

Mass transfer with surface reaction in arrays of cylinders at low Reynolds and high Peclet numbers: flow perpendicular to the axis of the cylinders

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Abstract

A problem of interest in the operation of trickle bed and liquid-fluidized bed reactors is convective transfer with surface reaction at low Reynolds and high Peclet numbers. The paper presents an analysis of the problem for flow across an array of cylindrical catalyst pellets under fast and intermediate kinetic regimes. The flow field is modelled by creeping flow hydrodynamics in conjunction with free surface cell model. Diffusion boundary layer equations are solved to obtain expressions for concentration distribution, mass flux to the surface, boundary layer thickness and average Sherwood number. The effect of system parameters such as Peclet number, Damkoehler number, and void fraction of the array on these quantities is numerically evaluated.

Key words: Convective transfer, surface reaction, creeping flow, diffusion boundary layer, cell model, cylindrical pellets.

Introduction

Analysis of convective transfer with surface reaction with flow past isolated simple bodies at low Reynolds numbers has received some attention in the literature; for example, past flat plates,¹⁻⁴ rotating discs and spheres¹ and cylinders.⁵ For such simple bodies the system equations are solved analytically for creeping flow¹ and numerically for laminar boundary layer flow.²⁻⁵ For multiparticle systems such as arrays of cylinders, packed beds and fluidized beds the flow field and consequently the concentration and temperature fields are complex. Here modelling is essential for the analysis. A model that finds wide application is Happel's free-surface model.⁶ The application of the model replaces the complex and difficult problem of the multiparticle assemblage by a set of concentric cells each cell containing a single particle surrounded by a hypothetical fluid envelope. The model assumes that a spherical particle is enclosed by a spherical envelope, and a cylindrical particle by a cylindrical envelope. The envelope has zero shear stress at its outer surface. Each envelope is assumed to contain the same amount of fluid, and the amount is such that the ratio of the particle volume to that of the cell is given by the concentration of the assemblage.

It is now sufficient to solve the simple problem of a single cell for analysing the multi-particle assemblage. The free-surface model has been successfully used for predicting pressure drop and transport in packed beds, in particular, in the range of voidages of 0.25 to 0.8, and at low Reynolds numbers.⁷⁻¹⁰ The application of the model for the analysis of deep-bed filtration is reported recently.¹¹ Brauer and Schlueter,⁸ and Govindarao and Lekshminarayanan¹² adopted the free surface model for multiparticle assemblage of spheres with surface reaction.

The purpose of this work is to present an analysis of the problem of convective mass transfer with surface reaction for creeping flow across an array of circular cylinders (see Fig. 1) at high Peclet numbers. Large Peclet and low Reynolds number conditions are encountered in the operation of multiphase systems involving liquids such as trickle bed and liquid-fluidized bed reactors. While the problem studied here is of direct interest in the analysis of systems such as filter mats, and reactors with catalyst deposited on fibers, etc., in general, in catalytic reaction engineering practice, beds of cylindrical particles are randomly packed. For such random assemblages one must employ a weighted average of the results for flow normal to the axis of cylinders and those for flow parallel to the axis.¹³

Model equations

We consider here a steady, isothermal and isobaric system. By application of the free-surface model the hydrodynamic problem reduces to one of a solid cylinder of radius a and length L placed at the origin of a cylindrical coordinate system and surrounded by a cylindrical envelope of fluid having a free surface at radius b , with the fluid envelope moving perpendicular to the axis of the cylinder at a constant velocity U . The radius b of the envelope is related to the voidage of the assemblage by

