MURPHREE POINT EFFICIENCIES IN MULTICOMPONENT SYSTEMS

By R. KRISHNA,* H. F. MARTINEZ,† R. SREEDHAR† and G. L. STANDART†

SUMMARY

The mass transfer characteristics during distillation of n-component mixtures on a well-mixed tray are analysed using matrix formulations of the interfacial transport rate relations. The Murphree point efficiencies of individual components are seen to be capable of exhibiting bizarre behaviour ($E_{oyi} \simeq 0$; $E_{oyi} < 0$; $E_{oyi} > 1$; $E_{oyi} \to \pm \infty$) arising out of diffusional interaction effects in multicomponent systems.

Experimental data on distillation of the ternary mixture ethanol/tert-butanol/water in a 76 mm diameter sieve tray column show that diffusional interaction effects are present to a significant extent for the system. It is observed that the Murphree point vapour efficiencies for the individual components are all different from one another; the efficiency for tert-butanol is strongly composition dependent and assumes negative values and values exceeding unity for different composition regions. The relative values of the component efficiencies experimentally observed are predictable qualitatively in terms of a film model for multicomponent mass transfer.

Introduction

In recent years there has been increasing interest in the area of multicomponent mass transport phenomena. This interest has been sparked off with the realisation that the mass transfer characteristics of multicomponent systems are significantly different from those exhibited by a simple two component system. As shown by Toor,[1] a multicomponent system may experience three interesting interaction phenomena: osmotic diffusion (diffusion of a species in the absence of its constituent driving force), diffusion barrier (a component fails to transfer even though a composition gradient exists for its transfer) and reverse diffusion (diffusion of a species in a direction opposite to that dictated by its constituent driving force). These interaction phenomena arise out of coupling between the diffusing species and are especially important for non-ideal mixtures made up of species of widely differing sizes and nature. The three interaction phenomena have been experimentally observed for diffusion in gaseous mixtures,[2] interphase mass transfer in vapour/liquid systems[3, 4] and more recently during interphase mass transfer in liquid/liquid systems.[5]

In order to take proper account of diffusional interaction effects and coupling between species transfer, the diffusion flux of species i in an n-component mixture must be written in the form

$$J_i = \sum_{k=1}^{n-1} k_{yik}^{\bullet}(y_{kI} - y_k), \qquad i = 1, 2, \ldots n-1 \quad (1)$$

The cross coefficients $k_{yik}^{\bullet}(i \neq k)$ allow for the coupling between the diffusing species. Equation (1) has been written for transfer in the vapour phase using partial composition driving forces: $y_{kI} - y_k$, differences between the interface and bulk vapour compositions. Analogous relations for the liquid phase may also be written. The superscript black dot on the elements of the matrix of mass transfer coefficients emphasises the fact that the coefficients defined in equation (1) are themselves functions of the interfacial transfer rates.[6, 7]

* Koninklijke/Shell Laboratorium, Badhuisweg 3, Amsterdam, The Netherlands.
† Department of Chemical Engineering, University of Manchester Institute of Science and Technology, Sackville Street, Manchester M60 1QD.

It is clear from equation (1) that each component in the multicomponent mixture transfers with a facility which is different for each species. The consequence of this in multicomponent distillation is that in general the component efficiencies will all be different. We might expect the differences in the component efficiencies to be small when the mixture is ideal and made up of species of similar size and nature. On the other hand for highly non-ideal mixtures we may expect the component efficiencies to be significantly different from one another. The experimental data available in the literature,[8-34] in general, confirm these expectations. Thus for the thermodynamically ideal systems benzene/toluene/xylene[8, 16, 27] and oxygen/nitrogen/argon,[15] the component efficiencies have been found to be nearly equal to one another. On the other hand for distillation of non-ideal mixtures: methanol/acetone/water,[10, 11] acetone/methanol/ethanol,[12] methanol/ethanol/propanol/butanol/water,[13] acetone/benzene/chlorobenzene,[16] methanol/isoporopanol/water[31, 32] and n-hexane/methyl cyclopentane/ethanol/benzene[33, 34] the component transfer efficiencies have been determined to be significantly different. There is also some conflicting information in the published literature; thus while Cermak[9] concludes that the distillation behaviour of the system methanol/isopropanol/water conforms with the postulate of mutually equal efficiencies, Vogelpohl[31, 32] has measured large interaction effects with the same system.

Though the theory of multicomponent mass transfer is fairly well developed[6, 35, 36] and has been applied to the prediction of component efficiencies in multicomponent distillation,[10, 31, 37] these predictive models have not been extensively, and critically, tested against experimental measurements. Thus there has been no experimental confirmation of the interesting possibilities of osmotic diffusion, diffusion barrier or reverse diffusion effects in multicomponent distillation as anticipated by Toor and Burchard.[38]

It is the objective of the current work to explore in detail the consequences of diffusional interaction effects in multicomponent distillation, to develop some general guidelines for the prediction of the relative magnitudes of the component efficiencies and to seek experimental confirmation of the interaction effects and the predictive mass transfer models. The system chosen for experimental study is ethanol/tert-butanol/water. The reasons for the choice of the system are the large thermodynamic non-idealities present in the system[39] and the expectation that diffusional interactions would be significantly large.

