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A calculation method for multicomponent mass transfer coefficient correlations

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Abstract

Mass transfer coefficients are usually based on measurements from binary mixtures. This leads to scalar correlation equation for mass transfer coefficient. These equations are usually obtained from dimensional analysis, and they include fractional powers of the system parameters, like the Reynolds number and the Schmidt number. Generalization according to the linearized Maxwell–Stefan theory (∇c_t and $\nabla[D]$ are assumed zero along the diffusion path) is then made by replacing the scalar values by corresponding matrix values. This leads to the problem of calculating the matrix fractional powers. This can be done by the similarity transform or by the Sylvester's expansion, but it is quite a tedious procedure. Krishna and Standart (1976) *American Institute of Chemical Engineers Journal 22*, 383–9 proposed that the binary mass transfer correlations could be used for each component pair in multicomponent systems. In this paper, another approximate approach is chosen for the simplification of the calculations. In the Maxwell–Stefan diffusion coefficient matrix, the off-diagonal elements describe diffusional interactions. These elements may be significant, but are usually smaller in magnitude than the diagonal elements. The method presented in this paper is based on that fact. The method gives more accurate results than the practice of using binary mass transfer coefficients. It is applicable to all mass transfer models, such as the film model, penetration model, and models resulting from boundary layer analyses. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Maxwell–Stefan theory; Mass transfer coefficient correlations; Matrix approximations

1. Introduction

Mass transfer correlations for binary systems are often in the form of

$$\mathrm{Sh} = a \cdot \mathrm{Sc}^p \tag{1}$$

where a is a scalar, which depends on some of the system parameters, especially the Reynolds number. p is a real number, usually in the range of 0.25–0.66.

These correlations can be generalized to multicomponent systems in a straightforward manner by substituting the dimensionless numbers by the corresponding matrix form

$$[\mathrm{Sh}] = a \cdot [\mathrm{Sc}]^p \tag{2}$$

where a remains scalar. In the approach of this paper, matrices in the Schmidt number are calculated from the Maxwell–Stefan theory. This manner of proceeding was proposed by Toor (1964) and by Stewart and Prober (1964). For a further reference, see Taylor and Krishna (1993), pp. 214–215.

This generalization leads to problem of computing matrix fractional powers. This can be done by similarity transform or Sylvester's expansion, after computing the eigenvalues (and eigenvectors in the similarity transform) of the [Sc] matrix. This might, however, be quite time consuming if this correlation is to be used again and again, for example in an inner loop of some iterative solution for a process simulation or optimization problem.

At this point it should be noted that the main root of the fractional power is always needed, because both [Sh] and [Sc] matrices have only real and positive eigenvalues. This root can be then proven unique. (Rudin, 1976, p. 10)

Krishna and Standart (1976) suggested that these correlations could be used with binary diffusion coeffi-

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cients to obtain the matrix of binary mass transfer coefficients. These coefficients are then used in the Maxwell–Stefan-theory mass transfer matrix formulation. This method might be most often used in practical calculations, even though it has come in for criticism. (Taylor & Krishna, 1993, pp. 214–215; Young & Stewart 1986)

The mass transfer coefficients are obtained from the Sherwood number matrix in the following way

$$[\mathrm{k}] = d \cdot [\mathrm{Sh}][\mathrm{D}] \tag{3}$$

where [D] is the Fickian diffusion coefficient matrix. It is calculated in the following way according to the Maxwell–Stefan theory: first calculate the matrix function of inverted binary diffusion coefficients, [B]

$$B_{ii} = \frac{x_i}{\mathcal{D}_{in}} + \sum_{\substack{k=1 \\ k \neq i}}^{n} \frac{x_k}{\mathcal{D}_{ik}}$$

$$B_{ij} = -x_i\left(\frac{1}{\mathcal{D}_{ij}} - \frac{1}{\mathcal{D}_{in}}\right) \tag{4}$$

