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Adsorption and Desorption Kinetics for Diffusion Controlled Systems with a Strongly Concentration Dependent Diffusivity

Douglas M. Ruthven
Department of Chemical Engineering
University of Maine
Orono, ME, 04469
USA

Abstract

The formal solution to the diffusion equation for transient adsorption in a semi-infinite medium with a strongly concentration dependent diffusivity, originally derived by Fujita (3), has been extended to desorption. Profiles for adsorption and desorption are compared and simplified asymptotic expressions which are useful when the diffusivity ratio is large are derived. The effect of a strongly concentration dependent diffusivity on adsorption and desorption kinetics is briefly considered.

1. Introduction

In contrast to gas and liquid phase systems in which the variation of diffusivity with composition is generally modest, for adsorbed phases and gases dissolved in polymers the diffusivity may vary very strongly with concentration. For sorption systems in which the sorption rate is controlled by intraparticle diffusion this leads to a qualitatively different pattern of behavior compared with a system in which the diffusivity is constant or only modestly concentration dependent. In particular, such behavior occurs when the equilibrium isotherm is highly favorable, approaching the rectangular or irreversible form. Since such systems are quite common and of some practical importance it is appropriate to consider their behavior in some detail.

As an example, we consider a system in which the equilibrium isotherm is of Langmuir form:

$$\frac{q}{q_s} = \frac{bp}{1+bp} \tag{1}$$

and diffusive transport is driven by the gradient of chemical potential with a constant (concentration independent) mobility. For such a system the Fickian diffusivity is given by (1):

$$D = D_o \left(\frac{\mathrm{dln}p}{\partial \mathrm{ln}q} \right)_T = \frac{D_o}{1-\lambda Q} \tag{2}$$

where $\lambda = q_o/q_s$ and $Q = q/q_o$. The diffusivity ratio (over the concentration range $0 < Q < 1$) is given by $r = (1 - \lambda)^{-1}$. If the equilibrium isotherm is highly favorable ($b \rightarrow \infty$) r can be very large.

2. Sorption Kinetics

For an isothermal parallel sided slab (thickness $2l$) subjected at time zero to a step change in the surface concentration of sorbate, the adsorption/desorption kinetics (assuming internal diffusion control) are governed by the partial differential equation:

$$\frac{\partial Q}{\partial \tau} = \frac{\partial}{\partial X}\left[\mathrm{f}(Q).\frac{\partial Q}{\partial X}\right] \tag{3}$$

where $\mathrm{f}(Q) = 1/(1-\lambda Q) = D/D_o$, $X = x/\ell^{*,}$ and $\tau = D_o t/\ell^2$, with the initial and boundary conditions:

$$\tau < 0,\ \ Q = 0 \text{ (ads.) or } Q = 1 \text{ (des.) for all } x$$

$$\tau \geq 0,\ \ Q(0, \tau) = 1 \text{ (ads.) or } Q(0, \tau) = 0 \text{ (des.) for all } \tau \tag{4}$$

$$\left.\frac{\partial q}{\partial x}\right|_{x=\ell} = \left.\frac{\partial Q}{\partial X}\right|_{X=1} = 0$$

Since Eq.3 is non-linear and the boundary conditions are finite, an analytic solution is not practical. Numerical solutions for the corresponding problem in spherical coordinates were presented many years ago by Garg and Ruthven $^{(2)}$.