Theory

Consider the distillation of an n-component mixture on a tray. If the vapour is assumed to be in plug flow, then the differential material balance for species i may be written for a thin vertical section of the tray as

$$\frac{dG_i}{dz} = N_i aH \qquad i = 1, 2, \ldots n \qquad . \qquad . \quad (2)$$

where N_i is the molar flux of species i across the vapour–liquid interface; G_i is the molar flow rate of species i in the vapour phase; z is height up the dispersion; a is the interfacial area per unit volume of dispersion; H is the volume of dispersion per unit height. If Z is the total height of dispersion, then $V = Z \times H$ is the total volume of dispersion in the section under consideration.

For the total mixture we have the material balance relationship

$$\frac{dG_t}{d\xi} = N_t aV \qquad . \qquad . \qquad . \qquad . \qquad . \qquad (3)$$

where G_t is the mixture molar flow rate, N_t is the total mixture flux across the interface and $\xi = z/Z$ is the fractional height of dispersion.

If we split the molar flux of species i, N_i, into a purely diffusive contribution, J_i, and the convective flux, $y_i N_t$, we get:

$$N_i = J_i + y_i N_t, \qquad i = 1, 2, \ldots n \qquad . \qquad . \quad (4)$$

In view of equations (3) and (4), we may write equations (2) in the form

$$G_t \frac{dy_i}{d\xi} = J_i aV, \qquad i = 1, 2, \ldots n-1 \qquad . \quad (5)$$

where we have used the relation

$$G_i = y_i G_t, \qquad i = 1, 2, \ldots n \qquad . \qquad . \qquad (6)$$

Only $n-1$ equations (5) have been written because only $n-1$ compositions y_i are independent. Further, only $n-1$ of the diffusion fluxes J_i are independent since

$$\sum_{i=1}^{n} J_i = 0 \qquad . \qquad . \qquad . \qquad . \qquad . \qquad . \qquad (7)$$

The interfacial mass transfer rate relations may be written using partial vapour phase driving forces, as in equation (1), or, more conveniently by use of overall driving forces as:

$$(J) = [K_{oy}^{\bullet}](y^* - y) . \qquad . \qquad . \qquad . \qquad (8)$$

where we use $n-1$ dimensional matrix notation. $[K_{oy}^{\bullet}]$ represents the matrix of overall vapour phase mass transfer coefficients.

If we further define a matrix of overall number of vapour phase transfer units by

$$[NTU_{oy}] \equiv \frac{[K_{oy}^{\bullet}]aV}{G_t} \qquad . \qquad . \qquad . \qquad (9)$$

then we may combine equations (5), (8) and (9) to give an $n-1$ dimensional matrix differential equation

$$\frac{d(y)}{d\xi} = [NTU_{oy}](y^* - y) . \qquad . \qquad . \qquad . \quad (10)$$

If the elements of $[NTU_{oy}]$ are assumed to be constant along the dispersion height and if liquid on the tray is assumed to be well mixed in the vertical direction, giving constant (y^*), equation (10) may be integrated with the boundary conditions

$$\xi = 0, (y) = (y_A);$$
$$(y^* - y) \equiv (\Delta y) = (y^* - y_A) = (\Delta y_A)$$

$$\xi = 1, (y) = (y_B);$$
$$(y^* - y) \equiv (\Delta y) = (y^* - y_B) = (\Delta y_B) \qquad (11)$$

to give

$$(\Delta y_B) = \exp\{-[NTU_{oy}]\}(\Delta y_A) \qquad . \qquad . \quad (12)$$

where the matrix exponential can be evaluated by use of Sylvester's theorem.[40] Thus, if we define

$$[G] \equiv \exp\{-[NTU_{oy}]\} . \qquad . \qquad . \qquad . \quad (13)$$

we get for a ternary system, for example,

$$G_{11} = \frac{\exp(-N\hat{T}U_{oy1})}{N\hat{T}U_{oy1} - N\hat{T}U_{oy2}}(NTU_{oy11} - N\hat{T}U_{oy2})$$
$$- \frac{\exp(-N\hat{T}U_{oy2})}{N\hat{T}U_{oy1} - N\hat{T}U_{oy2}}(NTU_{oy11} - N\hat{T}U_{oy1}) \quad (14)$$

$$G_{12} = \frac{\exp(-N\hat{T}U_{oy1}) - \exp(-N\hat{T}U_{oy2})}{N\hat{T}U_{oy1} - N\hat{T}U_{oy2}} NTU_{oy12} \quad (15)$$