[D] is then the inverse of [B]

$$[\mathrm{D}] = [\mathrm{B}]^{-1} \tag{5}$$

Matrices [D] and [B] are square matrices of size $n-1$, where n is the number of components. (Taylor & Krishna, 1993, pp. 19–21)

The Schmidt number matrix is defined for the multicomponent system as

$$[\mathrm{Sc}] = \nu[\mathrm{D}]^{-1} \tag{6}$$

Therefore, the required correlations for mass transfer coefficients for components $1 \ldots n-1$ are usually of the form

$$[\mathrm{k}] = b \cdot [\mathrm{D}]^{1-p} \tag{7}$$

2. The matrix fractional power approximation

Another way to calculate the matrix fractional power is to do it straightforwardly, but approximately. A general approximate method for all kinds of matrices cannot be derived without excessive loss of accuracy. However, if we use our knowledge of the [D] matrix structure, a reasonable approximation can be done. In the Maxwell–Stefan formulation, the diffusion coefficient matrix [D] is not diagonal, but the diagonal elements are usually greater than off-diagonal elements. This knowledge can be used in the approximation procedure.

Now we are presented with a problem of the form

$$[\mathrm{A}]^{n/m} = [\mathrm{B}] \tag{8}$$

where the matrix A is known and B is the desired result. At this point, only rational exponents are considered. Generalization to real numbers in discussed later.

We decompose the matrices A and B in diagonal and off-diagonal parts

$$[\mathrm{A}] = [\mathrm{F}] + [\mathrm{M}] \tag{9}$$

$$[\mathrm{B}] = [\mathrm{E}] + [\mathrm{N}] \tag{10}$$

So we can write this problem as

$$[\mathrm{A}]^n = ([\mathrm{F}] = [\mathrm{M}])^n = ([\mathrm{E}] = [\mathrm{N}])^m = [\mathrm{B}]^m \tag{11}$$

Now we use our knowledge that matrix A has larger diagonal elements than off-diagonal, and assume that the same is true for B, that is

$$\|[\mathrm{F}]\| > > \|[\mathrm{M}]\| \tag{12}$$

$$\|[\mathrm{E}]\| > > \|[\mathrm{N}]\| \tag{13}$$

and

$$\|[\mathrm{F}]^2[\mathrm{M}]\| > > \|[\mathrm{F}][\mathrm{M}]^2\| \tag{14}$$

$$\|[\mathrm{E}]^2[\mathrm{N}]\| > > \|[\mathrm{E}][\mathrm{N}]^2\| \tag{15}$$

where $\| \quad \|$ states for some suitable matrix norm.

The last two inequalities are assumed to be true for all the permutations of ([F], [F], [M]), ([F], [M], [M]), ([E], [E], [N]) and ([E], [N], [N]).

After expanding the binomial form (Eq. (11)) and using approximations (Eqs. (12)–(15)) we have

$$\begin{aligned} &[\mathrm{F}]^n + [\mathrm{F}]^{n-1}[\mathrm{M}] + [\mathrm{F}]^{n-2}[\mathrm{M}][\mathrm{F}] + \ldots + [\mathrm{F}][\mathrm{M}][\mathrm{F}]^{n-2} \\ &+ [\mathrm{M}][\mathrm{F}]^{n-1} = [\mathrm{E}]^m = [\mathrm{E}]^{m-1}[\mathrm{N}] \\ &= [\mathrm{E}]^{m-2}[\mathrm{N}][\mathrm{E}] + \ldots + [\mathrm{E}][\mathrm{N}][\mathrm{E}]^{m-2} = [\mathrm{N}][\mathrm{E}]^{m-1} \end{aligned} \tag{16}$$

Now it can be seen that

$$[\mathrm{F}]^n = [\mathrm{E}]^m \tag{17}$$

since [F] and [E] are diagonal and [M] and [N] are off-diagonal.

