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# Nonlinear driving force approximation for intraparticle mass transfer in adsorption processes

## Nonlinear isotherm systems with macropore diffusion control

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**Abstract**

A generalized nonlinear driving force (NLDF) approximation of intraparticle mass transfer rate for nonlinear isotherm systems with macropore diffusion control is presented. The obtained expression is compared with the solutions of the Fickian diffusion and adsorption model and excellent accuracy over the entire time (fractional uptake) domain and for all values of the Freundlich exponent (adopted as the isotherm nonlinearity measure) is demonstrated. The high accuracy of the model is further demonstrated by comparison with experimental data. The presented methodology for the derivation of driving force approximations is shown to be a useful alternative to the methodology based on intraparticle concentration profile approximations.

*Keywords:* Nonlinear driving force; Fickian diffusion; Macropore diffusion control; Kinetics; Freundlich isotherm

## 1. Introduction

The modeling of transient diffusion and adsorption/reaction processes in porous particles requires the numerical solution of a system of partial differential equations involving time and spatial variables [1–3]. The substantial simplification of computations resulting from the application of approximate models has motivated numerous studies whose aim was to develop and assess the applicability and accuracy of such models [4–40]. A detail review of the work done until 1995 is presented by Mendes et al. [4]. A careful analysis of the currently available models shows that:

(1) The majority of the available models is based on the assumption of a linear isotherm. In many systems of practical importance, however, the isotherm nonlinearity cannot be neglected. Nevertheless very often the same approximations are applied for linear and nonlinear systems, and the errors resulting from this fact are overlooked. In particular, the application of linear models to derive kinetic parameters for nonlinear sorption isotherm systems leads to significant errors. This issue is discussed in [5] and the necessity to apply nonlinear models for experimental data interpretation is stressed.
(2) Most of the models are highly inaccurate in the short time region because they do not capture the singular nature of the unit step [6]. This is particularly true for the widely applied linear driving force models. Such models cannot be used in the modeling of kinetic separations where the dimensionless diffusion time for the slow diffusing component is well below 0.003 [7].
(3) Some models lead to expressions where the time variable appears explicitly. Such models are difficult to be used in the modeling of distributed parameter systems (e.g. fixed-bed adsorbers).
(4) None of these models has been tested against experimental data for the prediction of integral step uptake curves.

In this study, an analysis of the case of pore diffusion control adsorption kinetics with a nonlinear isotherm is presented. As a result of this analysis, a new nonlinear driving force (NLDF) model is developed. The new model is highly accurate (maximum error 2.8%) significantly improving on currently available approximations for all values of time and for all values of the Freundlich exponent $\nu$ (adopted as the isotherm nonlinearity measure). The new model is asymptotically exact both for short and long times. Furthermore for $\nu = 0$ (irreversible isotherm), the model reduces to the exact analytical solution resulting from the shell model.

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**Nomenclature**

| | |
|---|---|
| $\bar{A} = m_A/m_{A\infty}$ | fractional uptake |
| $C$ | fluid phase concentration |
| $C_b$ | bulk fluid phase concentration |
| $D_p$ | diffusion coefficient |
| $m$ | parameter (Eq. (17)) |
| $m_A$ | mass of the adsorbed (desorbed) component |
| $m_{A\infty}$ | mass of the adsorbed (desorbed) component at equilibrium |
| $M$ | molecular weight of adsorbed component |
| $q_{mol}$ | solid phase concentration |
| $q_{mol\,b}$ | solid phase concentration in equilibrium with $C_b$ |
| $r$ | radial coordinate |
| $R_p$ | radius of pellet |
| $t$ | time |
| $x = r/R_p$ | dimensionless radial coordinate |
| $X = C/C_b$ | dimensionless fluid phase concentration |
| $Y = (q_{mol}/q_{mol\,b})$ | dimensionless solid phase concentration |

*Greek symbols*

| | |
|---|---|
| $\alpha$ | parameter (Eq. (9)) |
| $\mu$ | parameter (Eq. (14)) |
| $\nu$ | exponent in Freundlich equation |
| $\rho_p$ | particle density |
| $\tau = t/t_D$ | dimensionless time |

In fact, the presented model is the only known approximation which has this property, a feature which guarantees its accuracy for strongly nonlinear systems.