In the initial region the concentration front has not penetrated to the centre of the slab so the system behaves as a semi-infinite medium. In this situation the last boundary condition of Eq.4 may be replaced by:

$$\left.\frac{\partial q}{\partial x}\right|_{x\rightarrow\infty} = 0\ ;\ \left. Q\right|_{x\rightarrow\infty} = 0\,(\text{ads.})\ \text{ or }\ 1.0\,(\text{des.}) \tag{5}$$

This allows the Boltzmann transformation $\left(y = x/2\sqrt{D_o t}\right)$ to be used to reduce Eq.3 to the ordinary differential equation:

$$-2y\frac{dQ}{dy} = \frac{\mathrm{d}}{\mathrm{d}y}\left[f(Q)\frac{dQ}{dy}\right] \tag{6}$$

* Note that distance x is measured from the external surface at which $x = 0$.

with the initial boundary conditions:

$$
\begin{aligned}
t < 0 :&\quad Q(y) = 0 \text{ (ads.) or } 1.0 \text{ (des.)} \\
t \geq 0 :&\quad Q(0) = 1.0 \text{ (ads.) or } 0 \text{ (des.) for all } t \\
&\quad Q(y \rightarrow \infty) = 0 \text{ (ads.) or } 1.0 \text{ (des.)} \\
&\quad \frac{\mathrm{d}Q}{\mathrm{d}y}\Big|_{y\rightarrow\infty} = 0
\end{aligned}
\tag{7}
$$

Integration of Eq.6 yields:

$$\int_{y=0}^{\infty} y\mathrm{d}Q = \frac{1}{2}\left[\mathrm{f}\left(Q\right)\frac{\mathrm{d}Q}{\mathrm{d}y}\right]_{y=0} - \frac{1}{2}\left[\mathrm{f}\left(Q\right).\frac{\mathrm{d}Q}{\mathrm{d}y}\right]_{y\rightarrow\infty} \tag{8}$$

Since the gradient of concentration is zero for large y this simplifies to:

$$A = -\int_{Q=0}^{1} y\mathrm{d}Q = -\frac{r}{2}\frac{\mathrm{d}Q}{\mathrm{d}y}\Big|_{y=0}\left(\text{ads.}\right) = \frac{1}{2}\frac{\mathrm{d}Q}{\mathrm{d}y}\Big|_{y=0}\left(\text{des.}\right) \tag{9}$$

where A is the area under the Q vs y profile corresponding to the amount of material adsorbed or desorbed. Eq.9 provides a convenient check on the validity of numerical (or analytic) approximations to the solution for the concentration profile.

3. Adsorption Profiles

A formal analytic solution to this problem (for adsorption with $\mathrm{f}(Q) = (1-\lambda Q)^{-1}$) has been given, in parametric form, by Fujita $^{(3)}$ (summarized by Crank $^{(4)}$):

$$Q = \frac{r}{r-1}\left[1-\mathrm{e}^{-2\mathrm{I}(\phi)}\right] \approx 1-\mathrm{e}^{-2\mathrm{I}(\phi)} \quad \text{(for } r \text{ large)} \quad y = \frac{1}{\sqrt{2\mu}}\left[\mathrm{f}\left(\phi\right)-\phi\right]\mathrm{e}^{\mathrm{I}(\phi)} \tag{10}$$

where:

$$\mathrm{I}\left(\phi\right) = \int_{o}^{q}\frac{\mathrm{d}\phi}{\mathrm{f}\left(Q\right)};\ \mathrm{f}\left(Q\right) = \sqrt{\phi^2 - 2\mu\ln\phi};\ r = \frac{1}{1-\lambda} \tag{11}$$

The parameter μ is defined by the relationship:

$$\mathrm{I}(1)=\int_0^1 \frac{\mathrm{d}\phi}{\mathrm{f}(Q)}=\frac{1}{2}\ln r \tag{12}$$

When μ is small $\mathrm{f}(\phi)-\phi\approx-\frac{\mu\ln\phi}{\phi}$ and $\mathrm{I}(\phi)\approx\mathrm{I}(1)+\ln\phi=\ln\left(\phi\sqrt{r}\right)$ (13)

With these approximations the limiting expression for the concentration profile (for r large) may be obtained in explicit form:

$$Q=1-\frac{1}{r}\exp\left[2\sqrt{\frac{2}{\mu r}}.y\right] \tag{14}$$

The limiting slope is given by:

$$-r\frac{\mathrm{d}Q}{\mathrm{d}y}\bigg|_{y=0}=2\sqrt{\frac{2}{\mu r}} \tag{15}$$

This approximation is valid only for the region where $Q\rightarrow 1.0$ but the range of validity increases when r is large.