$$d = b/a = (1 - \epsilon)^{-1/2} \quad (1)$$

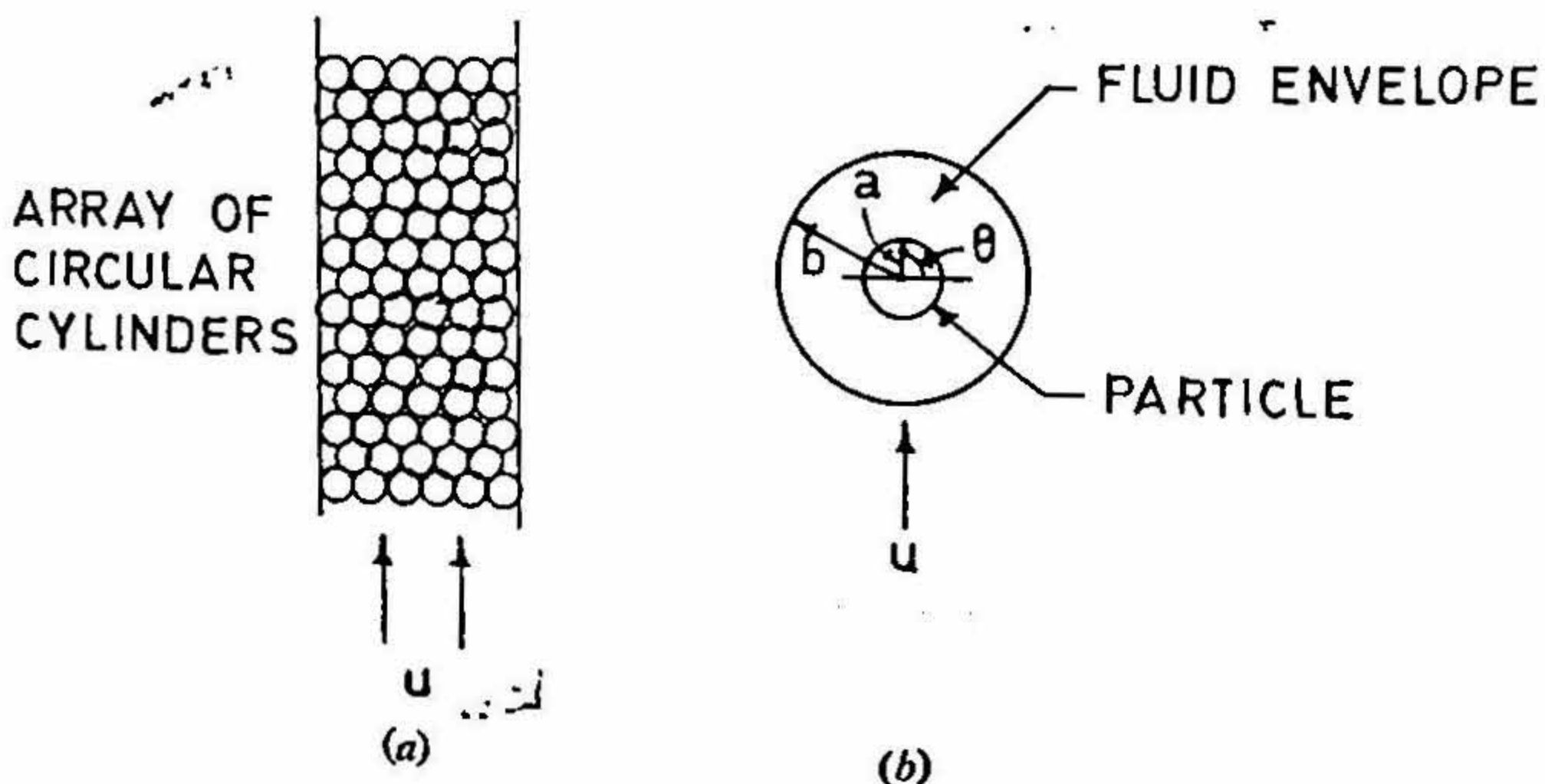


FIG. 1. (a) Assemblage of cylinders and (b) schematic of the unit cell.

We assume that (i) all the assumptions associated with the free-surface model⁶ hold good in the present analysis also, (ii) the concentration of the forward moving fluid is that of the cell boundary, (iii) the concentration of the dissolved reactant in the liquid is equal to its equilibrium value, (iv) at the forward stagnation point the incident flow is not depleted by diffusion, and therefore the concentration at this point is equal to the concentration in the bulk liquid.

For brevity, we consider the surface reaction to be irreversible, first-order with respect to the dissolved component and zero-order with respect to the liquid reactant. The reaction is assumed to take place only on the external surface of the particles; where pore diffusional effects are significant, they can be represented by the inclusion of an effectiveness factor in the rate equation. Also, the two faces of the cylindrical particle are assumed to be inactive.

Under these assumptions the flow of the liquid over the cylindrical particle is described by⁶

$$\psi = U w \sin \theta \quad (2)$$

For large Peclet numbers, normally encountered in problems with convective transfer in liquids, the change in the concentration from the bulk liquid phase to the catalyst surface occurs entirely in a thin boundary layer very close to the surface of the particle. For such thin boundary layers $y/a \ll 1$, where $y = r - a$. Then eqn. (2) reduces to

$$\psi \simeq \frac{2Ug}{a} y^2 \sin \theta \quad (3)$$

The diffusion equation is given by

$$v_r \frac{\partial c}{\partial r} + \frac{v_\theta}{r} \frac{\partial c}{\partial \theta} = D \left(\frac{\partial^2 c}{\partial r^2} + \frac{1}{r} \frac{\partial c}{\partial r} \right) \quad (4)$$

with boundary conditions

$$\text{at } r = a \quad \text{and} \quad \theta = 0 \quad c = c_0 \quad (5)$$

$$\text{at } r = b \quad c = c_0 \quad (6)$$

at $r = a$ and $\theta > 0$:

for intermediate kinetics (where the rate of reaction is comparable to the rate of transport):

$$D \frac{\partial c}{\partial r} = k_1 c \quad (7)$$

for fast kinetics (where the rate of reaction is very high):

$$c = 0 \quad (8)$$

Equation (5) arises because of the assumption iv.