## 2. Exact model and solutions

If pore diffusion is the rate controlling step and the isotherm is nonlinear (Freundlich, $Y = X^\nu$, $0 \le \nu \le 1$), the dimensionless equation describing the intraparticle diffusion and adsorption in an initially adsorbate free spherical pellet, subject at $\tau = 0$ to a unit step change of the concentration at its surface is

$$\nu X^{\nu-1}\frac{\partial X}{\partial \tau} = \frac{\partial^2 X}{\partial x^2} + \frac{2}{x}\frac{\partial X}{\partial x} \tag{1}$$

with the conditions

$$\tau = 0, \quad X = 0 \tag{2a}$$

$$x = 0, \quad \frac{\partial X}{\partial x} = 0 \tag{2b}$$

$$x = 1, \quad X = 1 \tag{2c}$$

Analytical solutions of the partial differential Eq. (1) with the conditions (2) are available only for the cases of irreversible ($\nu = 0$) and linear ($\nu = 1$) isotherms.

**Case I** (Irreversible isotherm). In the case of the irreversible isotherm the analytical solution resulting from the shell model is

$$\tau = \tfrac{1}{6}[1 + 2(1-\bar{A}) - 3(1-\bar{A})^{2/3}] \tag{3}$$

Differentiating Eq. (3) leads to the following expression for the fractional uptake rate:

$$\frac{d\bar{A}}{d\tau} = \left[3 + \frac{3(1-\bar{A})^{1/3}}{1-(1-\bar{A})^{1/3}}\right](1-\bar{A})^{1/3} \tag{4}$$

**Case II** (Linear isotherm). In the case of the linear isotherm the analytical solution is

$$\bar{A} = 1 - \frac{6}{\pi^2}\sum_{n=1}^{\infty}\frac{1}{n^2}\exp(-n^2\pi^2\tau) \tag{5}$$

with the uptake rate given by

$$\frac{d\bar{A}}{d\tau} = 6\sum_{n=1}^{\infty}\exp(-n^2\pi^2\tau) \tag{6}$$

As was shown in our earlier work [8], the fractional uptake rate for a linear isotherm system can be approximated by the following nonlinear driving force model

$$\frac{d\bar{A}}{d\tau} = \left[\pi^2 + \frac{18}{\pi}\frac{(1-\bar{A})^2}{\bar{A}}\right](1-\bar{A}) \tag{7}$$

The application of this model leads to a maximum error of 2.8% compared with the exact analytical solution (Eq. (5)).

## 3. Development of the nonlinear driving force model for the Freundlich isotherm

Let us now define the function $G(\bar{A}, \nu)$ which can be considered a generalization of the function $G(\bar{A})$ introduced by Georgiou and Kupiec [8] for linear systems

$$G(\bar{A}, \nu) = \left[\frac{d\bar{A}/d\tau}{(1-\bar{A})^m} - \alpha\right]\frac{1-(1-\bar{A})^m}{(1-\bar{A})^m} \tag{8}$$

where

$$\alpha = \lim_{\bar{A}\to 1}\frac{d\bar{A}/d\tau}{(1-\bar{A})^m} \tag{9}$$

and the parameter $m$ is a function of $\nu$ (Table 1). It should be noted that for a linear isotherm $\alpha = \pi^2$ and $m = 1$ which is basis for the LDF model [9,10].

In the case of the irreversible isotherm it can be easily shown from (Eq. (4)) that

$$G(\bar{A}, 0) = 3 \tag{10}$$

Table 1
Values of parameters $\mu$, $m$ and $\alpha$

| | $\nu = 0$ | $\nu = 1$ | $0<\nu<1$ |
|---|---|---|---|
| $\mu$ | $\sqrt{18}$[a] | $6/\sqrt{\pi}$[a] | $(1-\nu)\sqrt{18} + 6\nu/\sqrt{\pi}$ [3] |
| $m$ | $1/3$[a] | 1 [8] | $[2\nu + 1]/3$ [this work] |
| $\alpha$ | 3[a] | $\pi^2$[a] | $3 + \pi^2[1 - (3/\pi^2)^\nu]$ [this work] |
| $m\mu^2/2$ | 3 | $18/\pi$ | |

[a] Theoretical values.