$$G_{21} = \frac{\exp(-N\hat{T}U_{oy1}) - \exp(-N\hat{T}U_{oy2})}{N\hat{T}U_{oy1} - N\hat{T}U_{oy2}} NTU_{oy21} \quad (16)$$

$$G_{22} = \frac{\exp(-N\hat{T}U_{oy1})}{N\hat{T}U_{oy1} - N\hat{T}U_{oy2}}(NTU_{oy22} - N\hat{T}U_{oy2})$$
$$- \frac{\exp(-N\hat{T}U_{oy2})}{N\hat{T}U_{oy1} - N\hat{T}U_{oy2}}(NTU_{oy22} - N\hat{T}U_{oy1}) \quad (17)$$

where $N\hat{T}U_{oy1}$ and $N\hat{T}U_{oy2}$ are the eigenvalues of the matrix $[NTU_{oy}]$:

$$N\hat{T}U_{oy1,2} = \tfrac{1}{2}\{(NTU_{oy11} + NTU_{oy22}) \pm$$
$$\sqrt{[(NTU_{oy11} - NTU_{oy22})^2 + 4NTU_{oy12}NTU_{oy21}]}\} \quad (18)$$

For a two component system all the above matrix relations reduce to scalars and the Murphree point efficiency for component 1 may be obtained in view of equation (12) as

$$E_{oy1} = \frac{y_{1B} - y_{1A}}{y_1^* - y_{1A}} = 1 - \exp\left(-NTU_{oy}\right) \quad . \quad (19)$$

It can be easily verified that the Murphree point efficiency for component 1 is equal to the efficiency of component 2; there is thus only one characteristic efficiency describing the mass transfer behaviour of a binary system on a tray (just as the binary system is described by one diffusion coefficient, one mass transfer coefficient, one height of a transfer unit etc.).

For n-component systems the proper matrix generalisation of equation (19) is obtained by definition of a matrix of multi-component Murphree efficiencies by the relation:

$$(y_B - y_A) = [E_{oy}](y^* - y_A) \quad . \quad . \quad . \quad (20)$$

The matrix $[E_{oy}]$ is obtained in view of equations (12) and (13) as

$$[E_{oy}] = \ulcorner I_\lrcorner - \exp\left\{-[NTU_{oy}]\right\} = \ulcorner I_\lrcorner - [G] \quad (21)$$

If the elements of $[NTU_{oy}]$ are known, the elements of $[E_{oy}]$ can be calculated by use of Sylvester's theorem. For a ternary system, for example,

$$E_{oy11} = 1 - G_{11} \quad . \quad . \quad . \quad . \quad (22)$$

$$E_{oy12} = -G_{12} \quad . \quad . \quad . \quad . \quad (23)$$

$$E_{oy21} = -G_{21} \quad . \quad . \quad . \quad . \quad (24)$$

$$E_{oy22} = 1 - G_{22} \quad . \quad . \quad . \quad . \quad (25)$$

where the elements G_{ij} are given by equations (14)–(17).

It is more common in the published literature to define Murphree point efficiencies for each of the species in the n-component mixture in the pseudo-binary form

$$E_{oyi} = \frac{y_{iB} - y_{iA}}{y_i^* - y_{iA}}, \qquad i = 1, 2, \ldots n \quad . \quad . \quad (26)$$

Since the mole fractions add to unity, only $n-1$ of the efficiencies defined in (26) are independent. It is also possible to express these $n-1$ independent Murphree pseudo-binary point efficiencies in matrix notation by

$$(y_B - y_A) = \ulcorner E_{oy}\lrcorner(y^* - y_A) \quad . \quad . \quad . \quad (27)$$

and therefore we obtain from equation (20) the interrelation between the two efficiency definitions as

$$[E_{oy}](y^* - y_A) = \ulcorner E_{oy}\lrcorner(y^* - y_A). \quad . \quad . \quad (28)$$

For a ternary system we have from equations (22)–(25):

$$E_{oy1} = E_{oy11} + E_{oy12}/\Upsilon = 1 - G_{11} - G_{12}/\Upsilon \quad . \quad (29)$$

$$E_{oy2} = E_{oy22} + E_{oy21}\Upsilon = 1 - G_{22} - G_{21}\Upsilon \quad . \quad (30)$$

where we have further defined the ratio of driving forces of components 1 and 2:

$$\Upsilon = \frac{\Delta y_{1A}}{\Delta y_{2A}} = \frac{y_1^* - y_{1A}}{y_2^* - y_{2A}} \quad . \quad . \quad . \quad (31)$$

The pseudo-ginary efficiency for component 3 may be obtained from the efficiencies of components 1 and 2 as

$$E_{oy3} = \frac{\Upsilon E_{oy1} + E_{oy2}}{\Upsilon + 1}. \quad . \quad . \quad . \quad (32)$$

