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Film model for mass transfer in non-ideal multicomponent fluid mixtures

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Abstract

Multicomponent film model equations in the framework of generalized Maxwell–Stefan model were solved for non-ideal fluid mixtures for any given composition dependence of concentration, diffusivities and thermodynamic non-idealities. The solution is valid for planar, cylindrical and spherical film geometries This proposed solution was used to evaluate the available approximate solutions and to examine the conditions under which they perform well On the basis of calculations for the system acetone–benzene–carbon tetrachloride, it was observed that approximate methods generally give rise to greater errors in calculating small fluxes, i e when components transfer under small values of driving force. A parameter α was defined for each component to assess the influence of varying physical properties on the error associated with approximate methods When $\alpha \leqslant 15\%$ the error is about 6% and, when $\alpha \geqslant 25\%$, the corresponding errors are greater than 18% Whenever the approximate methods may be used for calculation, their performances are similar, but the method based on effective diffusivities has the advantage of being simple

1. Introduction

In many practical engineering operations such as absorption, distillation, extraction and ion exchange processes, it is essential to calculate rates of transport in the liquid phase Often the liquid-phase components exceed two and the transport occurs in a multicomponent environment. Transfer of species in multicomponent systems is complicated by thermodynamic non-idealities of the mixture, diffusional coupling between the transfer of the species, and composition dependence of these thermodynamic and diffusional interactions Diffusion in multicomponent fluid mixtures is described by the generalized Maxwell–Stefan (GMS) equations. The GMS equations for r-directional diffusion (in the absence of external forces) of an m-component fluid mixture at constant temperature and pressure may be written as·

$$\sum_{j=1}^{m-1} \Gamma_{ij}\frac{\mathrm{d}x_j}{\mathrm{d}r} = -\sum_{\substack{j=1\\(j\neq i)}}^{m} \frac{N_i x_j - N_j x_i}{c\text{Đ}_{ij}} \qquad \text{for } i=1, 2, .., m-1 \quad \text{(1a)}$$

$$= -\sum_{\substack{j=1\\(j\neq i)}}^{m} \frac{J_i x_j - J_j x_i}{c\text{Đ}_{ij}} \qquad \text{for } i=1, 2, \ldots, m-1 \quad \text{(1b)}$$

where Đ_{ij} are the GMS pair diffusivities and Γ_{ij} are thermodynamic factors defined by

$$\Gamma_{ij} = \delta_{ij} + \frac{x_i}{x_j}\frac{\mathrm{d}(\ln \gamma_i)}{\mathrm{d}(\ln x_j)} \quad (2)$$

The GMS equations are then commonly combined with the film model to analyse multicomponent mass transfer problems of chemical engineering interest. For steady state one-dimensional transport, the governing film model equations may be obtained as [1]

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$$\sum_{j=1}^{m-1} \Gamma_{ij} \frac{\mathrm{d}x_j}{\mathrm{d}r} = -\sum_{\substack{j=1 \\ (j \neq i)}}^{m} \frac{N_i x_j - N_j x_i}{c k_{ij}} \quad \text{for } i = 1, 2, \ldots, m-1 \tag{3a}$$

$$= -\sum_{\substack{j=1 \\ (j \neq i)}}^{m} \frac{J_i x_j - J_j x_i}{c k_{ij}} \quad \text{for } i = 1, 2, \ldots, m-1 \tag{3b}$$

subject to the following conditions at either ends of the film

$$\text{at } \eta = 0 \ (r = r_0) \quad (x) = (x_0) \tag{4a}$$

$$\text{at } \eta = 1 \ (r = r_\delta) \quad (x) = (x_\delta) \tag{4b}$$

k_{ij} in eqn. (3) are the GMS mass transfer coefficients defined as

$$k_{ij} = \frac{\text{Đ}_{ij}}{l} \tag{5}$$

The thermodynamic and diffusivity terms in eqn (3) generally exhibit highly non-linear dependence on mixture composition Any numerical technique to solve the equations may therefore be complicated by computational difficulties such as multiplicity of solutions as was observed with the parametric form of solution for ideal gas mixtures [1] and convergence problems especially when the concentration dependence of the terms is large as in the case of polymer solutions [2] Further, numerical calculations do not render easy interpretation of the results since the contributions to fluxes due to different effects such as thermodynamic non-idealities, relative component diffusivities and their concentration dependence are not brought out explicitly Hence, an analytical solution is desirable

Analytical solution of eqn. (3) is quite involved because of the concentration-dependent physical properties (*i e.* Γ_{ij}, Đ_{ij} and c) Several approximate solutions were proposed on the basis of (i) a pseudobinary assumption wherein the multicomponent transport problem is treated as a set of binary problems using a suitable effective diffusion coefficient for each component [3], (ii) linearization of eqn. (3) wherein the physical properties are assumed constant either separately [1] or in combination [4, 5] and (iii) the assumption that a combination of the properties remains constant across the film up to some distance and then varies linearly with composition [6]. In the case of ideal gas mixtures the approximate solutions of Krishna [1] and Kubaczka and Bandrowski [6] become exact while the other methods still remain approximate in nature The validity and limitations of the approximate methods have been well studied for gas mixtures but have not been evaluated in the case of liquid mixtures Such a study is important since it was shown [7] that, even for ideal gases, the Toor–Stewart–Prober [4, 5] linearization approximation can lead to significant errors in some cases

In the present work a method was proposed to solve the film model equations with composition-dependent properties The proposed method was then used to evaluate the various approximate methods and to examine the conditions where they are likely to perform well