For the off-diagonal elements ($i \neq j$) we obtain the following equality

$$\begin{aligned} &m_{ij}(f_{ii}^{n-1} + f_{ii}^{n-2}f_{jj} + \ldots + f_{ii}f_{jj}^{n-2} + f_{jj}^{n-1}) \\ &= n_{ij}(e_{ii}^{m-1} + e_{ii}^{m-2}e_{jj} + \ldots + e_{ii}e_{jj}^{m-2} = e_{jj}^{m-1}) \end{aligned} \tag{18}$$

Using the summation equation for a geometric series

$$u_i = a \cdot q^{i-1}$$

$$\sum_{i=1}^{n} u_i = a\frac{1-q^n}{1-q} \tag{19}$$

for both sides, we end up with

$$m_{ij}\left[f_{ii}^{n-1}\frac{1-\left(\frac{f_{jj}}{f_{ii}}\right)^n}{1-\left(\frac{f_{jj}}{f_{ii}}\right)}\right] = n_{ij}\left[e_{ii}^{m-1}\frac{1-\left(\frac{e_{jj}}{e_{ii}}\right)^m}{1-\left(\frac{e_{jj}}{e_{ii}}\right)}\right] \tag{20}$$

This and the next equation are valid for non-equal diagonal elements i.e. $e_{ii} \neq e_{jj}$ and $f_{ii} \neq f_{jj}$ for all i and j. This limiting case is considering later.

The final result for off-diagonal elements is obtained after using Eq. (17)

$$n_{ij} = m_{ij} \left[f_{ii}^{n/m-1} \frac{1-\left(\frac{f_{jj}}{f_{ii}}\right)^{n/m}}{1-\left(\frac{f_{jj}}{f_{ii}}\right)} \right] \tag{21}$$

With Eq. (17) we then observe that matrix fractional powers can be calculated termwise, when approximations (Eqs. (12)–(15)) hold. These results are valid for any fractional power n/m. However, by using the density argument for the rational field as a subfield of the real field, we can extend these results for any (here positive) real number p instead of rational n/m (Rudin, 1976, p. 9)

For a problem

$$[\mathrm{A}]^p = [\mathrm{B}] \tag{22}$$

we then have, after some manipulations, the following approximate equations

$$\mathrm{B}_{ii} = \mathrm{A}_{ii}^p \text{ for diagonal elements} \tag{23}$$

$$B_{ij} = A_{ij}\frac{A_{ii}^p - A_{jj}^p}{A_{ii} - A_{jj}} \text{ for off diagonal elements} \tag{24}$$

These equations reduce to the exact solution in special cases, two of which have practical importance. The first is the case of infinite dilution of all but one component. The second is the case, where the binary diffusion coefficients are equal, as usually is the case when closely similar chemical compounds diffuse. In these two cases the [D] matrix is diagonal.

The exact solution is also obtained when $p = 0$ or $p = 1$, but these two exponents have interest only as limiting cases.

3. Other matrix functions

We assume that there is a power series expansion for a general matrix function $f(\ )$ that we are interested in, so that

$$[\mathrm{B}] = f([\mathrm{A}]) = \sum_{n=0}^{\infty} a_n[\mathrm{A}]^n \tag{25}$$

So we can write using the notation of the previous section

$$[\mathrm{B}] = \sum_{n=0}^{\infty} a_n[[\mathrm{F}] + [\mathrm{M}]]^n \tag{26}$$

expanding this series and also using approximations from the previous section term by term, similarly to the matrix power approximation, we finally obtain

$$B_{ii} = f(A_{ii}) \text{ for diagonal elements} \tag{27}$$

$$B_{ij} = A_{ij}\frac{f(A_{ii}) - f(A_{jj})}{A_{ii} - A_{jj}} \text{ for off-diagonal elements} \tag{28}$$

If some two diagonal elements of the [A] matrix are equal or almost equal, we can use the derivative of the (now scalar) function $f(\ )$ at the point $A_{ii}(=A_{jj})$

$$B_{ij} = A_{ij}\frac{\mathrm{d}f(A_{ii})}{\mathrm{d}A} \text{ for off-diagonal elements, } A_{ii} = A_{jj} \tag{29}$$

This can be done also for the fractional power function, which is, in fact, only a special case here.