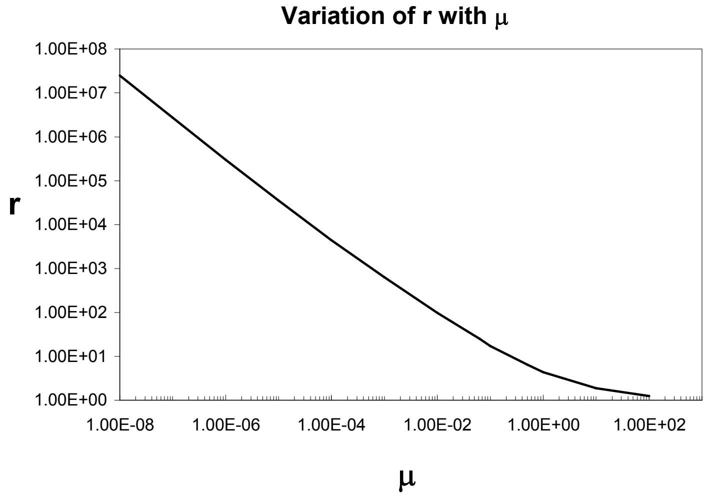

Fig. 1 Variation of diffusivity ratio r with parameter μ calculated from Eq.12.

Another limiting explicit approximation which is valid as $Q\rightarrow 0$ may be obtained by noting that, for $\phi\rightarrow 0$

$$\mathrm{I}(\phi) \approx \frac{1}{\sqrt{2\mu}} \int_0^{\phi} \frac{\mathrm{d}\phi}{(-\ln\phi)^{1/2}} \approx 2\sqrt{\frac{\pi}{\mu}} \operatorname{erfc}(u) \tag{16}$$

where $u^2 = -\ln\phi$. We thus obtain

$$y \approx 2\sqrt{\frac{\pi}{\mu}} \operatorname{erfc}(u); \; Q \approx 2\sqrt{\frac{\pi}{\mu}} \operatorname{erfc}(y) \tag{17}$$

as the asymptotic expressions for the limit $\phi \to 0, \; u \to \infty$.

The variation of the parameter μ with r calculated by numerical integration of Eq.12, is shown in figure 1. Concentration profiles for various values of r, calculated from Eq.10 are shown in figure 2. Also shown are the limiting profiles calculated from the asymptotic expressions (Eqs.14 and 17) for selected values of r. When r is large Eq.14 provides a good approximation over most of the range but Eq.17 is valid only at very low values of Q. Since $y = x/\left(2\sqrt{D_o t}\right) = X/2\sqrt{\tau}$ one may plot directly the profiles of Q vs X for a finite slab (for times less than the time at which the penetrating wave reaches the centre of the slab). Such a plot is shown in figure 3 from which the form of the penetrating wave is apparent. Note that, in contrast to the shockwave type of behavior observed for a macropore diffusion controlled system with irreversible adsorption $^{(5)}$ the concentration wave in the present system disperses as it penetrates.

