Diffusion Coefficients of n-Hexane in Particles of Molecular Sieve NaY
Determined by means of Chromatographic Measurements

D. BOBOK and M. ONDREJKOVÁ

Department of Chemical and Biochemical Engineering, Faculty of Chemical Technology,
Slovak Technical University, CS- 812 37 Bratislava

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The values of effective diffusion coefficients of n-hexane in the presence of nitrogen \((1.48-5.60) \times 10^{-9} \text{ m}^2 \text{s}^{-1}\) were determined at \(160-240 \degree \text{C}\) under the assumption that the particle of molecular sieve NaY can be described by a quasi-homogeneous model. Considering a biporous structure in this particle, the determined values of diffusion coefficients \(D_{ij}/r_{ij}^2\) of n-hexane in a molecular sieve crystal in the presence of nitrogen are ranging from 32.4 to 41.4 \text{s}^{-1}.

Values of diffusion coefficients in a single particle of adsorbent as well as equilibrium data are a necessary prerequisite for mathematical modelling of the adsorption separation units. With regard to the complexity of the adsorbent structure, a dependence of the diffusion coefficient on the properties of adsorbent, adsorptive, and carrier gas has not been formulated up to now. In characterizing the transport of adsorptive in a single adsorbent particle, experimental values of diffusion coefficients are used in models describing both adsorption and desorption.

In describing the transport of adsorptive in a complicated porous structure of adsorbent, mostly two approaches are applied. In the first one, the porous substance is supposed to be a quasi-homogeneous isotropic medium from the standpoint of mass transport [1, 2]. The second one proposes that the porous structure of the adsorbent particle can be approximated by two kinds of pores, i.e. by the so-called biporous structure [3, 4]. Particles of molecular sieve NaY employed in this study consist of zeolite crystals with dimensions in \(\mu\text{m}\), entrance openings of nm irregularly distributed in a particle of adsorbent and joined by the secondary pores having a most frequent radius of about 120 nm [5]. Therefore, the assumption to describe the mass transfer in a particle of adsorbent also by diffusion in a biporous particle of adsorbent is justified.

The relationships used for the determination of diffusion coefficients are presented in [5].

EXPERIMENTAL

n-Hexane (Lachema, Brno) had the following composition (\(\text{x/mole \%}\)): n-hexane 98.47; 3-methylpentane 1.13; 2-methylpentane 0.40.
Elution chromatographic curves for n-hexane from a molecular sieve bed NaY at temperatures of 160, 200, and 240 °C and flow-rates of carrier gas from 115 to 378 cm$^3$ min$^{-1}$ were estimated on an apparatus described previously [5]. The characteristics of columns and working conditions are given in Table 1.

Table 1. Characteristics of Columns and Working Conditions

<table>
<thead>
<tr>
<th>Quantities</th>
<th>Column</th>
<th>Column 2</th>
<th>Column 3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Length of bed /cm</td>
<td>3.70</td>
<td>3.80</td>
<td>3.60</td>
</tr>
<tr>
<td>Inside diameter of column /mm</td>
<td>8.3</td>
<td>8.3</td>
<td>8.3</td>
</tr>
<tr>
<td>Fraction of particles /mm</td>
<td>0.40—0.63</td>
<td>0.63—0.71</td>
<td>0.80—1.00</td>
</tr>
<tr>
<td>Equivalent radius of particles /mm</td>
<td>0.251</td>
<td>0.334</td>
<td>0.447</td>
</tr>
<tr>
<td>Bulk density / (kg m$^{-3}$)</td>
<td>706</td>
<td>636</td>
<td>562</td>
</tr>
<tr>
<td>Porosity of bed / (m$^3$ m$^{-3}$)</td>
<td>0.411</td>
<td>0.470</td>
<td>0.531</td>
</tr>
<tr>
<td>Flow of carrier gas / (cm$^3$ min$^{-1}$) / (25 °C, 101.3 kPa)</td>
<td>115—378</td>
<td>135—371</td>
<td>130—345</td>
</tr>
</tbody>
</table>

In the treatment of results, times for injecting samples into the column were neglected. The value $\hat{\Theta}/12$ was smaller than 5 % of the lowest value of the second statistical moment. Furthermore, correction with regard to dead volumes was omitted.

Statistical moments of n-hexane determined from measurements in columns filled with glass spheres having an equivalent radius of 0.433 mm did not reach 3 % of the values of statistical moments determined from measurements on particles of molecular sieve NaY.

RESULTS AND DISCUSSION

The values of $\mu'$ found for individual screened fractions of the particles of molecular sieve NaY and given temperatures are plotted as a function of $L/\nu$ in Fig. 1. In this figure the 95 % and 99 % confidence intervals of the slopes of the investigated relationship are also marked. The confidence intervals of the slope of the straight line were calculated according to the Student distribution $t$ on a chosen level of significance. The determined values of equilibrium constant $K$ and values of intervals of reliability $K_k$ are listed in Table 2.