4. Numerical comparison

The two approximate solutions of Krishna and Standart and the present method are compared to exact (eigenvalue) solution by numerical simulations. Random values are used as diffusion coefficients. The elements of the matrix of binary diffusion coefficients are assumed uniformly distributed at the interval 0.5×10^{-9} to 2×10^{-9} m^2/s. Random values are also used for mole fractions at two points of the system. The difference between these points represents the driving force for diffusion. Maxwell–Stefan diffusion coefficients (Eq. (4)) are calculated at the average compositions.

Two criteria are used in the comparison. The first criterion is the relative error ε_1 in the mass transfer coefficient matrices

$$\varepsilon_1 = \sqrt{\frac{\sum_{i=1}^{n-1}\sum_{j=1}^{n-1}(k_{ij,\text{approx.}} - k_{ij,\text{correct}})^2}{\sum_{i=1}^{n-1}\sum_{j=1}^{n-1}(k_{ij,\text{correct}})^2}} \tag{30}$$

The second criterion is the relative error ε_2 of the resulting diffusion fluxes. When the high flux correction to the mass transfer coefficient matrix is neglected, i.e. negligible convective flux is assumed, the criterion is

$$(J) = c[\mathrm{k}](\Delta x) \tag{31}$$

$$\varepsilon_2 = \sqrt{\sum_{i=1}^{n-1}\left(\frac{J_{i,\text{approx.}} - J_{i,\text{correct}}}{J_{i,\text{correct}}}\right)^2} \tag{32}$$

The first criterion is connected with the difference between the resulting matrices themselves. The second criterion is connected with the resulting error in the mass transfer calculations, and may thus be considered more important than the first criterion.

The numerical results for several cases are collected in Table 1. Cases with the number of components $n = 3$, 4, 5, 8, and 25, and the correlation (2) exponent $p = 0.25$, 0.33, 0.4, 0.5, and 0.66, are considered. One thousand cases are calculated for each combination of number of components and power p, so that in total 25 000 cases are calculated.

Both methods result in errors that are in most cases $< 10\%$. Slightly larger errors are observed, if the number of components is high. This statistical comparison shows that the present method rarely results in larger errors than the binary mass transfer coefficient method.

As an example of the numerical comparison, a liquid phase system of methyl isobutyl ketone (1), acetic acid (2), ethanol (3), ethyl acetate (4), and water (5) is considered. The estimated binary Maxwell–Stefan diffusion coefficients are (10^{-9} m²/s).

$$D_{12} = 1.20,\ D_{13} = 1.32,\ D_{14} = 1.84,\ D_{15} = 0.75,\ D_{23} = 1.11,\ D_{24} = 1.49,\ D_{25} = 1.22,\ D_{34} = 1.64,\ D_{35} = 1.27,\ D_{45} = 0.90$$

The matrix of binary diffusion coefficients is symmetric, i.e. $D_{ij} = D_{ji}$.

Average mole fractions in the mass transfer region are

$$x_1 = 0.0037,\ x_2 = 0.0328,\ x_3 = 0.0312,\ x_4 = 0.0067,\ x_5 = 0.9256$$

The Maxwell–Stefan [D] matrix is obtained from Eqs. (4) and (5)

$$[\mathrm{D}] = \begin{bmatrix} 0.7755 & -0.0017 & -0.0021 & -0.0021 \\ 0.0004 & 1.2170 & 0.0040 & -0.0056 \\ -0.0009 & 0.0052 & 1.2621 & -0.0066 \\ -0.0027 & -0.0033 & -0.0039 & 0.9294 \end{bmatrix} \cdot 10^{-9}\ \mathrm{m}^2/\mathrm{s}$$

Using the penetration theory, the matrix of average mass transfer coefficients is

$$[\mathrm{k}] = b \cdot [\mathrm{D}]^{0.5} \tag{33}$$

where $b = 2(\pi t)^{-0.5}$ according to the residence time model of Higbie (Taylor and Krishna, 1993, p. 232). For the numerical comparisons of the two methods, the parameter b is not important, since it cancels out when the relative errors are calculated.

