass fraction)$^{-1}$. Then,

$$\dot{G}_S = \frac{\mathrm{Re}\,\mu}{d_p} = \frac{30\text{x}1.15.10^{-5}}{0.85\text{x}10^{-3}} = 0.40588 \text{ kg m}^{-2}\text{s}^{-1}\text{=1 461.2 kg m}^{-2}\text{h}^{-1}.$$

The diffusion coefficient of n-heptane in the mixture with methylcyclohexane at 210ºC calculated according to the relation given in paper[5] is D_{AB} = 0.06224 cm^2 s^{-1}. The density of the gas phase at 210ºC calculated from the equation of state for an ideal gas is 2.4719 kg m^{-3}. The idividual mass transfer coefficient in the gas phase can be calculated from the relations derived in accordance with the Chilton and Colburn analogy published by Treybal[1], in the following way:

$$j_D.10^{-1} = \frac{k_y}{\dot{G}_S} Sc^{0,66}.10^{-1}$$

and for *Re* = 30 one obtains

$$k_y = \frac{0.033\dot{G}_S}{10^{-1}Sc^{0,66}} = \frac{0.33\text{x}1461{,}2}{0.7475^{0,66}} = 584.293 \text{kg.m}^{-2}\text{h}^{-1}\text{(mass fraction)}^{-1}$$

The volumetric outer surface of the molecular sieve bed of particles is defined as

$$a = a_p(1-\varepsilon) = \frac{6\left(1-\varepsilon\right)}{d_p} = \frac{6(1-0{,}4)}{0{,}85.10^{-3}} = 4235.3\text{m}^2\text{m}^{-3}$$

Then, k_ya = 584.293x4235.3 = 2 474 656 kg.m^{-3}h^{-1}. The relative high value of the individual volumetric coefficient in the gas phase manifests a small resistance against mass transfer in the gas phase. Hence, the resistance to mass transfer in the solid phase defined as

$$R_2 = \frac{1}{25000} - \frac{1}{2474656} = 4.0000\text{x}10^{-5} - 4.041\text{x}10^{-7} = 3.9596\text{x}10^{-5}\,\text{m}^3\text{.h.kg}^{-1}$$

accounts for 98.99 % of the overall resistance to mass transfer. With regard to the fact that the value of the individual resistance to mass transfer in the solid phase is approaching the value of the total resistance to mass transfer one can write:

$$m'' \cong m = \frac{y_A - y_{AS}}{x_{AG} - x_A} \tag{13}$$

It is obvious that the value of *m* is changed along the height of the mass transfer zone. Driving forces of the process are schematically shown in Fig. 5. One can see determination of driving forces at considered condition. The calculated values of individual mass transfer coefficients corresponding to the average relative mass fractions of adsorbate at the beginning, in the middle and at the end of the mass transfer zone are listed in Tab. 1.

Tab. I. The calculated values of individual mass transfer coefficients and effective diffusion coefficients in chosen places of the mass transfer zone.

$X_S.10^2$ kg.kg^{-1}	m 1	k_xa kg.m^{-3}h^{-1}(mass fraction)$^{-1}$	k_qa_p kg.m^{-3}h^{-1}(kg.m^{-3})$^{-1}$	$D_e.10^{10}$ m^{2}s^{-1}
6.50	3.042	76 817	114.311	3.824
7.18	7.421	187 415	278.891	9.329
7.85	11.80	298 011	443.469	14.834

From the values of k_xa the values of k_qa_p were computed from the relation

$$k_q a_p = \frac{k_x a}{(1-\varepsilon)\rho_p} \tag{14}$$

where ρ_p is the density of adsorbent particles. In Tab. I. are also given the values of the effective diffusion coefficients calculated from relation (11). These values increase with increasing adsorbate concentration. They are in agreement with the published values obtained for similar systems at corresponding measurement conditions.

In paper[6] are reported data of diffusion coefficients of n-heptane from air on particles of molecular sieve Calsit 5 and molecular sieve 5A (Union Carbide) at 30 ºC. For stepwise adsorption on the molecular sieve Calsit 5 and at X_S = 0.0383 kg.kg^{-1} the value of D_e = 3.71x10^{-11}m^{2}s^{-1}. With regard to the concentration the published value approaches D_e = 3.824x10^{-10}m^{2}s^{-1}. Supposing that diffusion in molecular sieves is an activated process, one can calculate from the above-mentioned two data the activation energy of diffusion from the following relation[7].

$$D_e = D_{e0} e^{-\frac{E}{RT}} \tag{15}$$

The calculated value of the activation energy of diffusion of n-heptane in the particles of molecular sieve Calsit 5 is 15.770 kJ.mol^{-1}, what corresponds to the system investigated.

REFERENCES

[1] Treybal R.E.: Mass Transfer Operations, Mc Graw-Hill Book Corp. INC., New York, 1968

[2] Knudsen J.G., Hottel H.C., Sarofim A.F., Wankat P.C., Knaebel K.S.: Heat and Mass Transfer, in Perry's Chemical Engineers' Handbook, Seventh Edition, Ed. By R.H. Perry, D. W. Green, J.O. Mahoney, International edition, 1977

[3] Post M.F.M.: Diffusion in Zeolite Molecular Sieves, in: Introduction to Zeolite Science and Practice, Ed.: H.van bechhum, E.M. Elaningen and J.C. Jansen, Elsevier (1991)

[4] Lightfoot E.N., Sanchez-Palma R.J., Edwards D.O.: Chromatography and Allied Fixed – Bed Separations Processes, in New Chemical Engineering Separations Techniques, Ed. By H.M. Schoen, Interscience Publishers, New York, London, 1962

[5] Fuller E.N., Schettler P.D., Giddings J.C.: Ind. Eng. Chem., **58**(3) 19 (1966)

[6] Bobok D., Besedová E., Petroleum and Coal, **45**(1-2) 19 (2003)

[7] Kärger J., Ruthven D.M.: Diffusion in Zeolites and Other Microporous Solids, John Wiley and Sons, INC., New York, 1992