In the case of the linear isotherm, the function $G(\bar{A}, 1)$ can be approximated [8] as

$$G(\bar{A}, 1) \cong \frac{18}{\pi}(1 - \bar{A}) \tag{11}$$

The behavior of the function $G(\bar{A}, \nu)$ at short times ($\bar{A} \to 0$) can be found from the following well known asymptotically exact expression [3]

$$\bar{A} = \mu\sqrt{\tau} \tag{12}$$

which upon differentiation leads to

$$\frac{\mathrm{d}\bar{A}}{\mathrm{d}\tau} = \frac{\mu^2}{2\bar{A}} \tag{13}$$

where the values of $\mu$ are shown in Table 1. The values of $\mu$ at the limiting cases can be obtained from theoretical considerations. For intermediate values of Freundlich exponent $\nu$ the linear interpolation

$$\mu = (1 - \nu)\sqrt{18} + \frac{6\nu}{\sqrt{\pi}} \tag{14}$$

can be applied [3].

At short times (small fractional uptakes) from Eq. (8) results

$$\lim_{\bar{A}\to 0} G \cong \lim_{\bar{A}\to 0} \left\{ \frac{\mathrm{d}\bar{A}}{\mathrm{d}\tau}[1 - (1 - \bar{A})^m] \right\} \cong \lim_{\bar{A}\to 0} \left( m\bar{A}\frac{\mathrm{d}\bar{A}}{\mathrm{d}\tau} \right) \tag{15}$$

Combining Eqs (12), (13) and (15) one obtains

$$\lim_{\bar{A}\to 0} G = \tfrac{1}{2}m\mu^2 \tag{16}$$

On the basis of the definition (Eq. (8)) it is understandable that any approximation of the function $G(\bar{A}, \nu)$ leads to an equivalent driving force model. In order to obtain the generalized NDLF model the following procedure was applied:

(a) The function $G(\bar{A}, \nu)$ was calculated from the available analytical solutions for $\nu = 0$ and 1.
(b) For intermediate values of $\nu$, the function $G(\bar{A}, \nu)$ was determined as follows:

**Step I.** The fractional uptake and the fractional uptake rate were obtained by the numerical solution of Eq. (1) with the boundary conditions (2). A finite difference scheme has been applied.

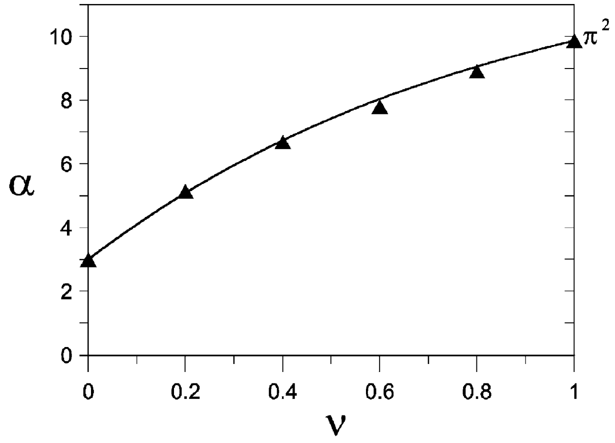

Fig. 1. The parameter $\alpha$ as a function of $\nu$: line—Eq. (18); symbols—Eq. (9).

**Step II.** The parameter $m$ was assumed to be a linear function of $\nu$

$$m = \tfrac{1}{3}(2\nu + 1) \tag{17}$$

satisfying the limiting cases.

**Step III.** The parameter $\alpha$ was determined on the basis of Eq. (9) and the results from Steps I and II. The so obtained values of $\alpha$ can be approximated with

$$\alpha = 3 + \pi^2 \left[ 1 - \left( \frac{3}{\pi^2} \right)^\nu \right] \tag{18}$$

A comparison of the numerical (Eq. (9)) and approximate (Eq. (18)) values of $\alpha$ is given in Fig. 1.

