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Overall mass-transfer coefficients in non-linear chromatography

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Abstract

In the case of mass transfer where concentration differences in both phases must be taken into account, one may define an overall mass-transfer coefficient based on the apparent overall concentration difference. If the equilibrium relationship is linear, i.e., in cases where a Henry's law relationship can be applied, the overall mass-transfer coefficient will be concentration independent. However, in mass-transfer operations, a linear equilibrium relationship is in most cases not a valid approximation wherefore the overall mass-transfer coefficient becomes strongly concentration dependent as shown in this paper. In this case one has to discard the use of overall mass-transfer coefficients and calculate the rate of mass transfer from the two-film theory using the appropriate non-linear relationship to calculate the equilibrium ratio at the interface between the two films. © 1998 Elsevier Science B.V. All rights reserved.

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1. Introduction

1.1. Mass transfer in dilute systems

In systems containing water as the solvent the mole fraction or the molar density of dissolved species are often quite low compared to the mole fraction or the molar density of water. In this case all transferred species behave as if the system is a pseudo binary system because the dissolved species do not interact. The local mass-transfer coefficients k_{ix} and k_{iy} are defined in terms of the rate of diffusion normal to the interface. Details and further important assumptions are given elsewhere [1,2]. The expressions for the flux of species i per unit transfer area is

$$J_i = k_{ix}(x_{i_0} - x_i) = -k_{iy}(y_{i_0} - y_i) \quad (1)$$

where x and y denote the bulk phase compositions and subscript 0 denotes a concentration at the interface. At the interphase the system is in equilibrium, that is:

$$y_{i_0} = F_{i_0}(x_{i_0}, y_0)x_{i_0} \quad (2)$$

where F_{i_0} is the interphase equilibrium ratio which depends on the thermodynamic variables x_0 and y_0 at the interphase; F_{i_0} is in general not a constant. In a non-linear system the equilibrium ratios will vary from the inlet to the outlet because x and y vary down the column. In Eq. (2) we have, out of simplicity, omitted temperature and pressure as thermodynamic variables, but they should of course be included.

We have assumed that the mixture is ideal, but strictly speaking, the force of flow of the individual species relative to each other is the gradient in the chemical potential and if the mixture is non-ideal the appropriate driving force must replace the concentration difference.

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The local mass-transfer coefficients are in most cases difficult to measure, except in experiments so designed that the concentration differences across one of the phases can be neglected. For convenience and in cases where concentration differences in both phases must be taken into account, one may define an overall mass-transfer coefficient K_{ix} or K_{iy} based on the apparent overall concentration difference

$$J_i = K_{ix}(x_i^* - x_i) = -K_{iy}(y_i^* - y_i) \quad (3)$$

where K_{ix} denotes the overall mass-transfer coefficient referring to the apparent overall driving force $(x_i^* - x_i)$, and K_{iy} denotes the overall mass-transfer coefficient referring to the apparent overall driving force $-(y_i^* - y_i)$. The mole fraction y_i^* is the y -phase composition that would be in equilibrium with the bulk x -phase composition x ; that is, $y_i^* = F(x, y^*)x_i$ and correspondingly, x_i^* is defined by $y_i = F(x^*, y)x_i^*$. If the overall mass-transfer coefficients so defined are treated as independent of the concentration it requires that the equilibrium ratio be constant otherwise Eq. (3) will not be in accordance with the fundamental assumptions in Eqs. (1) and (2). A fact that leads to erroneous results when neglected.

When the equilibrium ratio F_i is independent of the concentration the relationship between the film mass-transfer coefficients and the overall mass-transfer coefficients becomes quite simple

$$\frac{1}{K_{ix}} = \frac{1}{k_{ix}} + \frac{1}{F_i k_{iy}} \quad (4)$$

and

$$\frac{1}{K_{iy}} = \frac{F_i}{k_{ix}} + \frac{1}{k_{iy}} \quad (5)$$

where F_i then is a kind of Henry's law constant.

