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PENETRATION DEPTHS IN MULTICOMPONENT MASS TRANSFER

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Abstract—The concept of the depth of penetration during mass transfer of a multicomponent mixture within a fluid phase is examined It is shown that for mixtures exhibiting strong diffusional interactions, it is not possible to ascribe a simple physical significance to the penetration depth for each of the transferring species in the mixture Further, it is shown that in the film model description for multicomponent mass transfer, the film thicknesses of each individual species must be taken to be different from one another

The correct description of multicomponent mass transport phenomena is of obvious importance in chemical engineering Thus there are many applications which demand the use of a complete mass transfer formulation taking into account the possibility of diffusional interactions between the transferring species, these applications include distillation[1–3], liquid–liquid extraction[4–6], gas absorption[7, 8] and diffusion in catalytic reaction systems[9, 10] The ramifications of diffusional coupling effects in membrane separation processes are now becoming appreciated[11, 12]

For a rational design of processing equipment carrying out multicomponent mass transport processes it is necessary to predict the values of the appropriate mass transfer coefficients Further, it is desirable to have the capability of predicting multicomponent mass transfer coefficients from information on the transfer parameters of the corresponding binary pairs, such predictions are possible within the framework of the linearized theory of multicomponent mass transfer developed independently by Toor[13] and Stewart and Prober[14] The use of this theory requires the assumption that the matrix of diffusion coefficients $[D]$ remains constant along the diffusion path and with the aid of this assumption a majority of the mass transfer rate relations valid for binary systems may be extended to n-component mixtures by straightforward matrix generalization techniques The film, penetration and boundary layer theories of mass transfer have thus been extended to multicomponent mixtures[13–17]

One of the questions which remains in the development of the theory of multicomponent mass transfer concerns the film thicknesses of the individual species For a binary system there is only one independent concentration measure and the film thickness of the constituent species 1 and 2 are necessarily equal to each other, for an n-component system there are $n-1$ independent concentrations in the system and there is no requirement that the film thicknesses of the individual species should be equal to one another In the film theory development for multicomponent mass transfer it has been assumed that these film thicknesses are equal[13, 15, 17] and it is one of the objects of the present communication to examine this assumption Our approach to the problem makes use of the penetration model for mass transfer, with this approach the film thicknesses can be related to the penetration depths[18] We further aim to show that some basic concepts of binary mass transfer do not have a similar significance when extended to multicomponent mixtures

ANALYSIS

The instantaneous value of the mass transfer coefficient is obtained from the penetration theory applied to a binary mixture as

$$k = \left(\frac{D}{\pi t}\right)^{1/2} \tag{1}$$

which on combination of the film theory relation

$$k = D/\delta \tag{2}$$

yields the expression for the film thickness

$$\delta = (\pi D t)^{1/2} \tag{3}$$

Within the framework of the penetration theory the thickness δ is the distance from the interface when the concentration increase (or decrease) reaches 80% of the maximum concentration difference[18] δ may be viewed as the depth of penetration of the transferring component

For an n-component system, the proper description of the diffusion behaviour is obtained by use of a square matrix of diffusion coefficients $[D]$ of dimension $n-1 \times n-1$ The diffusion flux J_i is then given by the matrix generalization of Fick's law as

$$J_i = -\sum_{k=1}^{n-1} D_{ij}\frac{dc_j}{dz}, \quad i = 1, 2, \quad n-1 \tag{4}$$

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With the constitutive relations for diffusion given by eqn (4), the penetration theory development gives under conditions of negligible bulk flow the matrix of mass transfer coefficients as

$$[k] = \left(\frac{[D]}{\pi t}\right)^{1/2} \tag{5}$$

which is the generalization of eqn (1) The matrix analogue of eqn (3) leads to a matrix of penetration depths

$$[\delta] = (\pi[D]t)^{1/2} \tag{6}$$

which means that if we *define* a film thickness for each component in an n-component mixture $\bar{\delta}_i$ by the relation

$$[k] = [D]\left[\frac{1}{\bar{\delta}}\right] = [D][\delta]^{-1} \tag{7}$$

then the individual thicknesses $\bar{\delta}_i$ are necessarily different from one another unless the matrix $[D]$ is diagonal with the diagonal elements all identical

For the general case of non-ideal mixtures the matrix $[D]$ is non-diagonal with significant values for the cross-coefficients D_{ij} $(i \neq j)$[12], for such cases it is not possible to ascribe a physical significance to the matrix of penetration depths $[\delta]$, given by eqn (6), as is possible for a two-component system (eqn 3)