According to the van't Hoff equation, the relationship between log $K$ and $1/T$ represented in Fig. 2 enabled to determine the change in adsorption enthalpy ($-\Delta H_f$) = 39.3 kJ mol$^{-1}$.

The values of diffusion coefficients $D'$ determined according to eqns (13) and (14) in Ref. [5] on the assumption that a particle of adsorbent represents a quasi-homogeneous medium and using dependences illustrated in Figs. 3 and 4 are given in Table 3. The values of effective diffusion coefficients $D_e$ calculated by eqn (24) in Ref. [5] are also given in Table 3.

![Fig. 1. Relationship $\mu' = f(L/\nu)$. Screened fraction of particles of molecular sieve NaY with diameter of 0.80—1.00 mm (O), 0.63—0.71 mm (d), 0.40—0.63 mm (Δ); ---- 95 % confidence interval, ···· ···· 99 % confidence interval, —— obtained by the least squares method.](image-url)
Table 2. Values of Equilibrium Constants of n-Hexane on Molecular Sieve NaY and Intervals of Reliability

<table>
<thead>
<tr>
<th>Quantities</th>
<th>Temperature</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>160 °C</td>
</tr>
<tr>
<td>Number of measurements</td>
<td>21</td>
</tr>
<tr>
<td>$K/(m^3 \cdot kg^{-1})$</td>
<td>0.768</td>
</tr>
<tr>
<td>$\chi_y/(m^3 \cdot kg^{-1})$</td>
<td>0.179</td>
</tr>
<tr>
<td>95 % interval</td>
<td>0.243</td>
</tr>
</tbody>
</table>

Fig. 2. Relationship $K = f(1/T)$.

The validity of relationship (24) for $D_e$ is based on the presumption of an infinite rate of trapping the adsorptive in the solid surface from immediate proximity or an infinite rapid transformation of adsorptive into adsorbate at the adsorption surface.

The values of diffusion coefficients $D'$ of n-hexane in the pores of particles of molecular sieve NaY decrease with increasing temperature, which is in discrepancy with theoretical knowledge concerning the dependence of the diffusion coefficient on temperature. This discrepancy will be studied in more detail in further works. The above-mentioned anomaly can be explained in the following way:

The values $D'$ include the simultaneous course of adsorption and diffusion of adsorptive. Thus, these values depend not only on the transport properties of the system, but also on the rate of trapping adsorptive in the active surface. If one accepts the conditions of validity of the relation for $D_e$, then the adsorption rate is directly proportional to the equilibrium adsorption constant $K$.

Table 2 reveals that over the investigated range of temperature 160—240 °C, this constant decreases from 0.768 to 0.141 $m^3 \cdot kg^{-1}$, while the coefficient of molecular diffusion increases only about 1.3-times. Thus, it may happen that the temperature dependence of $D'$ is given by the dependence of the equilibrium adsorption constant on temperature. From the relation for $D_e$ the influence of the rate of adsorption on $D'$ and $D_e$ is evident. Relatively great changes of the value of the equilibrium constant with temperature caused that in contradistinction to $D'$, the values of $D_e$ increase with increasing temperature.
Fig. 4. Relationship \( \delta_1 + \delta_2 = f(R_0^2) \). ○ 160 °C, □ 200 °C, △ 240 °C.

Table 3. Diffusion Coefficients of n-Hexane in Particles of Molecular Sieve NaY

<table>
<thead>
<tr>
<th>( \theta/°C )</th>
<th>( D' \times 10^6 ) ( \text{m}^2 \text{s}^{-1} )</th>
<th>( D_e \times 10^6 ) ( \text{m}^2 \text{s}^{-1} )</th>
<th>( D_i \times 10^6 ) ( \text{m}^2 \text{s}^{-1} )</th>
<th>( D_e/R_0^2 ) ( \text{s}^{-1} )</th>
<th>( D_e \times 10^{12} ) ( \text{m}^2 \text{s}^{-1} )</th>
<th>( D_p \times 10^6 ) ( \text{m}^2 \text{s}^{-1} )</th>
<th>( D_{kp} \times 10^6 ) ( \text{m}^2 \text{s}^{-1} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>160</td>
<td>1.36</td>
<td>1.48</td>
<td>2.46</td>
<td>32.4</td>
<td>8.10</td>
<td>2.72</td>
<td>9.22</td>
</tr>
<tr>
<td>200</td>
<td>1.25</td>
<td>3.50</td>
<td>1.42</td>
<td>36.5</td>
<td>9.13</td>
<td>3.15</td>
<td>9.63</td>
</tr>
<tr>
<td>240</td>
<td>0.952</td>
<td>5.60</td>
<td>1.03</td>
<td>41.4</td>
<td>10.40</td>
<td>3.65</td>
<td>10.0</td>
</tr>
</tbody>
</table>

*Calculated for \( r_0 = 0.5 \times 10^{-6} \) m.