**Step IV.** The function $G(\bar{A}, \nu)$ was determined from the above results and the Eq. (8). A suitable approximation of the function $G(\bar{A}, \nu)$ (Fig. 2) is

$$G \cong \tfrac{1}{2}m\mu^2(1 - \bar{A})^\nu \tag{19}$$

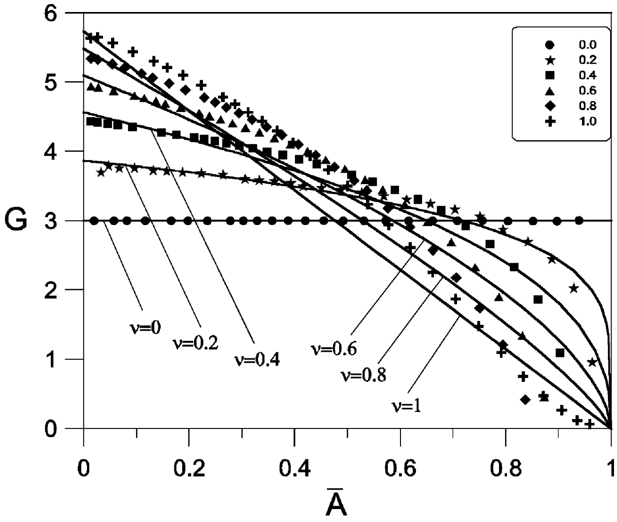

Fig. 2. The function $G(\bar{A}, \nu)$: lines—Eq. (19); symbols—numerical results.

(c) Combining Eqs. (8) and (19) leads to the following nonlinear driving force approximation (NLDF)

$$\frac{\mathrm{d}\bar{A}}{\mathrm{d}\tau}=\left[\alpha+\frac{m\mu^2}{2}\frac{(1-\bar{A})^{m+\nu}}{1-(1-\bar{A})^m}\right](1-\bar{A})^m \tag{20}$$

The values of the parameters $\mu$, $m$ and $\alpha$ are given in Table 1. This equation reduces to Eq. (7) in the case of linear systems and to the exact analytical solution resulting from the shell model (Eq. (4)) in the case of irreversible isotherm. At small times it reduces to asymptotically exact Eq. (13) and at long times to

$$\frac{\mathrm{d}\bar{A}}{\mathrm{d}\tau}=\alpha(1-\bar{A})^m \tag{21}$$

which may be regarded as a generalization of the linear driving force approximation to nonlinear systems.

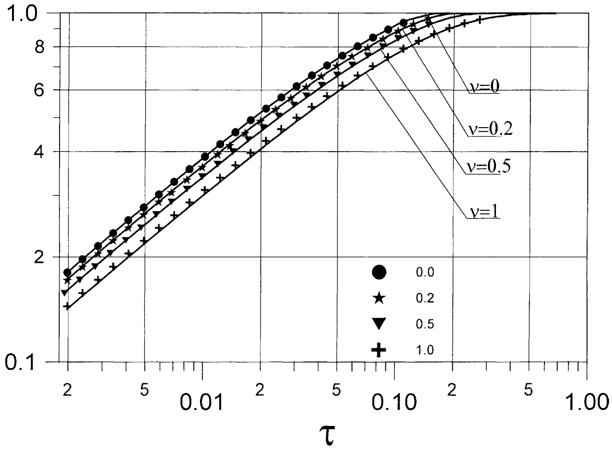

Fig. 3. Fractional uptake curves for various values of the Freundlich exponent: lines—approximate model (Eq. (20)); symbols—exact model (Eq. (1) with conditions (2)).

## 4. Numerical results and discussion

In order to evaluate the accuracy of the proposed nonlinear driving force approximation, the ordinary differential Eq. (20) was integrated with the initial condition $\tau = 0$, $\bar{A} = 0$ for various values of $\nu$. The obtained results $\bar{A}_{\mathrm{app}}(\tau)$ were compared with the numerical results $\bar{A}_{\mathrm{num}}(\tau)$ from the integration of Eq. (1) with the conditions (2). The results of these computations are illustrated in Fig. 3, where the fractional uptake curves resulting from the exact (Eq. (1)) and the approximate (Eq. (20)) models are shown. An excellent agreement of the two models is observed.