In order to understand fully the implications of eqn (6) it is necessary to consider the transient concentration profiles developed in the region adjacent to the interface due to a step change in the concentrations of the transferring species

For a binary system the transient profiles are given by

$$\frac{c - c_\infty}{c_0 - c_\infty} = \operatorname{erf}\,(z/(4Dt)^{1/2}) \tag{8}$$

where c is the concentration at position z and time t, c_0 is the interfacial concentration, c_∞ is the concentration in the bulk fluid The left hand side of eqn (8) represents the fractional unaccomplished change in concentration

For an n-component system the generalization of eqn (8) leads to the $n - 1$ dimensional relation

$$(c - c_\infty) = \operatorname{erf}\left(\frac{z}{(\pi D_{11} t)^{1/2}}[D']^{-1/2}\right)(c_0 - c_\infty) \tag{9}$$

where for convenience of comparison with the binary relation (6) we have defined a dimensionless matrix of diffusion coefficients $[D']$ whose elements are normalized with respect to the leading diagonal coefficient D_{11}, i e

$$D'_{ij} = D_{ij}/D_{11}, \quad i, j = 1, 2, \quad n - 1 \tag{10}$$

The argument of the error function in eqn (9) is a square matrix and this term may be evaluated by the use of Sylvester's theorem[13, 17] If the error function term is denoted by $[\mathcal{Y}]$, i e

$$[\mathcal{Y}] = \operatorname{erf}\left(\frac{z}{(\pi D_{11} t)^{1/2}}[D']^{-1/2}\right) \tag{11}$$

then we find for example for a ternary system that the fractional unaccomplished change for component 1 is given by

$$\chi_1 = \mathcal{Y}_{11} + \mathcal{Y}_{12}\frac{\Delta c_{20}}{\Delta c_{10}} \tag{12}$$

and similarly for component 2 we have

$$\chi_2 = \mathcal{Y}_{22} + \mathcal{Y}_{21}\frac{\Delta c_{10}}{\Delta c_{20}} \tag{13}$$

where the concentration difference Δc_{i0} are given by

$$\Delta c_{i0} = c_{i0} - c_{i\infty}, \quad i = 1, 2, \quad n - 1 \tag{14}$$

Equations (12) and (13) show how the concentration profiles of components 1 and 2 are coupled to one another through the cross coefficients $\mathcal{Y}_{12}$ and $\mathcal{Y}_{21}$ The ratio $\Delta c_{10}/\Delta c_{20}$ serves to increase the interaction effects When this ratio is large in magnitude, then the component 2 is strongly influenced by component 1 (see eqn 13), on the other hand when the ratio $\Delta c_{10}/\Delta c_{20}$ has a magnitude smaller than unity then eqn (12) shows that component 1 will be strongly influenced by component 2

In order to illustrate the influence of diffusional coupling on the concentration profiles and on the penetration depths, we consider transfer in the system acetone (1)–benzene (2)–methanol (3) For this system the diffusion coefficients in the liquid phase have been measured by Alimadadian and Colver[19] The system exhibits strong diffusional coupling Over a range of compositions we may represent the matrix of diffusion coefficients, normalized with respect to D_{11}, as

$$D'_{11} = 1, D'_{12} = 0\ 2, D'_{21} = -0\ 15, D'_{22} = 0\ 57 \tag{15}$$

Figure 1 shows the profiles for the unaccomplished change for the case $\Delta c_{10}/\Delta c_{20} = 4\ 5$ For this case the diffusional interaction effects have a strong influence on the benzene profile The unaccomplished change for

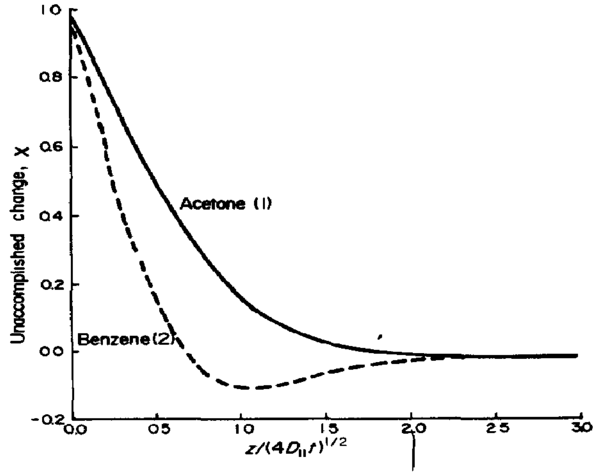

Fig 1 Unaccomplished change, χ, as function of dimensionless distance parameter $z/(4D_{11}t)^{1/2}$ for $\Delta c_{10}/\Delta c_{20} = 4\ 5$