Since the cross coefficients $K_{oyij}^\bullet(i \neq j)$ will in general be non-zero, it may be checked from (9), (21)–(25), that the elements $G_{ij}(i \neq j)$ and $E_{oyij}(i \neq j)$ will also be non-zero. The effect of non-zero $G_{ij}(i \neq j)$ and $E_{oyij}(i \neq j)$ is to make the pseudo-binary Murphree efficiencies, E_{oyi}, different for each of the individual species in the mixture [cf. equations (28)–(32)]. Further, the efficiencies E_{oyi} will be seen from equations (28)–(32) to be directly dependent on the ratio of driving forces Υ; this ratio is determined by the operating conditions and the vapour/liquid equilibrium relationship. The ratio Υ can be small or large in magnitude, positive or negative in sign. Thus depending on the signs and magnitudes of the elements G_{ij}, it may be seen from equations (29)–(32) that the component efficiencies E_{oyi} can assume values greater than unity or less than zero. If $\Upsilon \simeq -1$, then we see from equation (32) that $E_{oy3} \rightarrow \pm\infty$. For a binary system, on the other hand, it is clear from equation (19) that the Murphree point efficiency will always lie between 0 and 1.

From a design view point it is important to be able to predict the Murphree point efficiencies for n-component mixtures, preferably from information on the transport parameters of the constituent binary pairs alone. Further, it is also important to anticipate for a given mixture the occurrence of negative, low or unbounded efficiencies for any particular component. It is clear from equation (21) that the multicomponent transport behaviour can be predicted if we can estimate the elements of the matrix $[NTU_{oy}]$. From the addition of resistances formula for multicomponent systems,[35, 41] the overall matrix $[NTU_{oy}]$ may be expressed in terms of the partial number of transfer units in the vapour and liquid phases as

$$[NTU_{oy}]^{-1}[\beta^y]^{-1} = [NTU_y]^{-1}[\beta^y]^{-1}$$
$$+ [M]\frac{G_t}{L_t}[NTU_x]^{-1}[\beta^x]^{-1} \quad (33)$$

where $[M]$ is the matrix of equilibrium constants with elements

$$M_{ij} = \frac{\partial y_i^*}{\partial x_j}, \qquad i, j = 1, 2, \ldots n-1. \quad . \quad (34)$$

and $[\beta^y]$ and $[\beta^x]$ are "bootstrap" solution matrices which allow calculation of the molar fluxes from the diffusive fluxes in either fluid phase:

$$(N) = [\beta^y](J^y) = [\beta^x](J^x) \quad . \quad . \quad . \quad (35)$$

If conditions of equimolar transfer are assumed then the bootstrap solution matrices reduce to identity matrices. For the general case, the elements of the matrices $[\beta]$ will be obtained from an energy balance at the vapour liquid interface. The general procedure for obtaining the elements of $[\beta]$ is given by Krishna and Standart.[42]

The use of the linearised theory of multicomponent mass transfer to estimate the elements of $[NTU_y]$ and $[NTU_x]$ is discussed by Toor.[35, 37] If the effect of finite mass transfer rates on the values of the mass transfer coefficients is neglected, then for a ternary system, for example, the elements of the matrix $[NTU_y]$ can be written in terms of the numbers of transfer units of the constituent binary pairs NTU_{yij} as:

$$NTU_{y11} = NTU_{y13}(y_1 NTU_{y23} + (1-y_1)NTU_{y12})/S \quad (37)$$

$$NTU_{y12} = y_1 NTU_{y23}(NTU_{y13}-NTU_{y12})/S \quad . \quad (38)$$

$$NTU_{y21} = y_2 NTU_{y13}(NTU_{y23}-NTU_{y12})/S \quad . \quad (39)$$

$$NTU_{y22} = NTU_{y23}(y_2 NTU_{y13} + (1-y_2)NTU_{y12})/S \quad (40)$$

where

$$S = y_1 NTU_{y23} + y_2 NTU_{y13} + y_3 NTU_{y12} \quad . \quad (41)$$

The relations (37)–(41) follow from a simple film model for mass transfer,[11, 31, 43] which is based on a solution to the Maxwell–Stefan equations for gaseous diffusion. The binary numbers of transfer units NTU_{yij} can be evaluated from available experimental correlations.[44, 45, 46]

For transfer in the liquid phase, additional complications arise due to the thermodynamic non-idealities. Krishna[47] has developed a film model for liquid phase transport which yields relationships similar to equations (37)–(41) and in addition contains thermodynamic factors.

Since the NTU_{yij} for the binary pair $i-j$ is roughly proportional to the square root of the gas phase diffusivity D_{yij}, it can be seen from equations (37)–(41) that the cross coefficients NTU_{y12} and NTU_{y21} will be large in magnitude when the binary gas phase diffusivities of the constituent pairs are widely different. Since the cross coefficients are proportional to the differences in constituent NTU_{yij} it is clear that the NTU_{y12} and NTU_{y21} will in general be only a fraction of the main coefficients NTU_{y11} and NTU_{y22}. Further, the signs of the coefficients NTU_{y11} and NTU_{y22} will always be positive while the signs of NTU_{y12} and NTU_{y21} will depend on the relative magnitudes of NTU_{yij}. The cross coefficients can therefore be of either sign depending on the system numbering of the species.