In the case of a non-linear equilibrium relationship the overall mass-transfer coefficients K_{ix} and K_{iy} are calculable as

$$\frac{1}{K_{ix}} = \left(\frac{1}{k_{ix}} + \frac{1}{F_{i_0} k_{iy}} \right) \frac{F_i(x^*, y) - x_i}{F_{i_0} - x_i} \quad (6)$$

$$\frac{1}{K_{iy}} = \left(\frac{F_{i_0}}{k_{ix}} + \frac{1}{k_{iy}} \right) \frac{y_i - x_i F_i(x, y^*)}{y_i - x_i F_{i_0}} \quad (7)$$

which shows that although the overall mass-transfer coefficients are in principle calculable from the two-film mass-transfer coefficients, such formula will in general be of little use because the overall mass-transfer coefficients will be strongly concentration dependent. But even in cases where the equilibrium ratio is concentration dependent it is straight forward to calculate the flux in accordance with the two-film theory. First, we solve Eqs. (1) and (2) for the interfacial concentration and then substitute either x_{i_0} or y_{i_0} into Eq. (1) in order to calculate the rate of mass transfer. The relationship between x_i and y_i is of course in all cases given by the mass balance. In the next section we will show how strongly the non-linearity can effect the overall mass-transfer coefficient.

2. Mass transfer in chromatographic media

2.1. Linear isotherms

Let us consider an adsorbate with a linear isotherm

$$q = Ac \quad (8)$$

where A depends on the adsorbate, the ionic strength, pH and the adsorbent. As concentration variables we use the mass densities c and q wherefore Eqs. (1) and (3) become

$$J = k_f(c_0 - c) = -k_s(q_0 - q) \quad (9)$$

and

$$J = K_c(c^* - c) = -K_q(q^* - q) \quad (10)$$

where subscript 0 denotes a concentration at the interface and the superscript * denotes the hypothetical equilibrium concentration. Further, k_f denotes the film mass-transfer coefficient in the mobile phase, k_s denotes the film mass-transfer coefficient in the solid chromatographic medium, K_c denotes the overall mass-transfer coefficient referring to the apparent overall mobile phase driving force $(c^* - c)$, and K_q denotes the overall mass-transfer coefficient referring

to the apparent overall solid-phase driving force $-(q^* - q)$. The hypothetical equilibrium concentrations c^* and q^* are calculable from Eq. (8)

$$q^* = Ac \tag{11}$$

$$c^* = \frac{q}{A} \tag{12}$$

In the case of a linear isotherm the relationship between the film mass-transfer coefficients, k_f and k_s , and the overall mass-transfer coefficients K_c and K_q is given by the well known equations

$$\frac{1}{K_c} = \frac{1}{k_f} + \frac{1}{Ak_s} \tag{13}$$

$$\frac{1}{K_q} = \frac{A}{k_f} + \frac{1}{k_s} \tag{14}$$

which shows that the overall mass-transfer coefficients K_c and K_q are concentration independent when the isotherm is linear.

2.2. Non-linear isotherms

Let us now consider an adsorbate with a strongly favourable isotherm of the Langmuir type

$$q = \frac{q_{\max}bc}{1 + bc} = F(c)c \tag{15}$$

where the maximum binding capacity q_{\max} and the b parameter depend on the adsorbate, the ionic strength, pH and the adsorbent. The hypothetical equilibrium concentrations c^* and q^* in Eq. (10) are in this case calculable from Eq. (15)

$$q^* = F(c)c = \frac{q_{\max}bc}{1 + bc} \tag{16}$$

and

$$c^* = \frac{q}{F(c^*)} = \frac{q}{b(q_{\max} - q)} \tag{17}$$

From Eqs. (6) and (7) we can obtain relationships between the film mass-transfer coefficients k_f and k_s , and the overall mass-transfer coefficients K_c and K_q similar to but much more complex than the Eqs. (13) and (14). The result is

$$\frac{1}{K_c} = \left(\frac{1}{k_f} + \frac{1}{F(c_0)k_s} \right) \frac{\frac{q}{F(c^*)} - c}{\frac{q}{F(c_0)} - c} \tag{18}$$

