MODEL FOR PREDICTION OF POINT EFFICIENCIES FOR MULTICOMPONENT DISTILLATION

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This paper presents a model for the calculation of Murphree point efficiencies in distillation on non-ideal multicomponent fluid mixtures from information on tray hydrodynamics and diffusivity data for the constituent binary pairs in the mixture. A two-zone model is used to describe the hydrodynamic behaviour of the tray. Zone I consists of a *formation zone*, just above the tray floor, with the gas issuing as a cylindrical gas jet through the perforations. Above this zone is the *bulk froth zone*, Zone II, where the gas is dispersed in the form of rigid spherical bubbles of varying size populations. The interfacial mass transfer rate relations are based on the generalized Maxwell-Stefan diffusion equations and take proper account of differences in the binary pair Maxwell-Stefan diffusion coefficients in the vapour and liquid phases. Non-equimolar transfer effects are taken into account by invoking an energy balance at the vapour–liquid interface.

Calculations based on the model are used to demonstrate the strong influence of froth hydrodynamics (bubble sizes, size distributions and rise velocities) on the relative values of the component efficiencies. Using a particular example for distillation of ethanol—*tert* butanol–water, it is shown depending on the bubble size and residence time, the efficiency of *tert* butanol, could attain efficiency values in the range −20% to +50%. Channelling of the gas phase via fast-rising bubbles is also shown to have an effect on the extent of diffusional coupling experienced in the system.

The model developed in this paper could form the basis of an *a priori* method for the estimation of multicomponent distillation efficiencies.

INTRODUCTION

Though distillation occupies a position of pre-eminence amongst industrially used separation processes, there is still a lack of fundamental understanding concerning the interphase mass transfer behaviour on distillation trays. Industrially used design procedures usually proceed via the equilibrium stage calculations and departures from equilibrium are later incorporated by the use of an overall column efficiency; witness the recently expressed industrial view point by McEwan and Darton[1]. Such a procedure has little fundamental basis because for multicomponent distillation the mass transfer efficiencies of individual components, on any given tray, will be different from one another and these values will vary from one tray to the next[2]. In fact, to the author's knowledge the first published realisation of multicomponent distillation behavior dates back to 1941 when Walter and Sherwood[3], on the basis of an extensive experimental study of Murphree vapour and liquid plate efficiencies for absorption, desorption and rectification operations, concluded that "the results indicate that different efficiencies should be used for each component in the design of absorbers for natural gasoline and refinery gases".

Toor[4,5,6,7] was amongst the first to provide a theoretically based model for calculation of multicomponent distillation efficiencies. In an interesting computational study, Toor and Burchard[5] showed with the aid of a sample design problem with the system methanol–isopropanol–water that neglect of differences in component efficiencies could lead to severe underdesign. Toor's work served to kindle experimental and theoretical interest in this area and confirmation has been obtained on many of the theoretical predictions, see the fairly complete literature surveys of Krishna[2,8]. The most dramatic experimental results, in the opinion of the author, are with the system ethanol–tert butanol–water[2] for which it was observed that the component point efficiency of tert butanol exhibited efficiency values, under similar hydrodynamic conditions, $E_2^{ov} > 100\%$ and $E_2^{ov} < 0\%$. This bizarre, un-binary like, behaviour of tert butanol could be rationalized on the basis of multicomponent mass transfer formulations based on the Maxwell-Stefan diffusion equations[2]. It is interesting to remark that the un-binary like behaviour of the system ethanol–tert butanol–water was also observed during distillation in a completely different apparatus: a wetted-wall column[9], lending unequivocal confirmation of the interphase mass transfer models.

The analyses of multicomponent mass transfer on distillation trays have thus far concentrated on the setting up of the interphase mass transfer rate relations, using grossly simplified "black-box" type models for the tray hydrodynamics; see for example the recent paper by Burghardt et al.[10]. In recent years considerable progress has been made on understanding the influence of hydrodynamics on the efficiency of binary mixtures; see for example the recent papers by Lockett et al.[10-14]. In particular, the influence of bubble size distribution and gas channelling on binary tray efficiency has been noted as being of paramount importance[11,15]. It would perhaps not be out of place to point out that the deleterious effect of bubble size distribution on the mass transfer performance of bubble columns and gas fluidized beds, especially operating in the churn-turbulent regime, has long been appreciated and have been modeled with the help of the "two-phase" theory[16,17,18] in which the fast-rising bubble population is considered as the "dilute" phase. Tray hydrodynamics has not yet been tackled with the "two-phase" theory.

In the present communication we focus attention on the influence of tray hydrodynamics on the component efficiencies in multicomponent distillation. The analysis is restricted to the free-bubbling regime of operation of tray columns. Work is in progress to extend the treatment to the spray regime of operation. It is in the free bubbling regime that the analogy with the churn-turbulent flow of fluid beds is particularly striking.

The ensuing analysis is limited to the determination of *point* efficiencies in non-ideal n-component mixtures; liquid mixing effects, liquid channelling, liquid entrainment and vapour mixing effects are not considered.

INTERPHASE MASS TRANSFER RATE RELATIONS

Consider the mass transfer process between the vapour and liquid phases at any given position within the vapour–liquid dispersion (froth) on the tray. In this section we shall develop the proper form of the rate relations, postponing to the next section, the question of the estimation of the appropriate transfer coefficients.