For liquid phase transport the diffusional interaction effects will in general be much more pronounced than for gas phase transport; this is due to the additional interactions arising out of thermodynamic non-idealities. For molecular diffusion, cross coefficients in excess of the main coefficients have been experimentally measured.[48, 49]

The general conclusion to be drawn from the above analysis is that when the system is non-ideal and is made up of species of widely different size and nature (leading to widely different diffusional mobility), the cross coefficients of the matrices $[NTU_y]$ and $[NTU_x]$, and therefore of $[NTU_{oy}]$, will be significantly non-zero, leading to unequal component efficiencies [cf. equations (29)–(32)].

If the system numbering is chosen to give positive values for the cross coefficients NTU_{oy12} and NTU_{oy21}, it is clear from equations (13)–(18) that the elements G_{12} and G_{21} will be negative in sign. The coefficients G_{11} and G_{22} will always be positive. When Υ is small enough in magnitude

and negative in sign, it is seen from equation (29) that the Murphree point efficiency for component 1 could assume negative values; in any case E_{oy1} will be smaller than E_{oy2}. For large, but negative, values of Υ, E_{oy2} may assume negative values and will be smaller than E_{oy1}. If Υ is sufficiently small in magnitude and of positive sign, E_{oy1} can have a value exceeding unity. Similarly if Υ is sufficiently large in magnitude and of positive sign, E_{oy2} can assume values exceeding unity. Generally speaking, therefore, multicomponent interaction effects will be important for species i (giving rise to $E_{oyi} < 0$, $E_{oyi} > 1$ or $E_{oyi} \to \pm\infty$) when its constituent driving force Δy_{iA} is an order of magnitude smaller than the other constituent driving forces; in such cases the transfer of species i will be governed largely by the transfer rates of the other species in the mixture.

In the following we test the above interesting consequences of diffusional interactions by experimental measurement of efficiencies for distillation of the non-ideal mixture ethanol/ _tert_ butanol/water.

Experimental

The distillation experiments were carried out in a 76 mm internal diameter column made of QVF glass sections, each 305 mm long. The column has three test plates and one "cup tray" arranged in an alternate cross flow pattern. The test plates are constructed of 4·8 mm thick stainless steel. 84 holes, 2·4 mm diameter, are arranged in a triangular pitch of 4·8 mm in six rows. This arrangement gives a free area of 8·2% of the whole plate and 10·2% of the effective bubbling area. On each plate one 6·2 mm (1/4 inch BSP) and two 9·5 mm (3/8 inch BSP) holes for downcomers are tapped and an inlet weir of height 25·4 mm is screwed on to the plate. Two tubes of 6·2 mm and one of 11·2 mm diameter constitute the downcomers.

To get a good distribution of the vapour entering the lowest test plate, a cup tray with an opening in place of the perforations on the test trays is used above the reboiler outlet. A stainless steel knit mesh pad with 98% voidage located between the reboiler and the first glass section also serves to provide good vapour distribution.

The vapour samples were taken from the centre of the stream reaching each plate by means of PTFE sampling cups located underneath the plate. The vapour samples are fitted with small circular deflector plates to stop any entrainment from entering the sampling cup. The liquid samples were withdrawn through a 3·2 mm stainless tube located in the centre of the 11·2 mm downcomer with the inlet at 25·4 mm above the level of the plate to allow vapour disengagement from the liquid coming downwards and at the same time to avoid any mixing with the liquid on the plate. Such samples may be considered to be representative of the liquid leaving the plate above.

All the experimental measurements with the ternary mixture, and also the constituent binary pairs, were carried out at total reflux under similar hydrodynamic conditions. The trays operated in the spray regime in all the runs.

The liquid and vapour samples were analysed using a combined density and refractive index determination. The average error of the mole fraction determinations is less than 0.0020. The vapour/liquid equilibrium data for the ternary mixture were also obtained using a modified Hala flow still. The average deviation of the vapour/liquid equilibrium data fit is 0·002 in mole fraction.

Further details of the experimental set-up, operating conditions, composition determinations and vapour liquid equilibrium data are available.[39, 50, 51]

Results and Discussion

Tables giving the details of the results of 83 experimental measurements of Murphree point efficiencies for each individual species have been deposited with the Institution of of Chemical Engineers. An examination of the results shows that the individual Murphree point efficiencies are significantly different from one another; a representative small sample of the experimental results is given in the Table. The relative values of the pseudo binary Murphree point efficiencies E_{oyi} show strong dependence on the ratio of driving forces, Υ as anticipated earlier in this paper. The efficiency of *tert*-butanol is particularly sensitive to the magnitude and sign of Υ and assumes values less than zero and greater unity.