In Fig. 4, the functions

$$\delta_{\mathrm{app}}=\frac{\bar{A}_{\mathrm{ir}}-\bar{A}_{\mathrm{app}}}{\bar{A}_{\mathrm{ir}}} \tag{22}$$

$$\delta_{\mathrm{num}}=\frac{\bar{A}_{\mathrm{ir}}-\bar{A}_{\mathrm{num}}}{\bar{A}_{\mathrm{ir}}} \tag{23}$$

show the deviation from the irreversible isotherm case and allow the comparison of the numerical and approximate results. The fractional uptake $\bar{A}_{\mathrm{ir}}$ was calculated from Eq. (3). It should be noted that the relative error $\varepsilon$ can be calculated from

$$\varepsilon=\frac{\bar{A}_{\mathrm{app}}-\bar{A}_{\mathrm{num}}}{\bar{A}_{\mathrm{num}}}=\frac{\delta_{\mathrm{num}}-\delta_{\mathrm{app}}}{1-\delta_{\mathrm{num}}} \tag{24}$$

It is evident that the smaller the difference between $\delta_{\mathrm{num}}$ and $\delta_{\mathrm{app}}$ the more accurate is the model. Furthermore, the value of $\delta(0)$ can be obtained from Eqs. (12) and (14)

$$\delta(0)=\left(1-\frac{6}{\sqrt{18\pi}}\right)\nu\cong 0.2021\nu \tag{25}$$

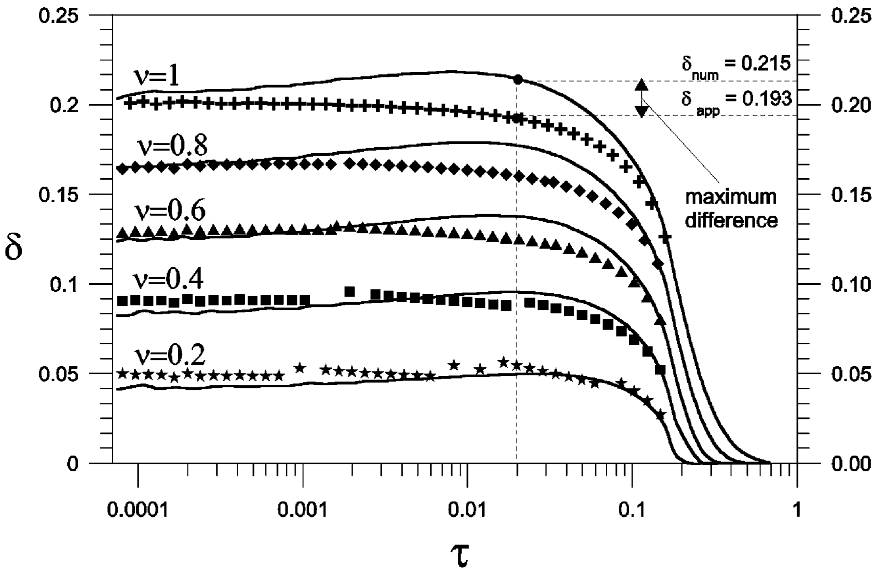

Fig. 4. The dependence of $\delta$ on dimensionless time $\tau$: lines—Eq. (23); symbols—Eq. (22).

As can be seen from Fig. 4, the accuracy of the proposed driving force approximation is excellent for all $\nu$ and over the entire time domain including small times. The maximum error arises in the case of a linear system (Fig. 4) and is equal to

$$\varepsilon_{\max} = \frac{0.215 - 0.193}{1 - 0.215} = 0.028 = 2.8\%$$

With decreasing $\nu$ the accuracy of the NLDF model increases as expected from the theoretical analysis.

## 5. Comparison with experimental data

The driving force approximation (Eq. (20)) was furthermore used in the analysis of the experimental data by Ruthven and Derrah [41] both for differential and integral steps. In these experiments, the adsorption and desorption of various hydrocarbons on Davison 5A (C-521) molecular sieves was studied under conditions where the external mass transfer resistance is negligible.