2. Analysis

The film model equations in eqn (3) may be generalized to any geometry (planar, cylindrical or spherical) when the fluxes N_i (which depend upon cross-sectional area) are replaced by those at $\eta = 0$, N_{0i}, and when the dimensionless distance η and characteristic length l are appropriately defined for different geometries [8] For a planar geometry, η and l are given by

$$\eta = \frac{r - r_0}{r_\delta - r_0} \qquad l = r_\delta - r_0 \tag{6}$$

Equation (3) can be written in a matrix form as

$$[\Gamma] \frac{\mathrm{d}}{\mathrm{d}\eta}(x) = [\Phi](x) + (\phi) \tag{7a}$$

$$= -\frac{l}{c}[B](J) \tag{7b}$$

$$= \frac{l}{c} N_{0t}[B]\left((x) - \frac{1}{N_{0t}}(N_0)\right)$$

where the elements of various matrices are defined as follows

$$B_{ii} = \frac{x_i}{\text{Đ}_{im}} + \sum_{\substack{k=1 \\ (k \neq i)}}^{m} \frac{x_k}{\text{Đ}_{ik}} \quad \text{for } i = 1, 2, \ldots, m-1 \tag{8a}$$

$$B_{ij} = -x_i\left(\frac{1}{\text{Đ}_{ij}} - \frac{1}{\text{Đ}_{im}}\right) \quad \text{for } i, j = 1, 2, \ldots, m-1 \ (i \neq j) \tag{8b}$$

$$\Phi_{ii} = \frac{N_{0i}}{c k_{im}} + \sum_{\substack{k=1 \\ (k \neq i)}}^{m} \frac{N_{0k}}{c k_{ik}} \quad \text{for } i = 1, 2, \ldots, m-1 \tag{9a}$$

$$\Phi_{ij} = -N_{0i}\left(\frac{1}{ck_{ij}} - \frac{1}{ck_{im}}\right)$$

for $i, j = 1, 2, \ldots, m-1$ $(i \neq j)$ (9b)

and

$$\phi_i = -\frac{N_{0i}}{ck_{im}} \quad \text{for } i = 1, 2, \ldots, m-1 \tag{10}$$

By introducing the matrices

$$[\theta] = [\Gamma]^{-1}[\Phi] \tag{11}$$

$$[D] = [B]^{-1}[\Gamma] \tag{12}$$

eqn (7) may be more compactly written as

$$\frac{\mathrm{d}}{\mathrm{d}\eta}(x) = [\theta]\left((x) - \frac{1}{N_{0t}}(N_0)\right) \tag{13a}$$

$$= \frac{l}{c} N_{0t}[D]^{-1}\left((x) - \frac{1}{N_{0t}}(N_0)\right) \tag{13b}$$

The fluxes N_{0t} in eqn. (13) are constant while $[\theta]$, $[D]$ and c are composition dependent Further, the fluxes of all m components (N_{0i}, $i = 1 - m$) are independent while eqn. (13) represents a set of only $m-1$ equations. This necessitates an additional relation among N_{0i} (termed the determinacy condition) for the problem to be fully determined We are interested in seeking a solution to eqn (13) for obtaining the fluxes N_{0i} for any given determinacy condition when the mixture composition at both ends of the film is specified It may be noted that eqns. (13a) and (13b) are equivalent and either of them may be used to obtain the solution. In the present work, eqn. (13a) was used. The solution to eqn (13a) with the boundary condition in eqn. (4a) can be given by [6, 9]

$$(x_\eta - x_0) = [\Omega_0^\eta(\theta) - I][\Omega_0^\delta(\theta) - I]^{-1}(x_\delta - x_0) \tag{14}$$

where the matrizant $[\Omega_0^\eta(\theta)]$ of $[\theta]$ is defined as

$$[\Omega_0^\eta(\theta)] = [I] + \int_0^\eta [\theta_{\tau_1}]\,\mathrm{d}\tau_1 + \int_0^\eta [\theta_{\tau_1}]\int_0^{\tau_1} [\theta_{\tau_2}]\,\mathrm{d}\tau_2\,\mathrm{d}\tau_1$$
$$+ \int_0^\eta [\theta_{\tau_1}]\int_0^{\tau_1} [\theta_{\tau_2}]\int_0^{\tau_2} [\theta_{\tau_3}]\,\mathrm{d}\tau_3\,\mathrm{d}\tau_2\,\mathrm{d}\tau_1 + \tag{15}$$

The matrizant incorporates the effect of thermodynamic non-idealities, component pair diffusivities and their composition dependence. For diffusion of ideal gas mixtures, $[\Gamma] = [I]$ and $Đ_{ij}$ are the corresponding binary gas diffusivities which are constant. The matrizant then equals $[\exp[\Phi]]$, and the general solution in eqn (14) reduces to the solution of Krishna and Standart [7].

To calculate the fluxes from the composition profiles, we first define the matrix $[K_0]$ of low-flux coefficients at $\eta = 0$ as

$$(J_0) = -c[K_0]\left(\frac{\mathrm{d}}{\mathrm{d}\eta}(x)\right)_{\eta=0} \tag{16}$$

It is clear from eqn. (7b) that $[K_0]$ is given by

$$[K_0] = \frac{1}{l}[B_0]^{-1}[\Gamma_0] = \frac{1}{l}[D_0] \tag{17}$$

For the computation of (J_0) from eqn. (16), low-flux coefficients can be obtained readily from the property values at $\eta = 0$ while the composition gradients can be obtained from eqn. (14) to give

$$\frac{\mathrm{d}}{\mathrm{d}\eta}(x) = [\theta_\eta][\Omega_0^\eta(\theta)][\Omega_0^\delta(\theta) - I]^{-1}(x_\delta - x_0) \tag{18}$$

Equations (16) and (18) may be combined and written in the form

$$(J_0) = -c[K_0][\Xi_0](x_\delta - x_0) \tag{19}$$

where the correction factor matrix $[\Xi]_0$ is given by

$$[\Xi_0] = [\theta_0][\Omega_0^\delta(\theta) - I]^{-1} \tag{20}$$

In ideal gas mixtures, $[\Xi_0]$ incorporates the correction due to the high flux while, in liquid mixtures, it additionally accounts for the effect of thermodynamic non-idealities, diffusional interactions and composition-dependent properties. Finally, the fluxes N_{0i} are required to be obtained from (J_0) to complete the problem

As mentioned earlier, in order to calculate the m independent fluxes N_{0i} ($i = 1$, m) a determinacy condition is required. This determinacy condition is often provided by the physical situation in the given problem (*e.g.* equimolar counterdiffusion or diffusion through a stagnant component), by enthalpy balance, or by momentum balance for the components [1, 10]. It is possible in most of the cases to express this condition as a bootstrap matrix $[\beta]$ relating N_{0i} and J_{0i}:

$$(N_0) = [\beta_0](J_0) \tag{21}$$

where the elements of $[\beta]$ can easily be derived from the given determinacy condition [10].