A complete test of the predictive relations (21)–(34) was not possible because of the lack of information on the diffusion coefficients in the ternary liquid mixture, and hence the matrix $[NTU_x]$ cannot be estimated. Experimental measurements for the constituent binary pairs ethanol/*tert*-butanol, ethanol/water and *tert*-butanol/water[50] under identical hydrodynamic conditions as the ternary runs show that the mass transfer process on the tray is predominantly gas phase diffusion controlled. The numbers of transfer units for the binary pairs were found to be $NTU_{oy12} = 0.35$, $NTU_{oy13} = 0.76$, $NTU_{oy23} = 0.66$ with about $\pm 10\%$ scatter in the experimental results. If the mass transfer during ternary distillation is also considered to be predominantly gas phase diffusion controlled, then the values of the NTU_{oyij} determined above may be used in equations (37)–(41) to generate the matrix $[NTU_y]$ which will approximate $[NTU_{oy}]$; the knowledge of the overall matrix of vapour phase transfer units allows predictions of the Murphree point efficiencies by use of relations (21)–(25), (29)–(32).

Since NTU_{oy12} is the lowest of the three constituent binary numbers of transfer units we might expect the cross coefficients NTU_{oy12} and NTU_{oy21} of the matrix $[NTU_{oy}]$ to be positive. From the discussions following equation (41), it is clear that we should expect E_{oy2} to exceed unity when $\Upsilon \gg 1$ and E_{oy2} should be negative when Υ has a large but negative value. The experimental results confirm these expectations and therefore we may conclude that the interactive mass transfer relations (8) are able to explain the experimental results qualitatively. When Υ is of the order unity, the interaction effects will not be large and the constituents E_{oyi} will be close to each other, as seen to be the case from the Table.

For a quantitative test of the multicomponent film model, consider Run S11C. Taking $NTU_{oy12} = 0.35$, $NTU_{oy13} =$

0.76 and $NTU_{oy23} = 0.66$, the matrix elements of $[NTU_{oy}]$ can be calculated using equations (37)–(41), assuming gas phase diffusion control. We obtain $NTU_{oy11} = 0.5198$; $NTU_{oy12} = 0.087$; $NTU_{oy21} = 0.1816$; $NTU_{oy22} = 0.5943$. The matrix $[G]$ can be calculated from equations (14)–(18); we thus obtain $G_{11} = 0.5992$; $G_{12} = -0.049$; $G_{21} = -0.1043$; $G_{22} = 0.5564$. From equations (29)–(32), we calculate the Murphree point efficiencies as $E_{oy1} = 0.403$; $E_{oy2} = 2.44$; $E_{oy3} = 0.504$ which gives the correct relative observed trend: $E_{oy1} < E_{oy3} < E_{oy2} > 1$. The actual component efficiency values are not predicted accurately because of the assumption of negligible liquid phase resistance and the scatter in the experimental data. It must be remarked here that to give large magnitudes of Υ we must have one of the driving forces very small. In the example above the driving force $\Delta y_{2A} = 0.0012$ which is of the order of magnitude of the accuracy of composition determination. For Run M12, using the same values of NTU_{oyij} as above we estimate the matrix $[NTU_{oy}]$ as: $NTU_{oy11} = 0.5854$; $NTU_{oy12} = 0.1533$; $NTU_{oy21} = 0.1320$; $NTU_{oy22} = 0.5441$. The elements of $[G]$ are calculated as: $G_{11} = 0.5626$; $G_{12} = -0.0874$; $G_{21} = -0.0753$; $G_{22} = 0.5862$ giving from equations (29)–(32) $E_{oy1} = 0.436$, $E_{oy2} = -4.16$; $E_{oy3} = 0.5129$. The observed trend $E_{oy3} > E_{oy1} > E_{oy2} < 0$ is again correctly predicted. But due to the fact that the driving force $\Delta y_{2A} = -0.0006$ is smaller than the accuracy of the composition determination, the actual magnitudes of the observed efficiencies are not predicted accurately.

Conclusions

Experimental measurements of Murphree point efficiencies for the system ethanol/*tert*-butanol/water show that the E_{oyi} ared significantly different from one another. The component with intermediate volatility, *tert*-butanol, has Murphree efficiency which is strongly composition dependent, exceeds unity and assumes negative values. The relative magnitudes of the Murphree point efficiencies can be predicted qualitatively by using a multicomponent film model assuming gas phase diffusion control.