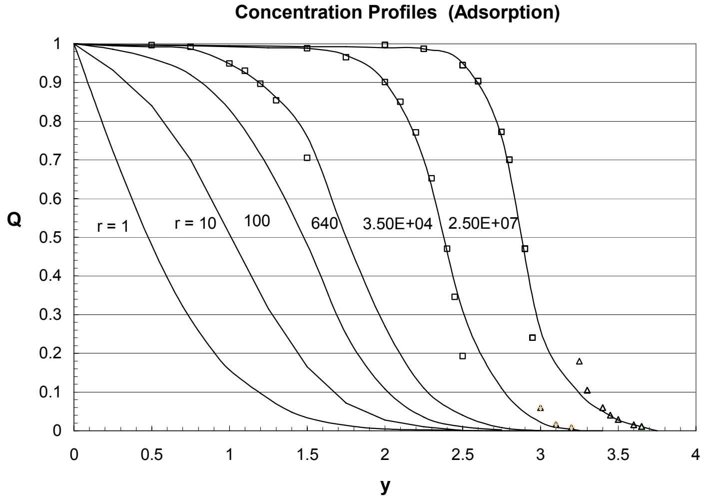

Fig. 2 Concentration profiles for adsorption showing how the form of the concentration wave changes with r. Note that when r is large the asymptotic expression (Eq.14) provides a good approximation except when Q is small.

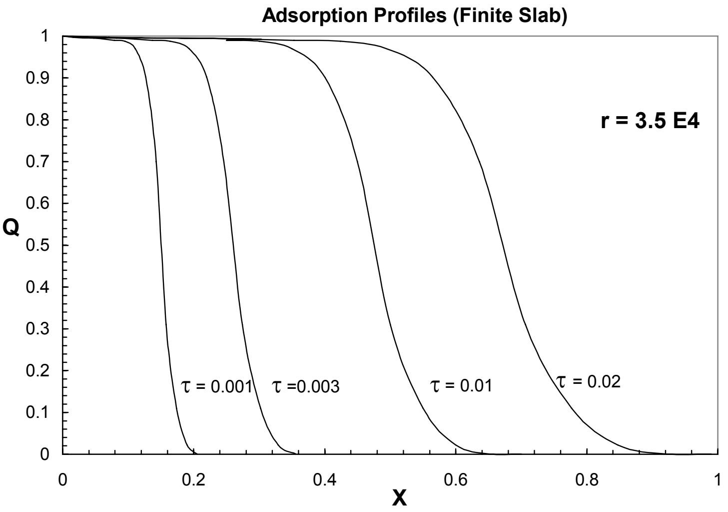

Fig. 3 Profiles of figure 2 replotted in the coordinates Q vs X (for a finite slab) for various values of τ. Note the increasing spread of the wave form as τ increases.

4. Desorption Profiles

Fujita presented only the solution for adsorption but by following his procedure the corresponding desorption problem may be solved to yield, for the transient profile:

$$Q = \left(\frac{r}{r-1}\right)\left[1-\exp\left\{2\left[\mathrm{I}(\phi)-\mathrm{I}(1)\right]\right\}\right]$$

$$y = \sqrt{\frac{r}{2\mu}}\left[\mathrm{f}(\phi)-\phi\right]\exp\left[\mathrm{I}(1)-\mathrm{I}(\phi)\right] \tag{18}$$

where the symbols and integrals have the same meanings as for the adsorption case. It is shown in the appendix that, when $r \to 1$, Eqs 10 and 18 both reduce to the well known error function forms for a constant diffusivity system. Following a procedure similar to that used to derive Eq.14 the following explicit approximation (valid only for small C and large r) can be obtained:

$$y \approx -\sqrt{\frac{\mu r}{8}}\,\frac{\ln(1-Q)}{(1-Q)} \tag{19}$$

Concentration profiles calculated from Eqs.18 are shown in figure 4. As is to be expected and in contrast to a linear system, the profiles for desorption and adsorption are quite different. The desorption profiles show no inflexion. The initial slope increases only slightly with increasing *r* but the curvature increases so that, when *r* is large, the gradient at some distance from the surface is small. Physically this form is to be expected since, when *r* is large, the desorption rate is controlled by diffusion through the surface region in which $D \rightarrow D_o$.