Rewriting equ. (4) in terms of the dimensionless concentration C and the dimensionless stream function ϕ , and noting that for $y/a \ll 1$, $\frac{\partial^2 c}{\partial r^2} \gg \frac{1}{r} \frac{\partial c}{\partial r}$, we get

$$\frac{\partial C}{\partial t} = \frac{\partial}{\partial \phi} \left[\phi^{1/2} \frac{\partial C}{\partial \phi} \right] \quad (9)$$

The boundary conditions now become

$$\text{at } \phi = 0 \text{ and } t = 0 \quad C = 1 \quad (10)$$

$$\text{as } \phi \rightarrow \infty \quad C = 1 \quad (11)$$

at $\phi = 0$:

$$\frac{D}{a} (8 \sin \theta)^{1/2} \left(\phi^{1/2} \frac{\partial C}{\partial \phi} \right) = k_1 C \text{ (for intermediate kinetics)} \quad (12)$$

$$C = 0 \quad \text{(fast kinetics)} \quad (13)$$

In writing eqn. (11), it is assumed that the stream function at the outer surface approaches infinity. This is logical since the quantity $(b - a)$ is always much larger than the thickness of the diffusion boundary layer.

Intermediate kinetics

Eqn. (9) with the boundary conditions of eqns. (10) to (12) can be solved rigorously by Levich's method¹ to get for the surface concentration

$$C = \frac{I}{\Gamma(2/3)} \quad (14)$$

where

$$I = \int_0^\infty \exp(-pz^{2/3}) \exp(-z) z^{-1/3} dz \quad (15)$$

Flux: The flux to the catalyst surface is

$$j = Dc_0 \frac{\partial C}{\partial y} \Big|_{y=0} = k_1 c_0 C$$

Substituting for C in this equation from eqn. (14) we get

$$j = \frac{k_1 c_0}{\Gamma(2/3)} I \quad (16)$$

Effective thickness of the diffusion boundary layer: The local thickness of the diffusion boundary layer (normalised with respect to the radius of the particle) is defined by

$$\delta = \frac{Dc_0(1-C)}{aj}$$

Substituting for C and j from eqns. (14), and (16), we have

$$\delta = \frac{2}{N_D} \left[\frac{\Gamma(2/3)}{I} - 1 \right] \quad (17)$$

As will be shown later, for small and large values of p , I can be approximated as a series in p (see eqns. 25 and 28).

Further simplifying these expressions for very small and very large p , we get

for $p \ll 1$

$$\delta_{vsD} \simeq \frac{1.32p}{N_D} = 1.078 N_{Pe}^{-1/3} g^{-1/3} f \quad (18)$$

and for $p \gg 1$

$$\delta_{vD} \simeq \frac{2\Gamma(2/3)p}{3N_D} = 1.474 N_{Pe}^{-1/3} g^{-1/3} f \quad (19)$$

Average surface concentration: The average surface concentration is given by

$$\bar{C} = \frac{1}{\pi} \int_0^\pi C d\theta$$

On substitution for C from eqn. (14), we get

$$\bar{C} = \frac{1}{\pi\Gamma(2/3)} \int_0^\pi I d\theta = 0.2352 \int_0^\pi I d\theta \quad (20)$$

Average Sherwood number: The average value of the Sherwood number, where the local mass transfer coefficient is defined based on the limiting flux, is given by

$$\bar{N}_{Sb} = \frac{N_D}{\pi} \int_0^\pi C d\theta = N_D \bar{C} \quad (21)$$

Fast kinetics

The governing equations for this situation are eqns. (9) to (11) and (13). These may be solved by the method of similarity transformation¹ to get

$$C = \frac{1}{1.17} \int_0^a \exp\left(-\frac{4}{9} q^3\right) dq \quad (22)$$

Flux: The flux to the surface is given by

$$j = 1.203 \frac{Dc_0}{a} (\sin \theta)^{1/2} t^{-1/3}$$

Effective thickness of the diffusion boundary layer: This is now given by

$$\delta = \frac{Dc_0}{aj} = 1.474 N_{Pe}^{-1/3} g^{-1/3} f \quad (23)$$

Equation (23) is the same as eqn. (19), the expression for the boundary layer thickness in the case of intermediate kinetics for very large values of p . This is expected since p becomes very large for large Damkohler numbers, and this corresponds to the surface reaction being very fast.

Since f becomes large for θ relatively close to π (greater than about 170°), the boundary layer thickness becomes very large and comparable to the radius of the particle for these values of θ . In fact, the solution predicts that for $\theta = \pi$, δ is infinity and the mass flux is zero. Actually, however, δ does not become infinity at $\theta = \pi$, and the flux is not zero. Thus, we note that the model presented here breaks down in the range of values of θ close to π . However, this range does not cause any significant effect on the total mass flow to the surface and thus on the average concentration. These observations are valid for the case of intermediate kinetics also.

Average Sherwood number: The average Sherwood number for fast kinetics is given by

$$\begin{aligned} \bar{N}_{Sh\infty} &= \frac{2a}{\pi Dc_0} \int_0^\pi j d\theta \\ &= 1.16 N_{Pe}^{1/3} g^{1/3} \end{aligned} \quad (24)$$

Equation (24) is similar in form to the one obtained for the average Sherwood number for transport (without reaction) to spheres at high Peclet numbers by Pfeffer,⁷

Analysis of results

The model and the solutions are evaluated numerically to determine the effect of the system parameters Damkoehler number, Peclet number and void fraction of the assemblage over wide ranges, namely $N_D : 0.05$ to $5,000$; $N_{Pe} : 5$ to $5,000$; and $\epsilon : 0.3$ to 0.8 .