$$\frac{1}{K_q} = \left(\frac{F(c_0)}{k_f} + \frac{1}{k_s} \right) \frac{q - cF(c)}{q - cF(c_0)} \tag{19}$$

which shows that K_c and K_q become concentration dependent when the isotherm is non-linear. To illustrate how concentration dependent the overall mass-transfer coefficients can be and thus to show how poor an approximation it can be to assume that they are constants we need a mass balance to relate c to q . To get a simple formula for the mass balance let us consider a frontal analysis where the conditions for obtaining a constant front is fulfilled; the mass balance becomes [3]

$$\frac{q}{c} = \frac{q_f}{c_f} = F(c_f) = \frac{q_{\max}b}{1 + bc_f} \tag{20}$$

where c_f is the feed concentration and q_f the corresponding equilibrium concentration in the medium. Further, the relative influence of the resistances will be accounted for by the scaled mass-transfer resistance ratio

$$\delta = \frac{k_f c_f}{k_s q_f} \tag{21}$$

where it is common practice to assume that $\delta < 0.1$ indicates that the mobile phase resistance is dominating, $\delta \approx 1$ indicates that both resistances are important, and $\delta > 10$ indicates that the solid-phase resistance is dominating.

To calculate the interfacial concentrations, c_0 and q_0 , one must proceed with the equation

$$k_f(c_0 - c) = -k_s(q_0 - q) \tag{22}$$

At the interface one can substitute the equilibrium concentration $q_0 = F(c_0)c_0$ by inserting Eq. (15) in the right hand side of Eq. (22); this gives the wanted relation for calculation of the interfacial concentration c_0

$$k_f(c_0 - c) = -k_s \left(\frac{q_{\max}bc_0}{1 + bc_0} - q \right) \tag{23}$$

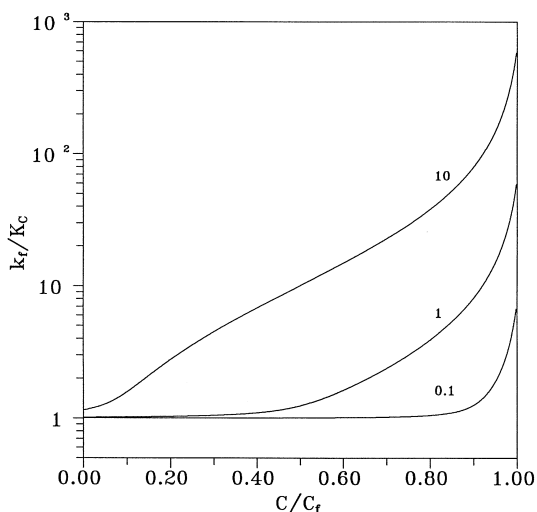


Fig. 1. The ratio of the mobile phase film mass-transfer coefficient k_f to the apparent overall fluid phase driving force mass-transfer coefficient K_c as function of the concentration and the scaled resistance ratio parameter δ at a feed concentration of 1.3 g/l. The equilibrium is calculated from a Langmuir isotherm with a maximum capacity q_{\max} of 125 g/l and a b parameter of 50 l/g.

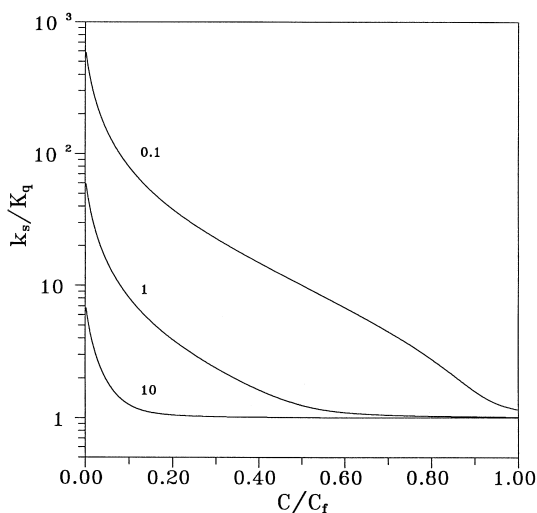


Fig. 2. The ratio of the solid-phase film mass-transfer coefficient k_s to the apparent overall solid-phase driving force mass-transfer coefficient K_q as function of the concentration and the scaled resistance ratio parameter δ at a feed concentration of 1.3 g/l. The equilibrium is calculated from a Langmuir isotherm with a maximum capacity q_{\max} of 125 g/l and a b parameter of 50 l/g.