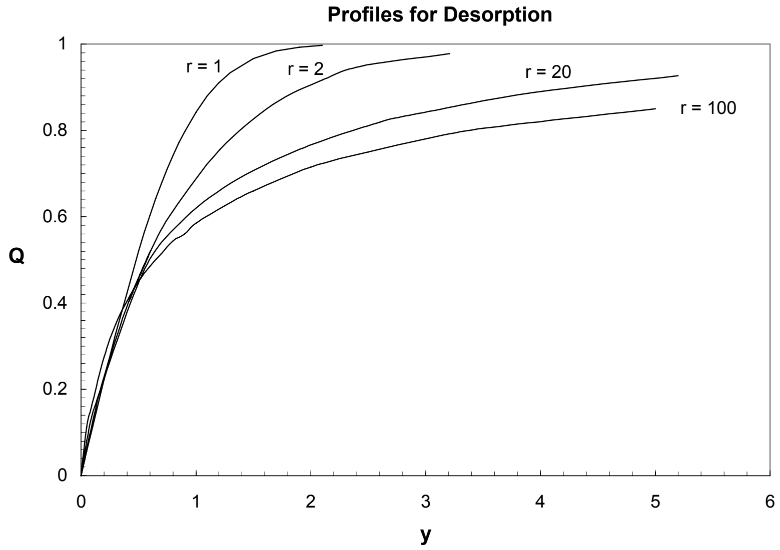

Fig. 4 Profiles for desorption from a semi-infinite medium for selected values of *r*.

5. Uptake Rates

The adsorption rate is given by:

$$\frac{\mathrm{d}m}{\mathrm{d}t} = -rD_0 \left.\frac{\mathrm{d}q}{\mathrm{d}x}\right|_{x=0} = -\frac{Dq_0}{2\sqrt{D_0 t}} \cdot \left.\frac{\mathrm{d}Q}{\mathrm{d}y}\right|_{y=0} \tag{20}$$

and, on integration:

$$m_\mathrm{t} = -r\sqrt{D_0 t}\;\; q_0 \;\; \left.\frac{\mathrm{d}Q}{\mathrm{d}y}\right|_{y=0} \tag{21}$$

When the diffusivity ratio is large ($\lambda \rightarrow 1.0$, $r \rightarrow \infty$) the concentration profile assumes the form of a penetrating wave (see figure 2) so the semi-infinite medium approximation will be valid throughout most of the uptake. In this regime the fractional approach to equilibrium ($m_\infty = q_o \ell$) will be given by :

$$\frac{m_{\mathrm{t}}}{m_{\infty}} = -r\sqrt{\frac{D_0 t}{\ell^2}}.\frac{\mathrm{d}Q}{\mathrm{d}y}\Big|_{y=0} = -r\sqrt{\tau}\frac{\mathrm{d}Q}{\mathrm{d}y}\Big|_{y=0} \qquad (22)$$

This expression shows that the "$\sqrt{t}$ law" is still valid even when the diffusivity is strongly concentration dependent.

Prediction of the uptake rate depends on estimating the concentration gradient at the surface $\left[\left(\mathrm{d}Q/\mathrm{d}y\right)\big|_{y=0}\right]$. When r is large we may use Eq. 15 which yields:

$$\frac{m_{\mathrm{t}}}{m_{\infty}} \approx 2\sqrt{\frac{2\tau}{\mu r}} \qquad (23)$$

By comparison with a linear system for which the approach to equilibrium is given by:

$$\frac{m_{\mathrm{t}}}{m_{\infty}} \approx 2\sqrt{\frac{D_0 t}{\pi \ell^2}} = 2\sqrt{\frac{\tau}{\pi}} \qquad (24)$$

we see that the "effective" diffusivity (D_{e}) for adsorption is given by:

$$\frac{D_{\mathrm{e}}}{D_0} = \frac{2\pi}{\mu r} \qquad (25)$$

The product μr decreases with increasing r so the effective diffusivity will increase continuously (rather than approaching an asymptotic limit) as the isotherm approaches the rectangular form.