For systems n-hexane—particles of molecular sieve NaY, we have not found values of diffusion coefficients measured in the presence of an indifferent component in available literature. Eberly [6] found out for the system n-hexane—particles of molecular sieve NaY at 93 °C by using the gravimetric method in the absence of an indifferent component that \( D_e/R_0^2 = 0.137 \text{ s}^{-1} \). This made possible to calculate \( D_e = 1.44 \times 10^{-5} \text{ m}^2 \text{s}^{-1} \) for the applied effective radius of particles of sieve 0.324 mm. Though, this value is consistent with the determined values of \( D_e \), it shows a significant difference between the values of effective diffusion coefficients of compounds in particles of molecular sieve determined in the absence or presence of an indifferent component.

In Table 3 are also presented diffusion coefficients of the molecular \( D_p \) and Knudsen diffusion \( D_{kp} \) found for the mean radius of straight pores of a molecular sieve particle \( r_a = 2.412 \times 10^{-7} \) cm, calculated on the porous medium according to eqn (26) in Ref. [5]. The value of the tortuosity factor was in accordance with [7, 8] chosen as \( \tau_m = 4 \). Calculated values of diffusion coefficients of the molecular and Knudsen diffusion in a porous medium are more than one decimal order higher than the determined values of effective diffusion coefficients. Thus, we can conclude that during the transport of n-hexane in a particle of molecular sieve NaY in the presence of nitrogen, besides the molecular and Knudsen diffusion, also diffusion in the crystal of zeolite plays an important role.

The values of diffusion coefficients of n-hexane in transport pores and in the zeolite crystals determined by means of eqns (15—18) in Ref. [5] from the curves given in Fig. 5 are listed in Table 3. The values of diffusion coefficients in transport pores \( D_v \), as well as the values of \( D' \) for the quasi-homogeneous model decrease with an increase in temperature. The cause of this apparent nonlogic consists in the fact that the experimental values \( D_i \) include also the influence of adsorption in crystals of zeolite, a so-called “sucking” of the adsorptive. This phenomenon is the higher, the higher is the equilibrium adsorbed amount, i.e. the equilibrium constant, under given conditions. A comparison of the values of \( D_i \) with calculated values of coefficients of molecular diffusion in a porous medium \( D_p \) and coefficients of Knudsen diffusion \( D_{kp} \) presented in Table 3 reveals that in the secondary pores of molecular sieve NaY the transport of n-hexane by molecular diffusion can be supposed.

Calculated values of \( D_a \) for \( r_0 = 0.5 \times 10^{-6} \) m listed in Table 3 are in agreement with the value of \( 4.23 \times 10^{-12} \text{ m}^2 \text{s}^{-1} \) found by Hsu and Haynes [9].
for the system n-hexane—crystals of molecular sieve NaY at 202 °C.

SYMBOLS

\[ \begin{align*}
D' & \quad \text{diffusion coefficient} \quad \text{m}^2 \text{s}^{-1} \\
D_a & \quad \text{diffusion coefficient} \quad \text{m}^2 \text{s}^{-1} \\
D_e & \quad \text{effective diffusion coefficient} \quad \text{m}^2 \text{s}^{-1} \\
D_i & \quad \text{diffusion coefficient} \quad \text{m}^2 \text{s}^{-1} \\
D_p, D_{kp} & \quad \text{coefficients of the molecular and Knudsen diffusion} \quad \text{m}^2 \text{s}^{-1} \\
K & \quad \text{equilibrium adsorption} \quad \text{m}^3 \text{kg}^{-1} \\
L & \quad \text{height of a bed of adsorbent} \quad \text{m} \\
r_0 & \quad \text{radius of zeolite crystals} \quad \text{m} \\
R_0 & \quad \text{radius of particles} \quad \text{m} \\
v & \quad \text{interparticle velocity} \quad \text{m s}^{-1} \\
\delta_a, \delta_i, \delta_l & \quad \text{moment contributions given by eqns (13—18) in [5]} \\
\mu_1 & \quad \text{the first simple statistical moment} \quad \text{s} \\
\mu_2 & \quad \text{the second central statistical moment} \quad \text{s}^2 \\
\tau_0 & \quad \text{time at the injection of sample into the column} \quad \text{s} \\
\tau_m & \quad \text{tortuosity factor} \quad -
\end{align*} \]

REFERENCES


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