Equations (17) and (19)–(21) provide the necessary relationships to compute N_{0i} using composition gradients at $\eta = 0$. These fluxes may also be computed by another set of equivalent equations using composition gradients at $\eta = 1$. An identical approach with that employed for obtaining the quantities at $\eta = 0$ gives the low-flux coefficients, correction factor matrix and the fluxes at $\eta = 1$. The resulting equations are

$$[K_\delta] = \frac{1}{l}\,[B_\delta]^{-1}[\Gamma_\delta] \tag{22}$$

$$(J_\delta) = -c[K_\delta][\Xi_\delta](x_\delta - x_0) \tag{23}$$

$$(N_0) = [\beta_\delta](J_\delta) \tag{24}$$

where

$$[\Xi_\delta] = [\theta_\delta][\Omega_0^\delta(\theta)][\Omega_0^\delta(\theta) - I]^{-1} \tag{25}$$

Finally the fluxes $N_{\delta i}$ at $\eta = 1$ may be obtained from N_{0i} using the following relationship for different geometries [8]

$$r_\eta^\nu N_{\eta i} = r_0^\nu N_{0i} = r_\delta^\nu N_{\delta i} \tag{26}$$

where ν is equal to 0, 1 and 2 for planar, cylindrical and spherical geometries respectively Equations (17)–(26) provide the required solution to the GMS equations Since these equations are highly nonlinear and implicit in N_{0i}, they need to be solved iteratively

3. Computational algorithm

Several algorithms have been proposed [7, 11–14] for the calculation of fluxes in the case of gas mixtures for which the integral equations (19)–(21) and (23)–(25) reduce to simple algebraic equations The computational scheme of Krishna and Taylor [13] is the most reliable, and it uses the dominant eigenvalue of $[\theta]$ for choosing one of the two equivalent sets of equations, eqns (19)–(21) and (23)–(25), for computing N_{0i} Since the present problem represents a set of integral equations, the following algorithm was used

Data

They are as follows composition (i e mole fraction x_{0i} and $x_{\delta i}$) at $\eta = 0$ and 1, c, $Ð_{ij}$ and Γ_{ij} as functions of the composition, geometry (planar, cylindrical or spherical), film thickness $r_\delta - r_0$, bootstrap condition

Step 1

Compute l, $[\beta_0]$, $[\beta_\delta]$, $[K_0]$ and $[K_\delta]$

Step 2

(a) Choose the number of points (say η_i, $i = 1$, $I + 1$) along the film thickness in the interval $0 \leqslant \eta \leqslant 1$ where the composition profiles are to be matched

(b) Assume the initial composition (i e mole fraction (x^{old})) at different η_i

(c) Assume initial values of (N_0)

Step 3

(a) Using previous values of (N_0) and (x^{old}) find $[\theta_0]$, $[\theta_\delta]$ and $[\Omega_0^{\eta_i}(\theta)]$ for $i = 1$, $I + 1$

(b) Find the latest mole fraction (x^{new}) at η_i using eqn (14)

Step 4

Check for convergence of (x^{old}) and (x^{new}) If not converged, go to step 3 with $(x^{\text{old}}) = (x^{\text{new}})$, else go to step 5

Step 5

Find

$$\hat{\theta}_{\text{av}} = \frac{1}{2(m-1)}\left(\sum_{i=1}^{m-1}(\theta_{0ii} + \theta_{\delta ii})\right)$$

If $\hat{\theta}_{\text{av}} < 0$, then find latest values of (N_0) using eqns (23)–(25) and go to step 6, else find latest values of (N_0) using eqns (19)–(21) and go to step 6

Step 6

Check for convergence of previous and latest value of (N_0) If converged, stop, else go to step 3

4. Evaluation of matrizant

Use of the above algorithm for solution of eqns (19)–(25) involves computation of the matrizant several times Any numerical evaluation for $[\Omega_0^{\eta_i}(\theta)]$ is computationally very expensive since the number of terms required for the convergence of the series in eqn (15) will be large when $|\theta_{ij}|$ are significantly away from zero, and the evaluation of each successive term involves increasingly greater number of $[\theta]$ calculations Hence an algorithm to evaluate $[\Omega_0^{\eta_i}(\theta)]$ economically to a good accuracy is important for the success of the algorithm

If $[\theta]$ varies linearly with η in the interval $\eta_1 \leqslant \eta \leqslant \eta_2$, $[\Omega_{\eta_1}^{\eta_2}(\theta)]$ can be easily obtained from analytical integration of the terms in the series in eqn (15) If the size of the interval is sufficiently small, the first five terms are usually sufficient for the convergence of the series Matrizants computed over small intervals can be used to obtain the matrizant value over a larger interval employing the chain rule of matrizants [9]

$$[\Omega_0^{\eta_i}(\theta)] = [\Omega_{\eta_{i-1}}^{\eta_i}(\theta)][\Omega_{\eta_{i-2}}^{\eta_{i-1}}(\theta)][\Omega_{\eta_{i-3}}^{\eta_{i-2}}(\theta)] \quad \cdot\ [\Omega_0^{\eta_1}(\theta)] \tag{27}$$

We compared the value of $[\Omega_0^{\eta_i}(\theta)]$ computed using the above procedure with that calculated from numerical integration of eqn (15) A composite Simpson rule with a sufficiently large number of intervals of integration was used to give good accuracy On the basis of calculations using different functional relationships of $[\theta]$ with η, it was observed that, when the size of the interval is appropriately chosen, the value of $[\Omega_0^{\eta_i}(\theta)]$ can be computed to the desired accuracy.