For desorption the semi-infinite medium approximation is valid only at short times since, as may be seen from figure 4, when r is large the concentration far from the surface decreases quite rapidly. The expression corresponding to Eq. 22 is:

$$\frac{m_{\mathrm{t}}}{m_{\infty}} = \sqrt{\tau}\ \frac{\mathrm{d}Q}{\mathrm{d}y}\Big|_{y=0} \qquad (26)$$

but this expression is of limited utility since it applies only in the limit of very short times. A more useful approximation for a finite slab may be obtained by recognizing that, when r is large, most of the desorbing material comes from the interior region where the concentration profile is quite flat. As a simple model we therefore approximate the system as a semi-infinite medium in which the concentration (q_{o}) is essentially uniform (except in the surface region) but decreases with time:

$$-\ell\frac{\mathrm{d}q_0}{\mathrm{d}t}=D_0\frac{\mathrm{d}q}{\mathrm{d}x}\bigg|_{x=0}=\frac{q_0}{2}\sqrt{\frac{D_0}{t}}.\frac{\mathrm{d}q}{\mathrm{d}y}\Big|_{y=0} \tag{27}$$

We assume that $\frac{\mathrm{d}q}{\mathrm{d}y}\Big|_{y=0}=\kappa$ remains approximately constant (true for large *r*). With this approximation Eq.27 can be easily integrated to yield:

$$\ln\left(\frac{\bar{q}}{q_0}\right)\approx-\kappa\sqrt{\tau} \tag{28}$$

Since $\bar{q}/q_0\approx 1-m_t/m_\infty$ this yields for the desorption curve:

$$\frac{m_\mathrm{t}}{m_\infty}=1-\mathrm{e}^{-\kappa\sqrt{\tau}} \tag{29}$$

This expression explains why, for strongly adsorbed species, desorption is very slow and plots of $\ln\left(1-m_\mathrm{t}/m_\infty\right)$ vs t which are linear for a constant diffusivity system, commonly show a decreasing slope$^{(2)}$.

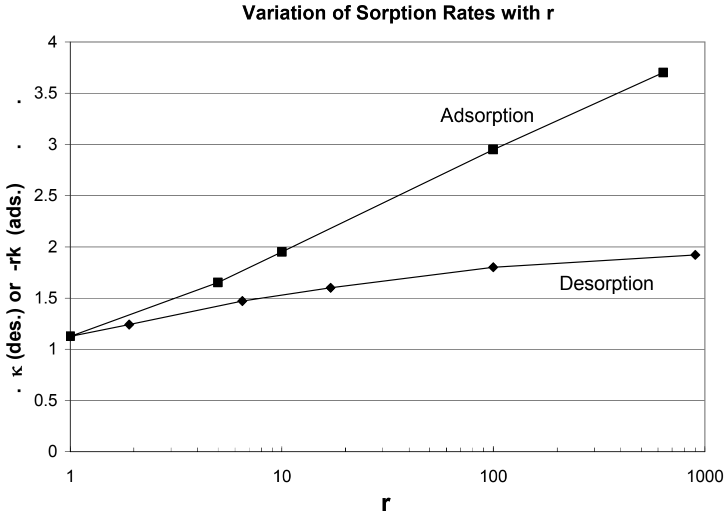

Fig. 5 Variation of initial adsorption and desorption rate (semi-infinite medium) with r calculated from the limiting slopes (κ) of the $Q-y$ profiles according to Eq.22 (ads.) or Eq.26 (des.).

At short times Eq.29 reduces to Eq. 26 (which is of the same form as Eq. 22 for adsorption) so the initial rates of adsorption and desorption for a semi-infinite medium may be compared simply on the basis of the limiting slopes and the diffusivity ratio. Such a comparison is shown in figure 5. For both adsorption and desorption the rate increases with r but the increase is greater for adsorption leading to an increasing difference between initial adsorption and desorption rates with increasing non-linearity$^{(6)}$.

6. Conclusion

Although the equations describing transient adsorption and desorption with a concentration dependent diffusivity can be solved numerically this task is not trivial when r is large and the equations are strongly non-linear. The analytic solutions originally obtained by Fujita and extended here to desorption yield greater understanding and provide a basis for simple asymptotic approximations which are practically useful for modelling adsorption/desorption kinetics.