Symbols Used

a interfacial area per unit volume of dispersion
D_{yij} binary diffusivity of gas pair $i-j$
E_{oyi} psuedo binary Murphree point efficiency of species i
$[E_{oy}]$ matrix of multicomponent Murphree point efficiencies

Table—Experimental results of the distillation of the mixture ethanol/tert-butanol/water

Run	y_{1A}	y_{2A}	y_1^*	y_2^*	Υ	E_{oy1}	E_{oy2}	E_{oy3}
S1A	0.1520	0.1405	0.2792	0.3343	0.6563	0.6829	0.6923	0.6886
S2B	0.1466	0.4088	0.1741	0.4628	0.5093	0.6259	0.5273	0.5660
S4A	0.1829	0.1412	0.3193	0.2994	0.8903	0.6019	0.5928	0.5971
S11A	0.1791	0.4203	0.1891	0.4637	0.2304	0.0699	0.6779	0.5638
M24	0.2324	0.3575	0.2606	0.4077	0.5618	0.4793	0.8334	0.7061
M32	0.0824	0.0801	0.2435	0.3363	0.6288	0.6268	0.5445	0.5762
S6C	0.2711	0.3488	0.3050	0.3753	1.2792	0.5013	0.8461	0.6525
S11C	0.1919	0.4627	0.2149	0.4639	19.1667	0.6491	2.0019	0.7162
M3	0.1924	0.4616	0.2143	0.4638	9.9545	0.6169	1.3577	0.6848
M6	0.1932	0.4579	0.2178	0.4601	11.1818	0.6455	1.2058	0.6906
M9	0.2280	0.4359	0.2490	0.4377	11.6667	0.5144	2.9244	0.7092
M34	0.3071	0.3499	0.3389	0.3533	9.0857	0.4463	1.0491	0.5050
M41	0.4733	0.1817	0.5317	0.1835	32.4	0.4433	1.5891	0.4780
M47	0.5242	0.1310	0.5928	0.1318	85.7	0.4605	5.2700	0.5170
M49	0.2198	0.4209	0.2417	0.4403	1.1289	0.5331	1.0735	0.7865
M1	0.1916	0.4646	0.2153	0.4645	−237.0	0.6509	−27.9812	0.7202
M12	0.3334	0.3297	0.3699	0.3291	−60.8	0.4790	−1.2888	0.5095
M40	0.4992	0.1846	0.5250	0.1833	−7.65	0.4811	0.1853	0.5256
M46	0.5558	0.1353	0.6040	0.1335	−26.8	0.3546	−2.9400	0.4800

G_i molar flow rate of species i in the gas phase
G_t mixture molar flow rate
[G]   matrix defined by equation (13)
H volume of dispersion per unit height
$\ulcorner I \lrcorner$ identity matrix
J_i molar diffusion flux of species i
$[k_y]$ matrix of partial mass transfer coefficients in gas phase
$[K_{oy}]$ matrix of overall mass transfer coefficients in gas phase
L_t molar flow rate of liquid across tray
[M]   matrix of equilibrium constants defined by eq (34)
n number of components in multicomponent mixture
N_i molar flux of species i relative to stationary coordinate reference frame
N_t mixture molar flux relative to stationary coordinate reference frame
NTU_{ij} number of transfer units for the binary pair ij
[NTU]   matrix of numbers of transfer units
$\widehat{NTU}_i$ ith eigenvalue of [NTU]
S summation parameter defined by equation (41)
V volume of dispersion
x_i mole fraction of species i ln liquid mixture
y_i mole fraction of species i in vapour mixture
z distance parameter up the height of dispersion on tray
Z total height of dispersion on tray

Superscripts
*   equilibrium value
•   eigenvalue of corresponding matrix
●   corresponding to finite mass transfer rates

Subscripts
A conditions corresponding to entry to tray
b bulk fluid phase property
B conditions corresponding to exit from tray
I interfacial property
i, j, k indices
o overall property
x pertaining to liquid phase
y pertaining to vapour phase

Greek Letters
$[\beta]$ "bootstrap" solution matrices
ξ dimensionless distance up the dispersion
Υ ratio of driving forces defined by equation (31)

Matrix Notation
( )   column matrix of dimension $n-1$
[ ]   matrix of dimension $n-1 \times n-1$
$[\ ]^{-1}$ inverted matrix $n-1 \times n-1$
$\ulcorner\ \lrcorner$ diagonal matrix