Since the NLDF model (Eq. (20)) was based on the assumption of a Freundlich isotherm, the first step was to fit the equilibrium data [41]. It should be noted, however, that Ruthven and Derrah [41] have used the Langmuir equation to fit the data. This shows that the application of the NLDF model is not limited to the Freundlich systems. The exponent $\nu$ is a convenient measure of the isotherm nonlinearity and can be estimated from equilibrium data. In the case of propylene at 50 °C the obtained Freundlich isotherm is

$$q_{\mathrm{mol}} = 1.72\, p^{0.080} \tag{26}$$

while the isotherm for propane at 75°C is given by

$$q_{\mathrm{mol}} = 0.278 p^{0.371} \tag{27}$$

For butylene at 75 °C isotherm equation is following

$$q_{\mathrm{mol}} = 1.53 p^{0.064} \tag{28}$$

where $q_{\mathrm{mol}}$ is the adsorbate concentration (moles of adsorbate/kg of adsorbent), and $p$ is the adsorbate pressure (mmHg). In Fig. 5 the equilibrium data are shown. It is evident that the Freundlich isotherm can describe the equilibrium data satisfactorily.

In the case of differential steps, the isotherm can be linearized and therefore Eq. (7) is applicable. In Fig. 6 the fractional uptake curve for the desorption of propylene (differential step, $p_0 = 22.3$ mmHg, $p_1 = 16.6$ mmHg) is shown. The symbols represent the experimental results by Ruthven and Derrah [41], while the line is the least-square fit of the experimental data using the NLDF model (Eq. (7)). The estimated value of the parameter $t_{\mathrm{D}} = 1255$ s. The excellent agreement between the NLDF prediction and the experimental data indicates the accuracy and applicability of the presented model.

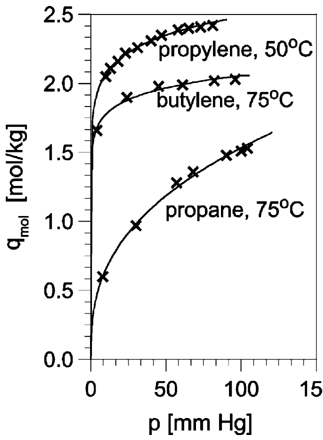

Fig. 5. Adsorption equilibrium: lines—Freundlich isotherms (Eqs. (26), (27) and (28)); symbols—experimental data [41].

Using the so obtained value of the parameter $t_{\mathrm{D}}$, the effective diffusivity was calculated:

$$D_{\mathrm{e}} = \frac{R_{\mathrm{p}}^2}{t_{\mathrm{D}}} \tag{29}$$

with $R_{\mathrm{p}} = 0.0023$ m [41], the effective diffusivity was found as $D_{\mathrm{e}} = 4.2 \times 10^{-9}\,\mathrm{m^2/s}$. The diffusion coefficient in the macropores is given by [41]:

$$D_{\mathrm{p}} = \frac{w(1-\varepsilon_{\mathrm{p}})}{\varepsilon_{\mathrm{p}}} \left(\frac{\mathrm{d}q_{\mathrm{mol\,b}}}{\mathrm{d}C_{\mathrm{b}}}\right) \rho_{\mathrm{p}} M D_{\mathrm{e}} \tag{30}$$

where

$$\frac{\mathrm{d}q_{mol\,\mathrm{b}}}{\mathrm{d}C_{\mathrm{b}}} = \frac{RT}{M}\frac{\mathrm{d}q_{mol\,\mathrm{b}}}{\mathrm{d}p} \tag{31}$$

In the case of propylene (Eq. (26)):

$$\frac{\mathrm{d}q_{\mathrm{mol\,b}}}{\mathrm{d}p} = 0.138 p^{-0.920} \tag{32}$$

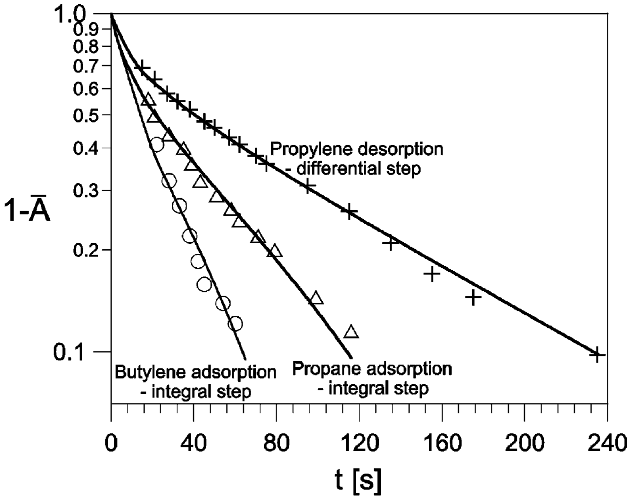

Fig. 6. Fractional uptake curves: lines—predictions of the NLDF model; symbols—experimental data [41].