5. Approximate methods

Kubaczka and Bandrowski [6] assumed the composition dependence of $[\theta]$ as

$$[\theta]=\begin{cases}[\theta_0] & \text{for } 0\leqslant\eta\leqslant\eta_L \quad (28a)\\ [\theta_0]-[[\theta_0]-[\theta_\delta]]\eta & \text{for } \eta_L\leqslant\eta\leqslant 1 \quad (28b)\end{cases}$$

This simplified composition dependence of $[\theta]$ is expected to be a better approximation than the constancy of $[\theta]$ assumed in Krishna's [1] model. This also allows easier determination of the matrizant from the relation

$$[\Omega_0^1(\theta)]=[\Omega_{\eta_L}^1(\theta)][\exp[\theta_0\,\eta_L]] \tag{29}$$

The first term can be determined using analytical integration of eqn. (15) as described earlier. The method, however, requires prior knowledge of η_L This method is designated as method 2

If the composition dependences of Γ_{ij}, $Đ_{ij}$ and c are ignored and these parameters are treated as constant at the values evaluated at the average composition, $[\theta]$ is a constant matrix The matrizant then is equal to $[\exp[\theta]]$ and the proposed solution is identical with the approximate solution of Krishna [1]. This method of computing fluxes is designed as method 3

As mentioned earlier, solution to eqns. (3) and (4) can also be arrived at through eqn (13b). When this approach is taken, the proposed solution in eqns (19)–(25) is still valid if $[\theta]$ is replaced by $[\Psi]$ which is defined as

$$[\Psi]=\frac{l}{c}N_{\mathrm{ot}}[\mathrm{D}]^{-1} \tag{30}$$

Further, if $[\Psi]$ is assumed constant and is evaluated at the average composition, the resulting solution is the approximate method suggested by Toor and Stewart and Prober [5] This method is designated as method 4

The effective diffusivity method [3, 10] as reported in the work by Krishna and Taylor [10] results from eqns. (7b) and (12) which may be rearranged to give

$$J_i=-\frac{c}{l}\sum_{j=1}^{m-1}D_{ij}\frac{\mathrm{d}x_j}{\mathrm{d}\eta}\quad\text{for } i=1, m-1 \tag{31}$$

If the derivatives are approximated by the ratio of corresponding difference in concentrations, eqn. (31) can be decoupled to give

$$J_i=-\frac{c}{l}d_i\frac{\mathrm{d}x_i}{\mathrm{d}\eta}\quad\text{for } i=1, m-1 \tag{32}$$

where the effective diffusivity d_i is defined as

$$d_i=D_{ii}+\sum_{\substack{j=1\\(j\neq i)}}^{m-1}D_{ij}\frac{\Delta x_j}{\Delta x_i} \tag{33}$$

Further, if D_{ij} and c are assumed constant and evaluated at the average composition, eqns (21) and (32) can be easily solved for the flux of each component. This method is designated as method 5

Method 5 is the crudest approximation but, when the convective flux is small, this method should produce results similar to those from method 3 because the underlying assumptions become equivalent. Likewise, method 3 (based on GMS coefficients) and method 4 (based on Fickian coefficients) are essentially equivalent when constant properties, evaluated at the average composition, are assumed; similar results would be expected in all cases Method 2 contains an adjustable parameter; so it might produce superior results if it is fitted to the proposed solution.

6. Results and discussion

The proposed solution was applied for the transfer of acetone(1)–benzene(2)–carbon tetrachloride(3) mixture (at $T=298.15$ K) across a planar film to find component fluxes for the given surface compositions and the determinacy condition When the initial composition profiles were taken as linear, and the initial fluxes obtained by assuming that the correction factor in eqn. (19) is unimportant (*i e* $[\Xi_0]=[I]$), solution was assured for all the cases studied The composition dependence of the thermodynamic quantities Γ_{ij} was described using the non-random two liquid (NRTL) equation with the reported parameters [15]. The composition dependence of the GMS diffusivities $Đ_{ij}$ can be predicted by any of the models of Bandrowski and Kubaczka [16], Kosanovich [17] or Wesselingh and Krishna [18]. In the present work the model of Wesselingh and Krishna was used. Their model describes the composition dependence of $Đ_{ij}$ as follows.

$$Đ_{ij}=(Đ_{ij}^0)^{(1+x_j-x_i)/2}(Đ_{ji}^0)^{(1+x_i-x_j)/2} \tag{34}$$

where $Đ_{ij}^0$ is the binary diffusion coefficient of components i and j at infinite dilution of component i The values of the ternary diffusivities predicted by eqn (34) agree with the reported data [19], and the accuracy of the predictions is comparable with that of other methods for the system considered [18] The composition dependence of the molar concentration of the mixture was calculated from eqn (35) which was obtained by assuming that volume change due to mixing is zero

$$c = 1 \Big/ \sum_i v_i x_i \qquad (35)$$

The NRTL parameters $Đ_{ij}^0$ and v_i necessary for the estimation of $Đ_{ij}$, Γ_{ij} and c are given in Table 1. The proposed solution, however, does not depend upon the model chosen for the estimation of these properties.

Solution of eqns. (19)–(25) with the proposed method depends upon the number of intervals (i e value of I) chosen For $I = 1$, the solution is identical with the method of Kubaczka and Bandrowski [6] with $\eta_L = 0$. When the number of intervals is sufficiently large, the assumed linear variation in $[\theta]$ within each interval is valid and the matrizant calculated by the method described earlier will approach the true value The proposed solution then becomes exact The influence of the number of intervals on computed fluxes for two sets of conditions (listed in Table 3) is shown in Table 2 It is clear that true solution is assured when $I \geqslant 20$.