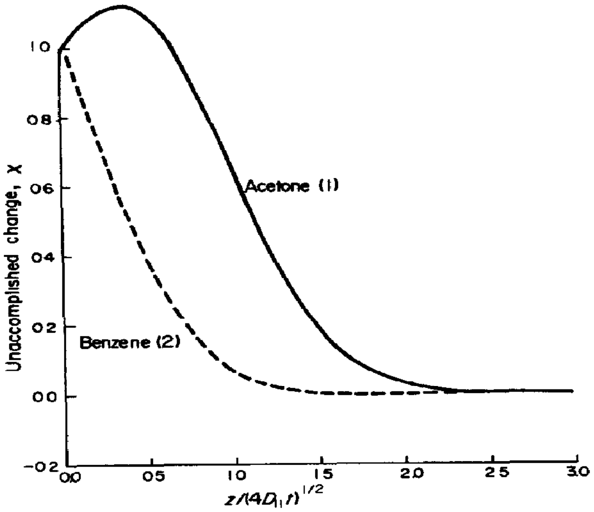

Fig 2 Unaccomplished change, χ, as function of dimensionless distance parameter $z/(4D_{11}t)^{1/2}$ for $\Delta c_{10}/\Delta c_{20} = 0\ 1$

benzene reaches negative values and shows a minimum in the profile On the other hand Fig 2 shows that when $\Delta c_{10}/\Delta c_{20} = 0\ 1$ the interaction effects are strongly felt by acetone which now shows the unaccomplished change exceeds unity and exhibits a maximum in the profile

If we consider the distances z reached when the unaccomplished change $\chi = 0\ 2$, it is easy to see from Figs 1 and 2 that the penetration depths for acetone and benzene are significantly different and show a dependence on the concentration driving forces Δc_{i0} This means that the equivalent film thickness for mass transfer will be a function of the operating composition range as well as a function of the system properties In contrast for a binary system the film thickness is not a function of the concentration driving forces

CONCLUDING REMARKS

The strict matrix generalization of the binary concept of the penetration depth leads to the definition of the matrix of penetration depths, given by eqn (6) This formal matrix generalization is without physical significance except for the trivial case when the matrix $[D]$ is diagonal with all diagonal elements equal In order to gain more insight into the concept of film thicknesses and penetration depths, the concentration profiles in the region of the interface have been considered The reason for the absurd definition for the multicomponent penetration depths, eqn (6), is seen to be the strong dependence of the concentration profiles on the concentration difference driving forces Thus unlike the simple binary system, for an n-component system the driving forces Δc_{i0} play a major role in determining the concentration profiles and hence the penetration depths

The commonly made assumption of equal film thicknesses for multicomponent mass transfer is thus clearly invalid

NOTATION

c_i	molar concentration of species i in mixture
Δc_{i0}	$= c_{i0} - c_{i\infty}$, concentration driving force
D	binary diffusion coefficient
D_{11}	leading diagonal coefficient of diffusion matrix $[D]$
$[D]$	matrix of diffusion coefficients
$[D']$	dimensionless matrix of diffusion coefficients
D_{ij}	elements of $[D]$
D'_{ij}	elements of $[D']$
J_i	diffusion flux of species i in mixture
k	binary mass transfer coefficient
$[k]$	matrix of multicomponent mass transfer coefficients
n	number of species in mixture
t	time
$[\mathscr{Y}]$	matrix defined by eqn (11)
z	distance from interface

Greek symbols

δ	film thickness or penetration depth
$[\delta]$	matrix of penetration depths
$\bar{\delta}_i$	film thickness of component i in multicomponent mixture
χ_i	fraction unaccomplished change, $= (c_i - c_{i\infty})/(c_{i0} - c_{i\infty})$

Matrix notation

( )	column matrix of dimension $n - 1$
[ ]	square matrix of dimension $n - 1 \times n - 1$
$\ulcorner\ \lrcorner$	diagonal matrix with $n - 1$ non-zero elements

Subscripts

i, j	indices
0	at interface
∞	in bulk fluid

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