Fast kinetics

Fig. 2 is a plot of the average Sherwood number for fast kinetics against voidage with N_{Pe} as parameter. The Sherwood number increases sharply with an increase in the Peclet number and a decrease in void fraction. For a given set of operating conditions higher rates of transfer are obtained with more closely packed arrays (small ϵ) than with dilute ones.

Intermediate kinetics

Computation of the average concentration and the average Sherwood number for the intermediate kinetics involves evaluation of the integral I , given by eqn. (15), an improper integral that involves infinity at the upper limit and a singularity at the lower limit.

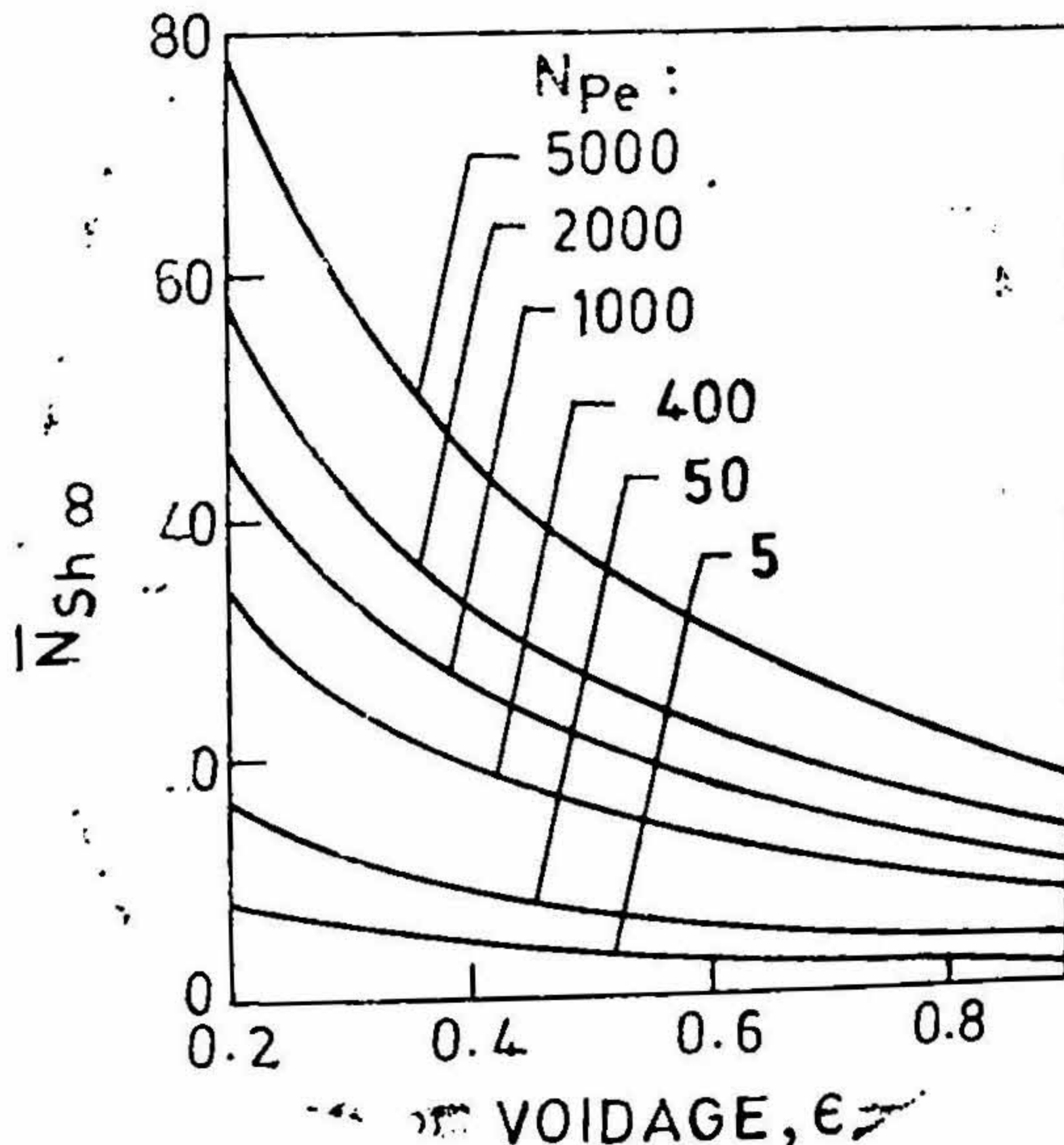


FIG. 2. Average Sherwood number for fast kinetics versus void fraction for different Peclet numbers.