The flux of a component depends upon the driving force (i e Δx_i) of all components, the physical properties and their variation across the film, and the contribution from the convective flux resulting from the diffusion process For a given system, the first two factors are decided by the boundary conditions while the determinacy condition decides the bootstrap matrix or the contribution from the convective flux The performance of different approximate methods may be assessed by examining the deviation between the fluxes calculated by them and the proposed method for different conditions Calculations were made with several sets of boundary and determinacy conditions Only a few results which emphasize the main features are presented in this work. A summary of conditions employed in these calculations is shown in Table 3 The determinacy conditions chosen in sets 1–6 are similar to those employed by Kubaczka and Bandrowski [6] and are such that the convective contribution is not important while the conditions in sets 7 and 8 ensure a significant contribution from the convective flux The percentage error ϵ in fluxes associated with approximate methods, is defined according to

$$\epsilon_i = \left| \frac{(N_i)_{\text{method } 1} - (N_i)_{\text{method } i}}{(N_i)_{\text{method } 1}} \right| \times 100 \qquad (36)$$

where $(N_i)_{\text{method } 1}$ are the fluxes obtained from the proposed method while $(N_i)_{\text{method } i}$ are the fluxes calculated by method i ($i = 2$–5) For each set of conditions given in Table 3, N_{0i} were calculated using the proposed method (method 1) as well as approximate methods (methods 2–5) and ϵ_i evaluated from eqn (36). These values are given in Table 4 The values of c_0, $Đ_{0ij}$, $[\Gamma_0]$ and $[\theta_0]$, together with their deviations across the film, are given in Table 5

The conditions in sets 1 and 2 (see Table 3) represent commonly encountered situations in many interphase mass transfer problems in which the driving forces (i.e Δx) of all three components are significant and all N_{0i} are of the same order of magnitude (see Table 4) It is clear from Table 4 that all the approximate methods calculate fluxes to a similar accuracy The errors in fluxes associated with the approximate methods is about 0 2–6% in set 1 and about 0 1–1.5% in set 2 It may be noted that errors in set 2 are smaller in spite of a similar magnitude of variation in the values of c, $Đ_{ij}$ and $[\Gamma]$ in both the sets (the average absolute deviation is 14 5% in set 1 and 13% in set 2) This suggests that deviation in the properties is not a reliable index for assessing errors As discussed earlier, the difference in various methods of calculating fluxes chiefly lies in the manner in which the composition dependence of $[\theta]$ is described Hence the deviation in $[\theta]$ may provide a better index in evaluating the errors The values of $[\theta_0]^{-1}[\theta_\delta]$ are presented in

TABLE 1 Data for the calculation of the system properties

Component pair (i, j)	τ_{ij} [a]	τ_{ji}	α_{ij}	$Đ_{ij}^0$ (10^{-9} m^2 s^{-1})	$Đ_{ji}^0$	v_i (m^3 kmol^{-1})
Acetone (i)–benzene(j)	−0 4650	0 7643	0 2	2 75	4 15	0 074
Benzene (i)–carbon tetrachloride (j)	−0 5182	0 7338	0 2	1 42	1 91	0 089
Carbon tetrachloride (i)–acetone (j)	1 5931	−0 4279	0 2	3 57	1 70	0 097

[a] $\tau_{ij} = (g_{ij} - g_{ji})/RT$ ($T = 298$ 15 K)

TABLE 2 Influence of the number of intervals on the values of fluxes calculated by the proposed method

I	Set 5[a] (N_{0i}) ($\times 10^5$ kmol m^{-2} s^{-1})			Set 7[a] (N_{0i}) ($\times 10^5$ kmol m^{-2} s^{-1})		
	$i=1$	$i=2$	$i=3$	$i=1$	$i=2$	$i=3$
1	207 89	−4 0842	−193 51	−337 21	−78 508	−5 8083
5	187 38	3 6781	−181 68	−349 60	−90 070	2 6641
10	186 75	3 8635	−181 28	−346 26	−89 973	3 4133
15	186 65	3 8944	−181 21	−345 62	−89 941	3 5520
20	186 61	3 9051	−181 18	−345 43	−89 932	3 5914
25	186 61	3 9051	−181 18	−345 43	−89 932	3 5914

[a]The boundary and determinacy conditions employed in sets 5 and 7 are given in Table 3

TABLE 3 Summary of the boundary conditions employed in the calculations

Set	Composition at $\eta=0$			Composition at $\eta=1$			Driving force			Determinacy condition
	x_{01}	x_{02}	x_{03}	$x_{\delta 1}$	$x_{\delta 2}$	$x_{\delta 3}$	Δx_1[a]	Δx_2[a]	Δx_3[a]	
1	0 8954	0 0948	0 0098	0 2989	0 3490	0 3521	0 5965	−0 2542	−0 3423	$N_1/N_t=15\ 3$
2	0 0098	0 8954	0 0948	0 3521	0 2989	0 3490	−0 3423	0 5965	−0 2542	$N_2/N_t=15\ 3$
3	0 8954	0 0948	0 0098	0 0933	0 8967	0 0100	0 8021	−0 8019	−0 0002	$N_2/N_t=-11\ 6$
4	0 5400	0 2500	0 2100	0 2900	0 4900	0 2200	0 2500	−0 2400	−0 0100	$N_1/N_t=24\ 0$
5	0 8954	0 0948	0 0098	0 0500	0 0500	0 9000	0 8454	0 0448	−0 8902	$N_1/N_t=20\ 0$
6	0 0948	0 8954	0 0098	0 0500	0 0500	0 9000	0 0448	0 8454	−0 8902	$N_2/N_t=20\ 0$
7	0 1000	0 1000	0 8000	0 7000	0 2000	0 1000	−0 6000	−0 1000	0 7000	$N_1/N_t=0\ 80$
8	0 1000	0 8000	0 1000	0 5000	0 2000	0 3000	−0 4000	0 6000	−0 2000	$N_1/N_t=-0\ 10$

[a]$\Delta x_i = x_{0i} - x_{\delta i}$

Table 5, and the extent of deviation in the matrix product from $[I]$ represents a measure of variation in $[\theta]$ across the film. It is clear from Table 5 that $[\theta]$ varies more strongly in set 1 than in set 2, and this is consistent with the greater errors observed in the former set

In sets 3 and 4, the driving force, and hence the flux, of one of the components is very small This is normally the case when solutions are dilute with respect to a component In such cases the value of the small flux is generally sensitive to the variation in properties For example, in set 3, the properties vary significantly (the average absolute deviation is about 14%), and the approximate methods fare very poorly for calculating the smaller flux although they calculate the larger fluxes to an accuracy (about 4%) similar to that in the previous cases In set 4 the deviation in the properties is small (the average absolute deviation is about 5%) and the values of fluxes including that of the smaller flux are calculated satisfactorily by the approximate methods. Thus, unlike the situation with sets 1 and 2, the performance of the approximate methods is consistent with the variation in the properties However, the criterion based on the variation in $[\theta]$ fails in this case since $[\theta_0]^{-1}[\theta_\delta]$ is significantly away from $[I]$ in both the sets

In sets 5 and 6 the boundary conditions are such that transfer of species occurs between two nearly pure components This is commonly the case when a small quantity of a valuable solute is to be extracted from one phase to the other In these sets the properties as well as $[\theta]$ vary significantly across the film. The approximate methods perform very well even for the smaller flux in set 6 while, in set 5, they totally fail for calculating the smaller flux and give rise to significant errors (about 10–20%) in calculating the larger fluxes. Thus neither of the criteria based on the variation in properties and $[\theta]$ can explain the observed performance of the approximate methods.