Table 1
Numerical comparison of binary mass transfer coefficient method and the method presented here to the exact eigenvalue solution

		Criterion 1				Criterion 2			
n	p	[a] $\varepsilon_{1,1}$%	[b] $\varepsilon_{1,2}$%	[a] $\varepsilon_{1,1} = \varepsilon_{1,2}$	[c] $N(\varepsilon_{1,1} = \varepsilon_{1,2})$	[a] $\varepsilon_{2,1}$%	[b] $\varepsilon_{2,2}$%	[a] $\varepsilon_{2,1} = \varepsilon_{2,2}$	[c] $N(\varepsilon_{2,1} = \varepsilon_{2,2})$
3	0.25	0.36	0.09	3.97	0	0.92	0.21	4.28	0
3	0.33	0.42	0.10	4.18	0	1.55	0.42	3.66	0
3	0.4	0.48	0.12	4.02	0	1.72	0.26	6.66	0
3	0.5	0.48	0.12	4.00	0	1.08	0.25	4.37	0
3	0.66	0.47	0.13	3.65	0	3.05	0.38	8.01	1
4	0.25	0.60	0.18	3.36	0	2.29	0.97	2.37	0
4	0.33	0.74	0.23	3.30	0	2.70	1.06	2.54	0
4	0.4	0.82	0.24	3.41	0	3.06	0.87	3.53	15
4	0.5	0.86	0.27	3.14	0	8.64	1.85	4.68	0
4	0.66	0.80	0.25	3.25	0	2.87	1.06	2.72	0
5	0.25	0.76	0.24	3.18	0	6.92	4.33	1.60	24
5	0.33	0.94	0.28	3.34	0	6.06	2.05	2.95	0
5	0.4	1.03	0.31	3.29	0	3.93	2.19	1.80	0
5	0.5	1.08	0.33	3.26	0	4.71	2.17	2.17	0
5	0.66	1.05	0.31	3.42	0	3.95	1.81	2.18	0
8	0.25	1.04	0.27	3.81	0	6.66	2.33	2.86	0
8	0.33	1.23	0.33	3.75	0	10.3	5.00	2.06	0
8	0.4	1.33	0.35	3.75	0	12.0	5.39	2.22	1
8	0.5	1.45	0.39	3.75	0	16.3	9.81	1.67	0
8	0.66	1.38	0.36	3.78	0	7.10	2.88	2.46	0
25	0.25	1.21	0.21	5.75	0	17.0	4.00	4.23	0
25	0.33	1.46	0.25	5.77	0	21.4	4.00	5.35	0
25	0.4	1.61	0.28	5.75	0	27.9	6.17	4.52	0
25	0.5	1.69	0.29	5.80	0	74.7	9.32	8.01	0
25	0.66	1.58	0.27	5.80	0	22.9	5.33	4.30	0

[a] $\varepsilon_{i,1}$, average error in the binary mass transfer coefficients according to criterion i.

[b] $\varepsilon_{i,2}$: average error in the present method according to criterion i.

[c] $N(\varepsilon_{i,1} < \varepsilon_{i,2})$: number of times the binary mass transfer coefficient method was more accurate than the present method according to criterion i (out of 1000 cases).

In the flux calculations, the following mole fraction differences are used

$$\Delta x_1 = 0.0050,\ \Delta x_2 = -0.0076,\ \Delta x_3 = -0.0094,\ \Delta x_4 = -0.0168$$

The following relative errors are calculated:
Criterion 1 (relative errors in the matrices)

Binary k_{ij}	$\varepsilon_{1,1} = 0.13\%$
Matrix approximation	$\varepsilon_{1,2} = 0.003\%$

Criterion 2 (relative errors in the fluxes)

Binary k_{ij}	$\varepsilon_{2,1} = 0.11\%$
Matrix approximation	$\varepsilon_{2,2} = 0.002\%$

Both these approximate methods gave results with a reasonable accuracy. However, the matrix approximation developed here gives results that are much more accurate than the binary mass transfer coefficient method.