Expanding $\exp(-p z^{2/3})$ in a series, we obtain¹ an expression for I in powers of p that is convergent for all values of p . However, it is convenient to use this series only for small values of p . Thus, for small values of p , I may be approximated, neglecting terms of the order of p^6 , by

$$I \simeq I_{sp} = \Gamma(2/3) - \Gamma(4/3)p + \frac{\Gamma(2)}{2!}p^2 - \frac{\Gamma(8/3)}{3!}p^3 + \frac{\Gamma(10/3)}{4!}p^4 - \frac{\Gamma(4)}{5!}p^5 \quad (25)$$

For large values of p , we make the substitution

$$p z^{2/3} = s \quad (26)$$

whereby I becomes

$$I = \frac{3}{2p} \int_0^{\infty} \exp(-s) \exp\left[-\left(\frac{s}{p}\right)^{3/2}\right] ds \quad (27)$$

Expanding $\exp[-(s/p)^{3/2}]$ in series we can now approximate I for large values of p by

$$I \simeq I_{lp} = \frac{1.5}{p} - \frac{1.5 \Gamma(5/2)}{p^{2.5}} + \frac{1.5 \Gamma(4)}{2! p^4} - \frac{1.5 \Gamma(11/2)}{3! p^{5.5}} + \frac{1.5 \Gamma(7)}{4! p^7} - \frac{1.5 \Gamma(17/2)}{5! p^{8.5}} \quad (28)$$

where terms of the order of p^{-10} are neglected.

The magnitude of p depends upon N_D , N_{pe} , ϵ as well as θ . Among these only the variation in N_D is reflected to the same fold variation in p , and thus for any range of the parameters the value of p being small or large mostly depends upon the value of N_D .

At $p = 0.9$ the contribution of the p^5 term in eqn. (25) to the quantity I is only about 0.5 per cent, and thus for $p < 0.9$, eqn. (25) may be used without making any significant error for approximating the value of I . Similarly at $p = 3$ the contribution of the last term in eqn. (28) is only about 0.5 per cent and therefore, for $p \geq 3$ eqn. (28) is satisfactory for estimating I . For values of p in the range 0.9 to 3, I should be evaluated numerically from eqn. (15) or (27). The form given in eqn. (27) is more convenient for this purpose, particularly because it avoids the problem of singularity at the lower limit. Suitable values that can be used to replace the upper limit of infinity in this integral giving a sufficiently good approximation were determined for the range $0.9 < p < 3.0$.

Based on the above observations the following procedure was adopted for the computations.

1. Since the solution, as stated earlier, fails in the close neighbourhood of π , the integral in eqn. (20) is carried out up to 176° only, and the average values were determined by using the corresponding surface area. Thus \bar{C} is now given by

$$\bar{C} = 0.2404 \int_0^{176} I d\theta \quad (29)$$

2. The quantity p for all values of θ will be ≤ 0.9 if this condition is satisfied by p at θ close to 176° . Therefore, for such combinations of N_{Pe} , ε and N_D we can replace I in eqn. (29) by I_{sp} given by eqn. (25), and the indicated integrations (now on the function f) may be carried out numerically. This gives for the average concentration:

$$\bar{C}_{sp} = 1 - 0.7149 h + 0.5494 h^2 - 0.5047 h^3 + 0.5517 h^4 - 0.6711 h^5 \quad (30)$$