In sets 7 and 8 the determinacy conditions were chosen such that the convective contribution to the flux is significant for all components. For the former set the approximate methods give rise to greater errors even for large fluxes while they fail to calculate even the correct direction of the small flux For set 8, however, the approximate methods fare well for both large and small values of flux It may be seen from Table 5 that the variation in properties is significant in both these sets while the change in $[\theta]$ is significant only in set 7. Thus the variation in $[\theta]$ is consistent with the observed performance of the approximate methods while the

TABLE 4 Comparison of the fluxes calculated by different methods

	Method 1	Method 2		Method 3	Method 4	Method 5
Set 1						
N_{01} (10^{-5} kmol m^{-2} s^{-1})	203 20	η_L=0 10	202 75	193 87	193 88	193 87
N_{02} (10^{-5} kmol m^{-2} s^{-1})	−100 16		−104 48	−94 162	−94 294	−94 298
N_{03} (10^{-5} kmol m^{-2} s^{-1})	−89 768		−85 028	−87 036	−86 910	86 897
ϵ_1	–		0 2	4 7	4 7	4 7
ϵ_2	–		4 3	6 0	6 0	6 0
ϵ_3	–		5 4	3 0	3 2	3 2
Set 2						
N_{01} (10^{-5} kmol m^{-2} s^{-1})	−108 22	η_L=0 00	−108 24	−108 10	−107 95	−107 96
N_{02} (10^{-5} kmol m^{-2} s^{-1})	168 37		−167 71	168 39	168 07	168 11
N_{03} (10^{-5} kmol m^{-2} s^{-1})	−49 140		−48 502	−49 284	−49 138	−49 166
ϵ_1	–		0 0	0 1	0 3	0 3
ϵ_2	–		0 4	0 0	0 2	0 2
ϵ_3	–		1 3	0 3	0 0	0 1
Set 3						
N_{01} (10^{-5} kmol m^{-2} s^{-1})	317 92	η_L=0 00	320 19	306 00	305 66	305 64
N_{02} (10^{-5} kmol m^{-2} s^{-1})	−292 68		−294 80	−281 80	−281 49	−281 45
N_{03} (10^{-5} kmol m^{-2} s^{-1})	−0 00831		0 01989	0 09018	0 08982	0 07466
ϵ_1	–		0 7	3 7	3 9	3 9
ϵ_2	–		0 7	3 7	3 8	3 8
ϵ_3	–		339	1185	1181	998
Set 4						
N_{01} (10^{-5} kmol m^{-2} s^{-1})	79 910	η_L=0 00	80 432	79 755	79 636	79 635
N_{02} (10^{-5} kmol m^{-2} s^{-1})	−75 309		−75 729	−75 191	−75 065	−75 062
N_{03} (10^{-5} kmol m^{-2} s^{-1})	−1 2716		−1 3529	−1 2409	−1 2531	−1 2679
ϵ_1	–		0 5	0 2	0 3	0 3
ϵ_2	–		0 4	0 2	0 3	0 3
ϵ_3	–		6 3	2 4	1 5	0 3
Set 5						
N_{01} (10^{-5} kmol m^{-2} s^{-1})	186 61	η_L=0 00	207 89	149 54	149 44	149 45
N_{02} (10^{-5} kmol m^{-2} s^{-1})	3 9051		4 0842	6 9412	6 6922	6 9241
N_{03} (10^{-5} kmol m^{-2} s^{-1})	−181 18		−193 51	−149 00	−148 89	−148 90
ϵ_1	–		11 4	19 9	19 9	19 9
ϵ_2	–		4 5	77 8	71 3	77 4
ϵ_3	–		6 8	17 8	17 9	17 9
Set 6						
N_{01} (10^{-5} kmol m^{-2} s^{-1})	−4 6427	η_L=0 10	−4 6541	−4 7153	−4 7430	−4 7972
N_{02} (10^{-5} kmol m^{-2} s^{-1})	161 10		164 70	157 01	157 05	157 08
n_{03} (10^{-5} kmol m^{-2} s^{-1})	−148 40		−151 81	−144 45	−144 45	−144 48
ϵ_q	–		0 2	1 5	2 1	3 3
ϵ_2	–		2 1	2 5	2 5	2 5
ϵ_3	–		2 2	2 7	2 7	2 7
Set 7						
N_{01} (10^{-5} kmol m^{-2} s^{-1})	−345 43	η_L=0	−337 21	−259 38	−259 77	−259 33
N_{02} (10^{-5} kmol m^{-2} s^{-1})	−89 932		−78 508	−69 941	−70 095	−70 016
N_{03} (10^{-5} kmol m^{-2} s^{-1})	3 5914		5 8083	5 0955	5 1531	5 0953
ϵ_1	–		2 3	24 9	24 8	24 9
ϵ_2	–		12 7	22 3	22 1	22 3
ϵ_3	–		260	41 9	43 5	41 9
Set 8						
N_{01} (10^{-5} kmol m^{-2} s^{-1})	−36 340	η_L=0 15	−36 395	−36 535	−36 285	−36 453
N_{02} (10^{-5} kmol m^{-2} s^{-1})	379 87		380 50	382 75	379 16	379 81
N_{03} (10^{-5} kmol m^{-2} s^{-1})	19 870		19 850	19 137	19 973	21 168
ϵ_1	–		0 2	0 5	0 2	0 3
ϵ_2	–		0 2	0 8	0 2	0 1
ϵ_3	–		0 1	3 8	0 5	6 5