Notation

A	defined by Eq.8
b	Langmuir constant (Eq.1)
D	Fickian diffusivity
D_o	Limiting or "corrected" diffusivity (Eq. 2)
D_e	"effective" diffusivity
$\mathrm{I}(\phi),\mathrm{I}(1)$	Integrals defined by Eqs.11 and 12
ℓ	half-thickness (of parallel sided slab)
m_t	mass of sorbate adsorbed or desorbed during time t
m_∞	value of m_t as $t \rightarrow \infty$ (i.e. at equilibrium)
p	sorbate partial pressure
q	adsorbed phase concentration
q_o	value of q at equilibrium with external gas phase
q_s	saturation limit (Eq.1)
Q	dimensionless concentration q/q_s
r	diffusivity ratio $D(Q)/D_0$
t	time
u	$-\ln\phi$
x	distance (measured from external surface)
X	dimensionless distance x/ℓ
y	dimensionless distance $x/2\sqrt{D_0 t}$
κ	limiting slope $(\mathrm{d}Q/\mathrm{d}y)_{y=0}$ for desorption (Eq.28)
μ	constant defined by Eq.12
λ	q_o/q_s
τ	dimensionless time $D_o t/\ell^2$
$\phi\,(Q)$	parameter defined by Eqs.11 and 12.

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Appendix: Reduction to Linear System for r → 1.0

The linear limit ($r \to 1.0$) corresponds to $\mu \to \infty$ (as may be seen from figure 1). When μ is large we have:

$$\mathrm{f}(\phi) \approx \sqrt{2\mu}\sqrt{-\ln u} = \sqrt{2\mu}.u \quad \text{where } u^2 = -\ln\theta$$

$$\mathrm{I}(\phi) = \int_0^{\phi} \frac{\mathrm{d}\phi}{\phi} = \sqrt{\frac{2}{\mu}} \int_u^{\infty} \mathrm{e}^{-u^2}\,\mathrm{d}u = \sqrt{\frac{\pi}{2\mu}}\,\mathrm{erfc}(u)$$

$$\mathrm{I}(1) = \sqrt{\frac{\pi}{2\mu}} = \frac{1}{2}\ln r,\ r = \exp\left(\sqrt{\frac{2\pi}{\mu}}\right),\ \frac{r}{r-1} \to \sqrt{\frac{\mu}{2\pi}}$$

Both $\mathrm{I}(\phi)$ and I(1) are small so exp $[-\mathrm{I}(\phi)] \approx 1 - \mathrm{I}(\phi) = 1 - \sqrt{\frac{\pi}{2\mu}}\,\mathrm{erfc}(u)$

Hence we have:

Adsorption:

$$Q = \frac{r}{r-1}\left[1 - \mathrm{e}^{-2\mathrm{I}(\phi)}\right] \to \mathrm{erfc}(u)$$

$$y = \frac{1}{\sqrt{2\mu}}\left[\mathrm{f}(\phi) - \phi\right]\mathrm{e}^{\mathrm{I}(\phi)} \to u\mathrm{e}^{\mathrm{I}(\phi)} \approx u$$

$$Q = \mathrm{erfc}(y)$$

Desorption:

$$Q = \frac{r}{r-1}\left[1 - \exp\left[2\left(\mathrm{I}(\phi) - \mathrm{I}(1)\right)\right]\right] \to \mathrm{erf}\ u$$

$$y = \sqrt{\frac{r}{2\mu}}\left[\mathrm{f}(\phi) - \phi\right]\exp\left[\mathrm{I}(1) - \mathrm{I}(\phi)\right] \to u\exp\left[\sqrt{\frac{\pi}{2\mu}}\ \mathrm{erf}\ u\right] \approx u$$

$$Q = \mathrm{erf}(y)$$

These are the well known solutions for a constant diffusivity system.

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