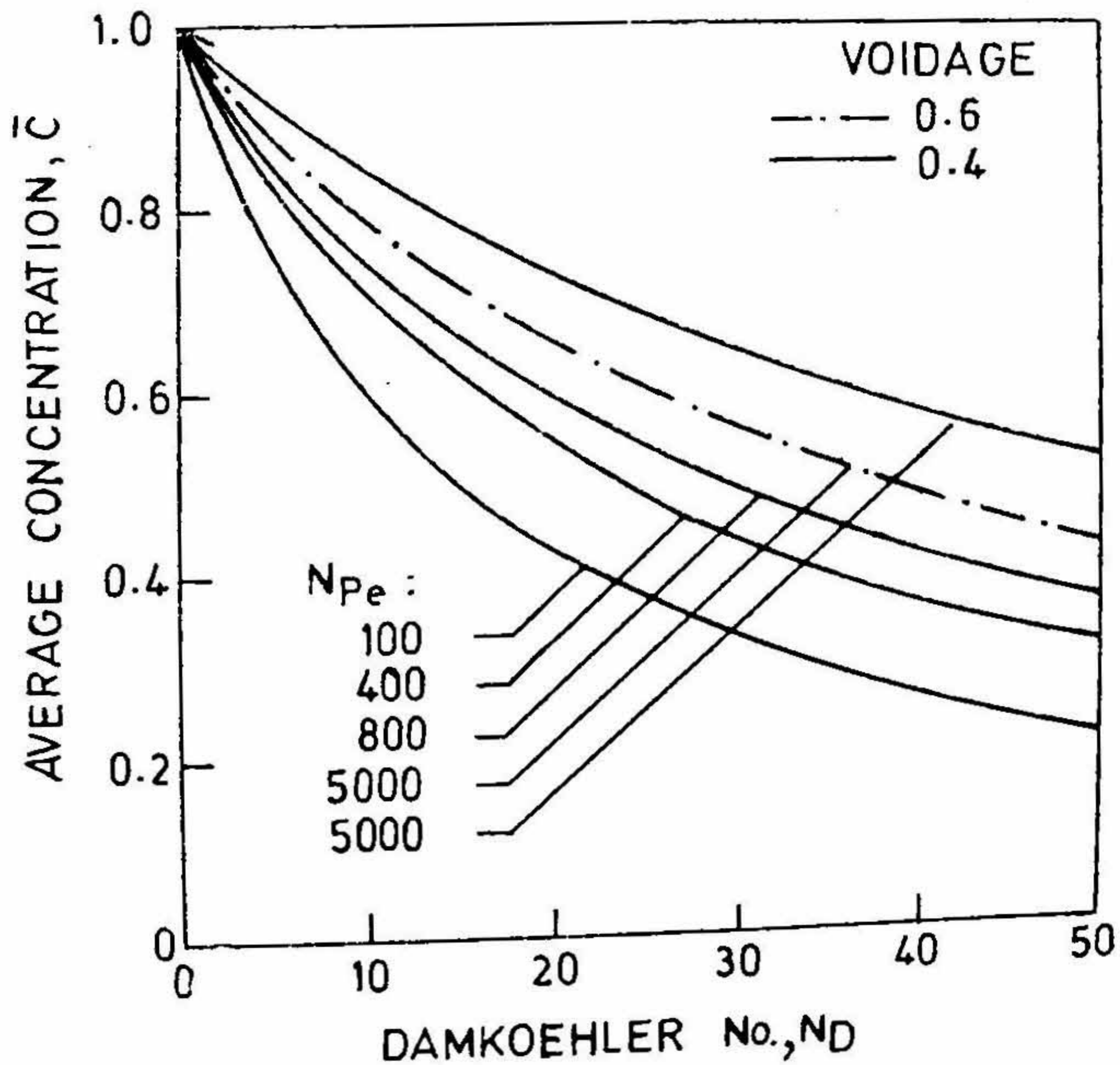


FIG. 3. Average surface concentration against Damkoehler number for different values of Peclet number and void fraction.

3. Similarly, for values of N_{Pe} , ε and N_D that give a p of about 3 for θ close to zero degrees, p for all the other values of θ will be ≥ 3 , and I in eqn. (29) may be replaced by I_{1p} . With this substitution and performing the resulting integrations on f we get for \bar{C}

$$\begin{aligned} \bar{C}_{1p} = & 1.16 h^{-1} - 2.0013 h^{-2.5} + 6.3134 h^{-4} - 26.539 h^{-5.5} \\ & + 136.3825 h^{-7} - 809.0075 h^{-8.5} \end{aligned} \quad (31)$$

4. For combinations of N_{Pe} , ε and N_D that do not fall into either of the above two situations, I for a given θ is calculated from eqn. (25) whenever the corresponding $p \leq 0.9$, from eqn. (28) whenever $p \geq 3$, and by numerical integration of eqn. (27) for the other values of p . The average concentration is then computed by numerical integration by using eqn. (29) and these I values.

Fig. 3 shows the average concentration as a function of the Damkohler group for different Peclet numbers and different void fractions. All the three quantities have a strong effect on the average surface concentration and thus on conversion and rate of reaction. As N_D increases the average concentration falls steeply first and approaches zero asymptotically. At large values of N_D the rate of reaction becomes very rapid and the surface concentration approaches zero, and consequently diffusional effects become predominant. This is the case of fast kinetics analysed above. On the other hand, as N_D approaches zero the average concentration approaches unity and the effects of diffusion are negligible compared to those of the surface reaction. Thus kinetics become the controlling step. The curves also indicate that transport effects are significant even at as low a N_D as about 2; the effects are more significant at lower N_{Pe} and higher void fraction.

The average Sherwood number (in the intermediate kinetics regime) is plotted against N_D with N_{Pe} and ε as parameters in Fig. 4. Fig. 5 gives a plot of the ratio of this Sherwood number to that for fast kinetics against the same parameters as in Fig. 4. As N_D increases \bar{N}_{Sh} approaches $\bar{N}_{Sh\infty}$. For N_{Pe} upto about 1,000 the ratio $\bar{N}_{Sh}/\bar{N}_{Sh\infty}$ approaches unity for N_D of about 400 itself; for lower N_{Pe} at still lower N_D values. For higher Peclet numbers the corresponding N_D value is much larger indicating that for such conditions both transport and kinetic processes must be considered even for fairly fast reactions. For a particular N_D , the average Sherwood number (and thus the rate of the overall process) increases with increase in N_{Pe} , the effect being more significant for closely packed assemblages.