References

1 Toor, H. L., *AIChE J*, 1957, 3, 198.
2 Duncan, J. B., and Toor, H. L., *AIChE J*, 1962, **8**, 38.
3 Toor, H. L., and Sebulsky, R. T., *AIChE J*, 1961, 7, 558, 565.
4 Modine, A. D., PhD Dissertation, Carnegie Institute of Technology, Pittsburgh, 1963.
5 Paybarah, A., PhD Thesis, University of Manchester Institute of Science and Technology, 1973.
6 Stewart, W. E., and Prober, R., *Ind & Eng Chem Funda*, 1964, 3, 224.
7 Stewart, W. E., *AIChE J*, 1973, 19, 398.
8 Burns, M. D., PhD Dissertation; Oklahoma State University, 1969.
9 Cermák, J., *Coll Czech Chem Comm*, 1970, **35**, 1844.
10 Diener, D. A., PhD Dissertation, University of Delaware, 1967.
11 Diener, D. A., and Gerster, J. A., *Ind & Eng Chem Process Des & Dev*, 1968, 7, 339.
12 Free, K. W., and Hutchison, H. P., in *Distillation*, 1960, p 231, (IChemE Symp Series No 6).
13 Gelbin, D., *Br Chem Eng*, 1965, 10, 301.
14 Gücalp, U., PhD Thesis, University of Birmingham, 1966.
15 Haselden, G. G., and Thorogood, R. M., *Trans IChemE*, 1964, **42**, 81.
16 Hutchinson, H. P., and Lusis, M. A., *Trans IChemE*, 1968, 46, T158.
17 Konstantinov, E. N., and Nikolaev, A. M., *Izv Vyssh Ucheb Zaved Neft Gaz*, 1964, 7, 53.
18 Konstantinov, E. N., and Nikolaev, E. N., *Izv Vyssh Ucheb Zaved, Khim Khim Tekh*, 1964, 7, 492.
19 Lutigina, N. V., and Kislyakova, L. I., *Zh Prikl Khim*, 1969, 42, 218.
20 Lutugina, N. V., and Kovalichev, O. F., *Zh Prikl Khim*, 1966, 39, 1587.
21 Lutugina, N. V., and Kovalichev, O. F., *Massoobmennye Potsessy Khim Tekh*, 1969, 4, 71.
22 Lutugina, N. V., Kolbina, V. N., and Pukinskii, I. B., *Zh Prikl Khim*, 1968, 41, 444.
23 Lutugina, N. V., Molodenko, P. Y., and Orlievskaya, O. V., *Zh Prik Khim*, 1968, 41, 850.
24 Lutugina, N. V., and Nikandrova, G. I., *Massoobmennye Protsessy Khim Tekh*, 1969, 4, 64.
25 Lutugina, N. V., and Nikandrova, G. I., *Massoobmennye Protsessy Khim Tekh*, 1969, 4, 73.
26 Miskin, L. G., Ozalp, U., and Ellis, S. R. M., *Br Chem Eng & Proc Tech*, 1972, **17**, 153.
27 Nord, M., *Trans AIChE*, 1946, **42**, 863.
28 Qureshi, A. K., and Smith, W., *J Inst Petroleum*, 1958, **44**, 137.
29 Shporin, V. I., Konstantinov, V. N., and Nikolaev, A. M., *Teor Osn Khim Tekh*, 1968, 2, 505.
30 Vertuzaev, E. D., Lysko, E. A., and Ganenok, N. I., *Theor Found Chem Eng*, 1970, 45, 284.
31 Vogelpohl, A., and Ceretto, R., *Chem Ing Tech*, 1972, 44, 936.
32 Vogelpohl, A., Paper presented at the European Federation of Chemical Engineers Working Party on Distillation and Absorption, Toulouse, April 1975.
33 Young, G. C., PhD Dissertation, University of Nebraska, 1971.
34 Young, G. C., and Weber, J. H., *Ind & Eng Chem Process Des & Dev*, 1972, 11, 440.
35 Toor, H. L., *AIChE J*, 1964, 10, 448, 460.
36 Cullinan, H. T., *Ind & Eng Chem Funda*, 1965, 4, 133.
37 Toor, H. L., *AIChE J*, 1964, 10, 545.
38 Toor, H. L., and Burchard, J. K., *AIChE J*, 1960, 6, 202.
39 El-Yafi, A. H., Martinez, H. F., Newsham, D. M. T., and Vahdat, N., *J Chem Thermodynamics*, 1976, **8**, 1061.
40 Amundson, N. R., *Mathematical Methods in Chemical Engineering*, 1966, Prentice Hall, Englewood Cliffs, NJ.
41 Krishna, R., and Standart, G. L., *Letters Heat & Mass Transfer*, 1976, 3, 41.
42 Krishna, R., and Standart, G. L., *Letters Heat & Mass Transfer*, 1976, 3, 173.
43 Krishna, R., and Standart, G. L., *AIChE J*, 1976, 22, 383.
44 *Bubble Cap Tray Design Manual*, 1958, AIChE, New York.
45 Smith, B. D., *Design of Equilibrium Stage Processes*, 1963, McGraw-Hill, New York.
46 Sherwood, T. K., Pigford, R. L., and Wilke, C. R., *Mass Transfer*, 1975, McGraw-Hill, New York.
47 Krishna, R., *Letters Heat & Mass Transfer*, 1976, 3, 153.
48 Cussler, E. L., and Lightfoot, E. N., *J Phys Chem*, 1965, 69, 1135, 2875.
49 Alimadadian, A., and Colver, C. P., *Can J Chem Eng*, 1976, 54, 208.
50 Martinez, H. F., PhD Thesis, University of Manchester Institute of Science and Technology, 1975.
51 Sreedhar, R., MSc Dissertation, University of Manchester Institute of Science and Technology, 1975.