TABLE 5 Variation in the physical properties across the film

Set	c_0 (kmol m^{-3})	$\begin{pmatrix}Đ_{12}\\Đ_{13}\\Đ_{23}\end{pmatrix}_0$ (10^{-9} m^2 s^{-1})	$\begin{bmatrix}\Gamma_{11} & \Gamma_{12}\\ \Gamma_{21} & \Gamma_{22}\end{bmatrix}_0$	$\begin{bmatrix}\theta_{11} & \theta_{12}\\ \theta_{21} & \theta_{22}\end{bmatrix}_0$	$\Delta c/c_0{}^a$ $\times 100$	$\begin{pmatrix}\frac{\Delta Đ_{ij}}{Đ_{0ij}}\end{pmatrix}$ $\times 100$	$\begin{bmatrix}\frac{\Delta\Gamma_{ij}}{\Gamma_{0ij}}\end{bmatrix}$ $\times 100$	$[\theta_0]^{-1}[\theta_\delta]$
1	13.2	$\begin{pmatrix}3.98\\3.42\\1.67\end{pmatrix}$	$\begin{bmatrix}0.93 & -0.03\\ 0.06 & 1.03\end{bmatrix}$	$\begin{bmatrix}0.05 & 0.05\\ -0.24 & -0.44\end{bmatrix}$	13.5	$\begin{pmatrix}16.1\\29.4\\1.30\end{pmatrix}$	$\begin{bmatrix}26.6 & -\\ - & -1.0\end{bmatrix}$	$\begin{bmatrix}5.1 & 5.9\\ -2.3 & -2.3\end{bmatrix}$
2	11.1	$\begin{pmatrix}2.82\\2.39\\1.85\end{pmatrix}$	$\begin{bmatrix}0.99 & -0.03\\ 0.06 & 0.99\end{bmatrix}$	$\begin{bmatrix}-0.05 & -0.06\\ 0.28 & 0.23\end{bmatrix}$	-4.0	$\begin{pmatrix}-21.1\\-3.3\\11.8\end{pmatrix}$	$\begin{bmatrix}32.5 & -\\ - & -5.0\end{bmatrix}$	$\begin{bmatrix}1.2 & 0.2\\ 0.5 & 1.2\end{bmatrix}$
3	13.2	$\begin{pmatrix}3.99\\3.42\\1.67\end{pmatrix}$	$\begin{bmatrix}0.94 & -0.03\\ 0.06 & 1.03\end{bmatrix}$	$\begin{bmatrix}0.13 & 0.08\\ -0.73 & -0.68\end{bmatrix}$	14.0	$\begin{pmatrix}28.1\\25.7\\-12.6\end{pmatrix}$	$\begin{bmatrix}3.3 & -\\ - & 1.0\end{bmatrix}$	$\begin{bmatrix}3.3 & 1.7\\ -2.9 & -1.3\end{bmatrix}$
4	12.1	$\begin{pmatrix}3.39\\2.78\\1.66\end{pmatrix}$	$\begin{bmatrix}0.72 & -0.12\\ 0.10 & 1.06\end{bmatrix}$	$\begin{bmatrix}0.05 & 0.04\\ -0.20 & -0.19\end{bmatrix}$	4.5	$\begin{pmatrix}9.6\\9.2\\-3.4\end{pmatrix}$	$\begin{bmatrix}-2.3 & -\\ - & 0.0\end{bmatrix}$	$\begin{bmatrix}3.5 & 2.4\\ -2.7 & -1.6\end{bmatrix}$
5	13.2	$\begin{pmatrix}3.98\\3.42\\1.67\end{pmatrix}$	$\begin{bmatrix}0.94 & -0.03\\ 0.06 & 1.03\end{bmatrix}$	$\begin{bmatrix}0.02 & 0.04\\ -0.02 & -0.35\end{bmatrix}$	20.7	$\begin{pmatrix}15.2\\47.5\\12.9\end{pmatrix}$	$\begin{bmatrix}8.3 & -\\ - & 2.0\end{bmatrix}$	$\begin{bmatrix}1.7 & 19.5\\ 0.0 & -2.4\end{bmatrix}$
6	11.4	$\begin{pmatrix}2.87\\2.54\\1.88\end{pmatrix}$	$\begin{bmatrix}0.90 & -0.04\\ 0.09 & 1.04\end{bmatrix}$	$\begin{bmatrix}-0.03 & 0.00\\ 0.25 & 0.04\end{bmatrix}$	7.8	$\begin{pmatrix}-17.9\\29.3\\22.6\end{pmatrix}$	$\begin{bmatrix}4.9 & -\\ - & 2.0\end{bmatrix}$	$\begin{bmatrix}14.2 & 0.4\\ -68.2 & -0.4\end{bmatrix}$
7	10.6	$\begin{pmatrix}3.38\\1.90\\1.48\end{pmatrix}$	$\begin{bmatrix}0.76 & -0.10\\ -0.07 & 0.98\end{bmatrix}$	$\begin{bmatrix}-2.0 & -0.9\\ -0.39 & -1.2\end{bmatrix}$	-21.2	$\begin{pmatrix}-10.8\\-62.0\\-12.6\end{pmatrix}$	$\begin{bmatrix}-5.0 & -\\ - & -2.0\end{bmatrix}$	$\begin{bmatrix}0.57 & -0.20\\ -0.12 & 0.71\end{bmatrix}$
8	11.3	$\begin{pmatrix}2.93\\2.46\\1.83\end{pmatrix}$	$\begin{bmatrix}0.89 & -0.05\\ 0.04 & 1.03\end{bmatrix}$	$\begin{bmatrix}1.27 & 0.08\\ 0.63 & 1.78\end{bmatrix}$	-12.1	$\begin{pmatrix}-22.8\\-7.6\\11.2\end{pmatrix}$	$\begin{bmatrix}24.4 & -\\ - & 1.0\end{bmatrix}$	$\begin{bmatrix}1.12 & 0.20\\ 0.14 & 0.99\end{bmatrix}$