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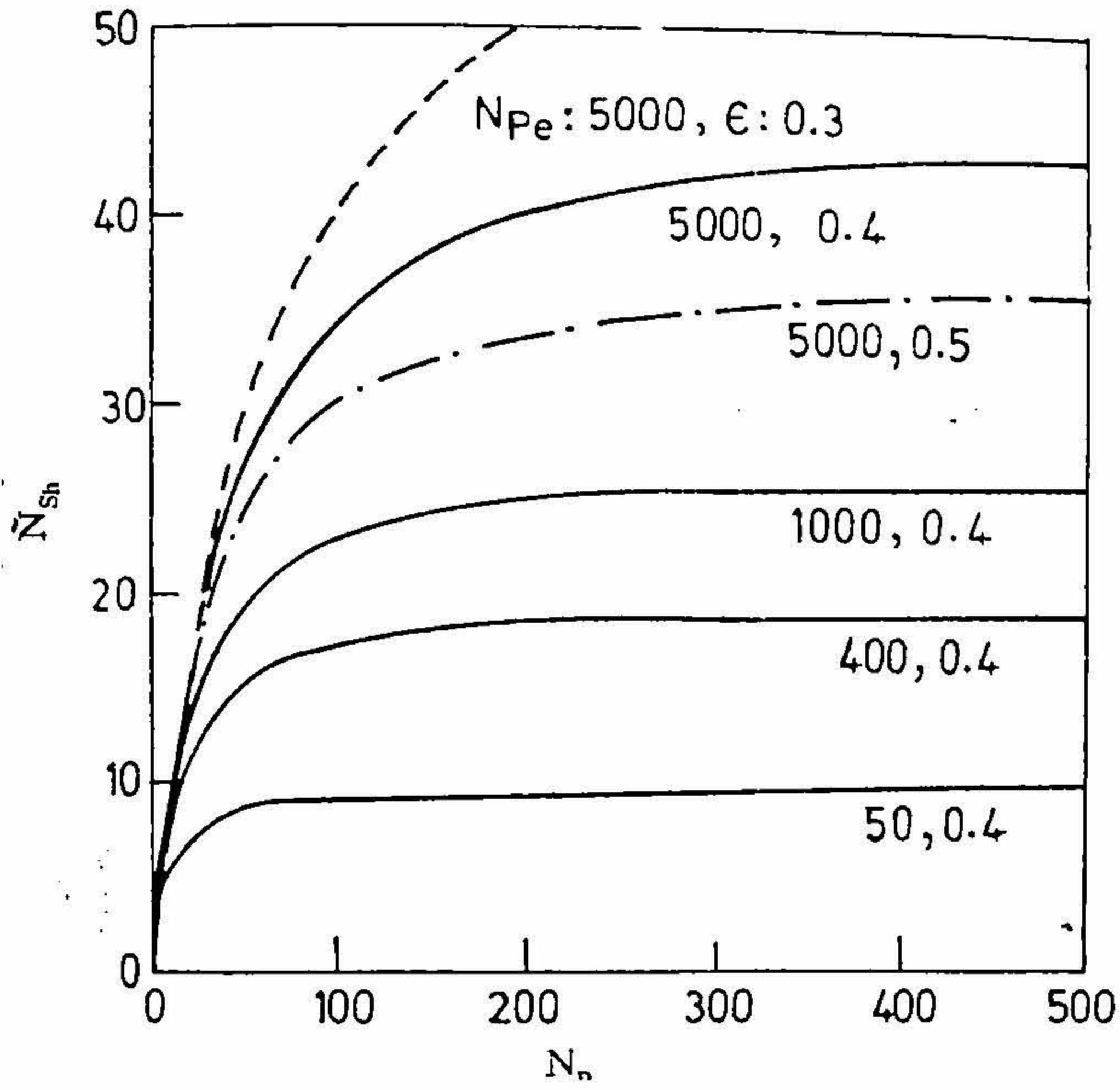


FIG. 4. Average Sherwood number (intermediate kinetics) against Damkoehler number for different values of Peclet number and void fraction.