Table 2
Comparison of effective diffusion coefficients calculated in different ways

| | Effective diffusion coefficients $D_e$ $10^9$ m$^2$/s | | | |
|---|---|---|---|---|
| | Shell model (Eq. (3)) $\nu = 0$ | NLDF model (Eq. (20)) | Linear isotherm model (Eq. (5)) $\nu = 1$ | Values from [41] |
| Butylene, 75 °C, $\nu = 0.064$ | 7.7 | 8.1 | 14.4 | 14.1 |
| Propane 75 °C, $\nu = 0.371$ | 4.4 | 5.6 | 8.1 | 8.0 |

Using the above equations and the data [41]:

$$\varepsilon_p = 0.26, \quad w = 0.83, \quad \rho_p(\text{kg/m}^3) = 1160,$$
$$T = 323\,K, \quad M(\text{kg/mol}) = 0.042$$

the estimated value was $D_p = 2.1 \times 10^{-6}$ m$^2$/s which agrees very well with the result $D_p = 2.0 \times 10^{-6}$ m$^2$/s obtained by Ruthven and Derrah [41].

In the case of integral steps the isotherm nonlinearity must be taken into account. Using the estimated value of the Freundlich exponent $\nu = 0.371$ (Eq. (27)) for the adsorption of propane at 75 °C [41] the following values of the parameters $\mu$, $m$ and $\alpha$ were calculated from Eqs. (14), (17) and (18):

$$\mu = 3.92, \quad m = 0.581, \quad \alpha = 6.52$$

In Fig. 6 the fractional uptake curve for the adsorption of propane (integral step, $p_0 = 29$ mmHg, $p_1 = 105$ mmHg) is shown. The symbols represent the experimental results by Ruthven and Derrah [41], while the line is the least-square fit of the experimental data using the NLDF model (Eq. (20)). The estimated value of the parameter $t_D = 945$ s. Again an excellent agreement between the NLDF prediction and the experimental data is observed.

Computations were also performed for the case of butylene adsorption at 75 °C (integral step, $p_0 = 1.1$ mmHg, $p_1 = 86$ mmHg). In this case $\nu = 0.064$ and, therefore,

$$\mu = 4.19, \quad m = 0.376, \quad \alpha = 3.72$$

The estimated value of the parameter $t_D = 652$ s (Fig. 6).

For comparison purposes the time constants $t_D$ were calculated using the assumptions of rectangular isotherm (shell model Eq. (3)) and linear isotherm (Eq. (5)). The so obtained time constants were used to calculate the effective diffusivities. The results of these computations are shown in Table 2. A comparison of these results shows that the values obtained by Ruthven and Derrah [41] are almost identical to those resulting from the linear isotherm model (Eq. (5)). In the case of the strongly adsorbed butylene ($\nu = 0.064$), the value obtained using the NLDF model is very closed to the value resulting from the shell model, while the value obtained using the linear isotherm assumption is much higher. This shows that the application of the linear isotherm model (Eq. (5)) in the case of strongly adsorbed substances leads to highly overestimated effective diffusivities. In the case of the moderately strongly adsorbed propane ($\nu = 0.371$), the NLDF model leads to intermediate values between the two extreme cases.

The above results indicate that the NLDF model can be successfully applied in parameter estimation from integral step experiments.

## 6. Conclusions

In this study, a nonlinear driving force approximation of intraparticle mass transfer rate in pore diffusion controlled nonlinear adsorption systems has been presented. This approximation is proved to be very accurate and applicable both for linear and nonlinear systems. In the case of an irreversible isotherm, the NLDF model reduces to the exact analytical solution resulting from the shell model, a feature that indicates its accuracy for highly nonlinear systems. The NLDF model is shown to successfully predict the uptake curves both for differential and integral steps and to be valid over the entire time domain. These properties of the presented approximation show that the methodology introduced in our earlier work for diffusion/adsorption [8,11] and diffusion/reaction [12] systems is a useful and efficient alternative to the much exploited methodology based on intraparticle concentration profile approximations.

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