It is interesting that in this case even better results are obtained, if the matrix approximation is applied in the form $[\mathrm{k}] = b \cdot [\mathrm{B}]^{-0.5}$, where [B] is the matrix of inverted binary diffusion coefficients. The errors are then 0.002% and 0.0009% for the two criteria. Usually the approximate inversion of the [B] matrix increases the error to some extent. The errors are, however, the same order of magnitude whether the matrix inversion is carried out approximately or not.

5. Computational work

For matrix eigenvalue calculations with QR decomposition, we need about $5n^3$ operation counts, where n is the dimension of the matrix. Then we need n arbitrary functional calculations, one for each eigenvalue, and one matrix inversion and two matrix multiplications. In the present method we need only n arbitrary functional calculations, and $2n^2$ other operation counts (one for each element), and one matrix inversion, which is of order $(1/3)n^3$. Thus our method is certainly time saving in practical calculations, especially for large n. If time saving is of primary importance, matrix inversion can also be avoided by using the inverted diagonal elements of the [B] matrix straightly. Then we have a true $O(n^2)$ process. This is obtained at the expense of slight increase in the approximation error. (Press, Teukolsky, Vetterling and Flannery, 1994).

In the relative computational time calculations it was assumed that either the form of the diffusion coefficient matrix or the value of the power p affects the computational time. Results for the different methods are presented in Table 2.

Table 2
Relative computational times

Number of components	Eigenvalue solution	Matrix approximation	Binary k_{ij}
3	1.00	0.29	0.32
4	3.00	0.52	0.65
5	5.36	0.84	1.09
8	20.2	2.91	3.56
11	44.6	7.06	7.76
15	109	16.2	18.5
20	223	35.6	41.8
25	426	71.2	74.1

It is clearly seen that the eigenvalue solution is much more time consuming than either of the other two. The use of the present matrix approximation is slightly faster than the use of the binary mass transfer coefficients.

6. Conclusion

The present approximate method for multicomponent mass transfer coefficient correlations yields generally very accurate results. Up to four components the errors are usually within 1%, and for a larger number of components the errors are usually within 10%, also when the binary diffusion coefficients are very unequal and when no single component has a mole fraction near unity.

The comparison of the present method with the binary mass transfer coefficient method of Krishna and Standart shows that the present method is significantly more accurate. A further advantage of the present method is that the matrix forms in the eigenvalue solution and in the present approximate solution are the same. The present method can be used with the matrix of inverted binary diffusion coefficients in a straightforward manner. In this case, no matrix inversions are needed in the Maxwell–Stefan mass transfer coefficient formulation.

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Appendix A. Notation

ε_1, ε_2	approximation errors according to different criteria
λ	eigenvalue of a matrix
(Δx)	vector of mole fraction differences

[A], [B]	arbitrary diagonal controlling matrices appearing in the Maxwell–Stefan mass transfer calculations
[B]	matrix function of inverted binary diffusion coefficients (Eqs. (5) and (6)) (s/m^2)
[D]	matrix of diffusion coefficients (m^2/s)
[E], [F]	arbitrary diagonal matrices
(J)	vector of diffusion fluxes (mol/m^2s)
[k]	matrix of mass transfer coefficients (m/s)
[N], [M]	arbitrary off-diagonal matrices
a, b	scalars
a_n	coefficient of a power series
c	total concentration (mol/m^3)
D_{ij}	binary diffusion coefficient (m^2/s)
$f(\ )$	arbitrary function
J_i	diffusion flux of component i (mol/m^2s)
n	number of components
p	scalar (power)
Sc	Schmidt number, dimensionless
Sh	Sherwood number, dimensionless

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