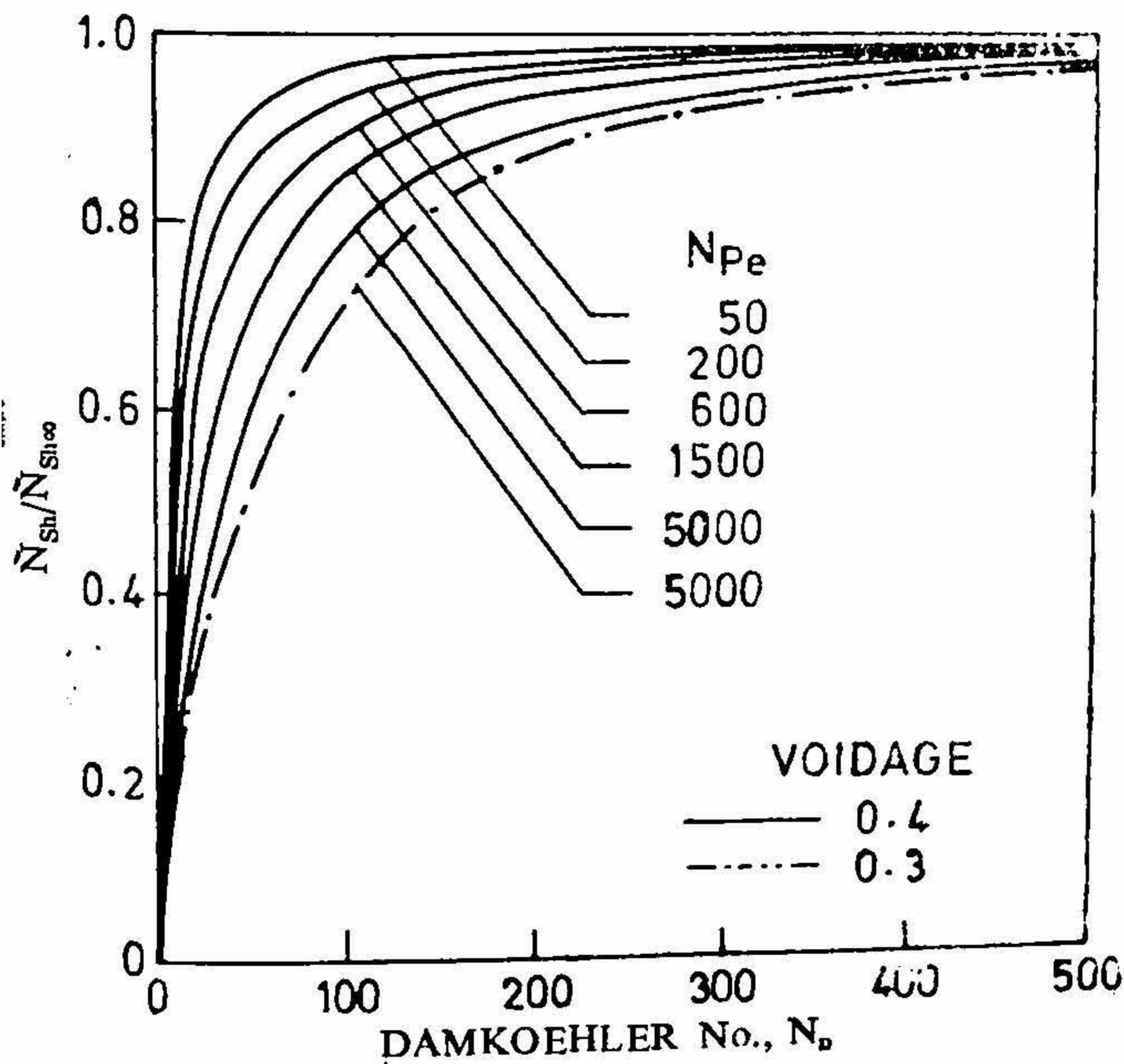


FIG. 5. Ratio of average Sherwood number for intermediate kinetics to that for fast kinetics against Damkoehler number for different values of Peclet number and void fraction,

Notation

- a : radius of the cylinder
 b : radius of the fluid envelope
 c : concentration
 c_0 : free stream concentration
 C : normalized concentration, c/c_0
 \bar{C} : average surface concentration
 \bar{C}_{sp} : average concentration where $I \simeq I_{sp}$ for all values of θ
 \bar{C}_{lp} : average concentration where $I \simeq I_{lp}$ for all values of θ
 d : defined by eqn. (1)
 D : diffusivity
 f : $m^{1/3} (\sin \theta)^{-1/2}$
 g : $(d^4 - 1)/g'$
 g' : $2 + (1 + d^4)(2 \ln d - 1)$
 h : $N_D N_{Pe}^{-1/3} g^{-1/3}$
 I : integral defined by eqn. (15)
 I_{sp} : I for small values of p
 I_{lp} : I for large values of p
 j : flux to the surface
 k_1 : first-order rate constant
 k_a : mass transfer coefficient
 L : length of the cylinder
 m : $\int_0^\theta (\sin \theta)^{1/2} d\theta$
 N_D : Damkoehler number, $2a k_1/D$
 N_{Pe} : Peclet number, $2a U/D$
 N_{Sh} : Sherwood number, $2a k_a/D$
 \bar{N}_{Sh} : average Sherwood number
 $\bar{N}_{Sh\infty}$: average Sherwood number for fast kinetics

- p : $0.8165 hf$
 q : $\phi^{1/2} t^{-1/3}$
 r : radial coordinate
 s : defined by eqn. (25)
 t : $5.6569 m/N_{Pe} g$
 U : free stream velocity
 v_r : radial velocity component
 v_θ : angular velocity component
 w : $\frac{r}{g'} \left[-\frac{r^2}{a^2} + (1 + d^4)(2 \ln r - 1) + 2 \{1 + (1 + d^4) \ln a\} \frac{a^2 d^4}{r^2} \right]$
 y : $r - a$
 z : independent variable

Greek letters

- δ : normalized (with respect to the radius of the particle) thickness of the diffusion boundary layer
 δ_{vSD} : δ for very small values of p ($p \ll 1$)
 δ_{vLD} : δ for very large values of p ($p \gg 1$)
 ε : voidage of the assemblage
 θ : angular coordinate
 ϕ : normalized stream function, $\psi/U ag$
 ψ : stream function

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