or

$$\delta(c_0 - c) = -\frac{c_f}{q_f} \left(\frac{q_{\max} b c_0}{1 + b c_0} - q \right) \quad (24)$$

where c to q are related by the mass balance Eq. (20). We insert δ and the equilibrium ratios $F(c_0)$ and $F(c_f)$ in Eqs. (18) and (19) and get

$$\frac{k_f}{K_c} = \left(1 + \delta \frac{F(c_f)}{F(c_0)} \right) \frac{\frac{q}{F(c^*)} - c}{\frac{q}{F(c_0)} - c} \quad (25)$$

and

$$\frac{k_s}{K_q} = \left(\frac{1}{\delta} \frac{F(c_0)}{F(c_f)} + 1 \right) \frac{q - cF(c)}{q - cF(c_0)} \quad (26)$$

3. Results and conclusion

In order to calculate the influence of the non-linearity on the overall mass-transfer coefficients from Eqs. (25) and (26) we choose a Langmuir isotherm with a maximum binding capacity q_{\max} of 125 g/l, a b of 50 l/g, and a feed concentration c_f of 1.3 g/l. Calculate q_f and $F(c_f)$ from Eq. (20), and given c , calculate q from the mass balance Eq. (20), c_0 from Eq. (24), $F(c_0)$ from Eq. (15), and finally $F(c)$ and $F(c^*)$ from Eqs. (16) and (17). As δ values we choose 0.1, 1 and 10. The results are shown in Figs. 1 and 2. Figs. 1 and 2 show that the assumption of a constant overall mass-transfer coefficient K_c or K_q is only valid when δ is small or large. As expected, when δ is small K_c is a constant and when δ is large K_q is a constant. When $\delta \approx 1$ neither K_c nor K_q are constants but depend strongly on the concentration due to the non-linear isotherm. One must therefore in general discard the use of overall mass-transfer coefficients and calculate the flux from the formula

$$J = k_f(c_0 - c) \quad (27)$$

by solving the equations

$$k_f(c_0 - c) = -k_s(q_0 - q) \quad (28)$$

and

$$q_0 = F(c_0, q_0)c_0 \quad (29)$$

for the interfacial concentration c_0 and insert in Eq.

(27). The relationship between c and q is in general given by the mass balance which in case of a constant form front reduces to Eq. (20).

q_{\max}	Maximum equilibrium capacity in the solid-phase, g/l particle
x	Mole fraction in the x -phase
y	Mole fraction in the y -phase

4. Symbols

A	Equilibrium ratio, linear isotherm
b	Langmuir parameter, l/g
c	Mobile phase concentration, g/l
F	Equilibrium ratio
J	Flux, mol or g/cm ² s
k_f	Mobile phase film mass-transfer coefficient, cm/s
k_s	Solid-phase film mass-transfer coefficient, cm/s
K_c	Overall mobile phase mass-transfer coefficient, cm/s
K_q	Overall solid-phase mass-transfer coefficient, cm/s
k_{ix}	x -Phase film mass-transfer coefficient of species i , mol/cm ² s
k_{iy}	y -Phase film mass-transfer coefficient of species i , mol/cm ² s
K_{ix}	Overall x -phase mass-transfer coefficient of species i , mol/cm ² s
K_{iy}	Overall y -phase mass-transfer coefficient of species i , mol/cm ² s
q	Solid-phase concentration, g/l particle

Greek letters

δ	Scaled mass-transfer resistance ratio
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Subscripts

i	Species i
0	Concentration at the interphase of the two films
f	Feed concentration

Superscripts

*	Hypothetical equilibrium concentration
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References

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