$^a\Delta$ indicates the difference between the values at $\eta = 0$ and 1

variation in properties does not explain these trends

It is clear from the above discussion that the variation in properties or $[\theta]$ does not consistently explain the performance of the approximate methods. It may be attributed to the fact that (N_{0i}) in eqns. (19)–(25) are related to the properties through the matrix functions of $[\theta]$ in a complicated manner, and the deviations in c, $Đ_{ij}$, $[\Gamma]$ or $[\theta]$ do not directly correspond to ϵ_i. A parameter α_i is defined for each component according to the following equation in order to understand the performance of the approximate methods

$$\alpha_i = \left|\frac{(N_i)_{\text{method 3}} - (N_i)_{\text{method 6}}}{(N_i)_{\text{method 3}}}\right| \tag{37}$$

In method 6, the fluxes are calculated by treating $[\theta]$ in eqn (13a) as constant and equal to $0.5[[\theta_0]+[\theta_\delta]]$ while the fluxes obtained by method 3 are obtained by treating $[\theta]$ as constant at its value evaluated for the average composition. The values of (N_{0i}) calculated from methods 3 and 6, α_i and ϵ_i (obtained for method 3) are presented in Table 6. It is clear from the table that, for a given set, ϵ_i are consistent with α_i. In the pairs of sets 3 and 4, 5 and 6, and 7 and 8, the greater errors in the former set of pairs is satisfactorily explained by the corresponding values of α_i. Further, errors associated with the approximate methods are about 6% when α_i is less than 15% while the errors are generally greater than about 18% when $\alpha_i > 25\%$

TABLE 6 Test of α as an index for the influence of property variation on the performance of approximate methods

Set	(N_{0i}) ($\times 10^{-5}$ kmol m^{-2} s^{-1})		(α_i)	(ϵ_i) for method 3
	Method 3	Method 6		
1	193 87	211 80	9 2	4 7
	−94 162	−105 00	11 5	6 0
	−87 036	−92 963	7 0	3 0
2	−108 10	−108 69	0 5	0 1
	168 39	168 83	0 4	0 0
	−49 284	−48 906	0 8	0 3
3	306 00	336 12	10 0	3 7
	−281 80	−309 35	9 9	3 7
	0 09018	−0 11886	232	1185
4	79 755	−80 222	1 3	0 2
	−75 191	−76 049	1 1	0 2
	−1 2409	−1 4053	3 2	2 4
5	149 54	244 30	63 4	19 9
	6 9412	−0 2503	104	71 3
	−149 00	−231 83	55 6	17 9
6	−4 7153	−4 4586	5 4	1 5
	157 01	166 46	6 0	2 5
	−144 45	−153 68	6 3	2 7
7	−259 38	−364 50	40 5	24 9
	−69 941	−87 798	25 5	22 3
	5 0955	−3 3269	165	41 1
8	−36 535	−37 057	1 4	0 5
	382 75	387 62	1 3	0 8
	19 137	20 004	4 5	3 8

It is clear from Table 5 that, whenever approximate methods may be used for the computation of fluxes, their performance is similar The method based on the work of Kubaczka and Bandrowski [6] requires an appropriate value of η_L The best value of η_L, designated as η_L^*, was chosen in the present work so as to give minimum deviation in the larger fluxes It is clear from Table 4 that η_L^* is specific to a given set of conditions For example, $\eta_L^* = 0$ for sets 2–5 and 7 while it is 0 1 for sets 1 and 6, and 0 15 for set 8 Use of $\eta_L^* = 0$ in sets 1, 6 or 8 gives greater errors than those obtained by other approximate methods Method 2 thus does not offer any particular advantage even if the best value of η_L specific to a given set of conditions is used. The other approximate methods are almost identical in their performance while method 5 has the advantage of being simple but is inapplicable when Δx of a component is zero

7. Conclusion

Multicomponent film model equations in the framework of GMS model were solved for non-ideal fluid mixtures for any composition dependence of concentration, diffusivities and thermodynamic non-idealities The solution is valid for planar, cylindrical and spherical film geometries The proposed solution was used to examine the existing approximate methods suggested for non-ideal fluid mixtures A parameter α was defined for each component to assess the influence of varying the physical properties on the error associated with the approximate methods On the basis of the calculations for an example system, it is generally recommended that the proposed solution should be used when accurate results are required especially for those components transferring under the conditions of small driving forces. However, when $\alpha_i \leqslant 15\%$, any of the approximate methods, including the simplest which is based on effective diffusivities, may be used with a maximum error of about 6%

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Appendix A: Nomenclature

c	molar concentration (kmol m^{-3})
d	effective diffusion coefficient of component i (eqn. (33)) (m^2 s^{-1})
$Đ_{ij}$	GMS pair diffusivity of components i and j in a multicomponent mixture (m^2 s^{-1})
$Đ^0_{ij}$	binary diffusivity of component mixture i–j at infinite dilution of component i (m^2 s^{-1})
$[D]$	matrix of Fickian diffusion coefficients (eqn. (12)) (m^2 s^{-1})
$[I]$	identity matrix
J	molar diffusive flux with respect to molar average velocity (kmol m^{-2} s^{-1})
k_{ij}	GMS mass transfer coefficient of component pair i–j in a multicomponent mixture (eqn (5)) (m s^{-1})
$[K]$	matrix of low-flux Fickian mass transfer coefficients (eqn (17)) (m s^{-1})
l	characteristic length (eqn. (6)) (m)
N	molar total flux with respect to fixed coordinates (kmol m^{-2} s^{-1})
r	distance coordinate (m)
v	molar volume of mixture (m^3 kmol^{-1})
x	mole fraction

Greek Letters

$[\beta]$	bootstrap matrix
$[\Gamma]$	matrix of thermodynamic factors (eqn (2))
γ	activity coefficient
δ_{ij}	Kronecker delta
ϵ	error in flux value calculated by approximate methods (eqn. (36))
η	dimensionless distance
$[\Xi]$	correction factor matrix (eqns. (20) and (25))
$[\Omega]$	matrizant (eqn. (14))

Subscripts

i, j	components i, j
t	total value
0	position at $\eta=0$
δ	position at $\eta=1$

Superscripts

new	latest values
old	current values

Symbols

[ ]	$(m-1)\times(m-1)$ square matrix
( )	$(m-1)$ column matrix