The diffusion process is most conveniently described by the generalized Maxwell-Stefan diffusion equations. Consider first the diffusion within the non-ideal liquid phase. The Maxwell-diffusion equations for the n-component mixture[19] can be written as

$$\frac{x_i}{RT}\nabla_{T,p}\mu_i = \sum_{\substack{j=1\\ j\neq i}}^{n} \frac{x_i N_j - x_j N_i}{c_t \text{Đ}_{ij}}, \quad i = 1, 2, \ldots, n \tag{1}$$

Due to the Gibbs-Duhem relationship

$$\sum_{i=1}^{n} x_i \nabla_{T,p}\mu_i = 0 \tag{2}$$

only $n-1$ of the equations (1) are independent and so to determine the n interfacial fluxes N_i we need to supplement equation (1) with an additional relationship. This additional relationship is provided by an energy balance at the interface[20,21], which simplifies to

$$\sum_{i=1}^{n} N_i \lambda_i = 0 \tag{3}$$

for the case where temperature equilibration is rapid, as is the case for distillation tray operations. When the molar latent heats of vaporization of the individual species:

$$\lambda_i = \bar{H}_i^{v} - \bar{H}_i^{l}, \quad i = 1, 2, \ldots, n, \tag{4}$$

are equal to one another the relation (3) degenerates to the requirement of equimolar counter transfer:

$$N_t = \sum_{i=1}^{n} N_i = 0, \tag{5}$$

a condition almost always implicitly assumed in textbook treatments of the subject of distillation mass transfer; see for example King[22]. It has been pointed out that the approximation (5) could lead to large errors in some cases of multicomponent transfers[20,21]; we therefore recommend the routine use of the more general relationship (3).

The energy balance relation (3) enables us to "eliminate" the nth flux N_n from the relations (1) and the further analysis is facilitated if we express the $n-1$ independent equations (1) in $n-1$ dimensional matrix notation:

$$(N) = -c_t[\beta][B]^{-1}[\Gamma](\nabla x) \tag{6}$$

where we introduce three separate coefficient matrices, each of dimension $n-1 \times n-1$ as follows:

(1) a bootstrap matrix $[\beta]$, with elements

$$\beta_{ij} = \delta_{ij} - x_i\left[\frac{\lambda_i - \lambda_n}{\sum_{i=1}^{n} x_i\lambda_i}\right], \quad i,j = 1, 2, \ldots, n-1 \tag{7}$$

This matrix portrays the non-equimolar transfer character of the process considered. When the constituent molar latent heats of vaporization are close to one another, the bootstrap matrix $[\beta]$ degenerates to the identity matrix [I]:

$$[\beta] = [\mathrm{I}] \quad \text{(equimolar transfer)} \tag{8}$$

(2) the matrix $[B]$ of the inverted Maxwell-Stefan diffusion coefficients with the elements

$$B_{ii} = \frac{x_i}{\text{Đ}_{in}} + \sum_{\substack{k=1\\ k\neq i}}^{n} \frac{x_k}{\text{Đ}_{ik}}, \quad i = 1, 2, \ldots, n-1 \tag{9}$$

$$B_{ij} = -x_i\left(\frac{1}{\text{Đ}_{ij}} - \frac{1}{\text{Đ}_{in}}\right), \quad i,j = 1, 2, \ldots, n-1 \quad (i \neq j) \tag{10}$$

which are calculable from information on the pair diffusivities Đ_{ij}. For ideal vapour mixtures the Đ_{ij} are identical to the Fickian binary diffusion coefficient in the binary mixture $i-j$ and can be estimated from the semi-empirical models based on the kinetic theory of gases[23]. It is interesting to note that for ideal vapour mixtures while the binary pair diffusivities are *independent* of composition, use of the formulation (6) for n-component transfer, renders the multicomponent diffusion coefficient matrix $[B]^{-1}$ composition *dependent*. For non-ideal liquid mixtures the pair diffusivities Đ_{ij} are composition dependent, even for binary mixtures. For binary mixtures, the Đ_{ij} show a much simpler dependence on the composition than the corresponding Fickian diffusivity, as shown by Vignes[24], who suggested the following rule for the prediction of Đ_{ij} from the two infinite dilution coefficients Đ_{ij}^0 and Đ_{ji}^0:

$$\text{Đ}_{ij} = (\text{Đ}_{ij}^0)^{x_j}(\text{Đ}_{ji}^0)^{x_i} \quad \text{(binary mixture)} \tag{11}$$

The infinite dilution coefficients Đ_{ij}^0 and Đ_{ji}^0 can be estimated by the methods discussed in Reid et al.[23].

For n-component mixtures, the methods for prediction Đ_{ij} are still under development; see for example the references (25–27). In the absence of reliable prediction procedures we recommend the following generalization of the Vignes relationship:

$$\text{Đ}_{ij} = (\text{Đ}_{ij}^0)^{(x_j/(x_i+x_j))}(\text{Đ}_{ji}^0)^{(x_i/(x_i+x_j))}, \quad i,j = 1, 2, \ldots, n-1 \tag{12}$$

Our unpublished calculations indicate that the above relationship (12) is of adequate accuracy for engineering design purposes.

Let us now examine some limiting forms of the matrix $[B]$. When the components making up the mixture are similar in size and nature and the mixture is nearly thermodynamically ideal, then the pair diffusivities Đ_{ij} become nearly equal to one another and the matrix $[B]$ degenerates to the form:

$$[B] = \text{Đ}^{-1}[\mathrm{I}] \tag{13}$$

which will be a good engineering approximation for close-boiling hydrocarbon mixtures. Indeed, measurements of the diffusion coefficients in the ternary system toluene–chlorobenzene–bromobenzene[28] show that the diffusion process can be characterized by one characteristic diffusion coefficient Đ. For non-ideal mixtures made up of components of differing size, nature, polarity and hydrogen bonding characteristics the pair Đ_{ij} typically vary by a factor of four. We do not therefore recommend the use of a single diffusivity to describe the transfer behaviour in either fluid phase.

Another limiting case of interest is when one component, say component 1, in the mixture is present in vanishingly small concentrations. In this case the relations (6), (9) and (10) reduce to

$$\mathbf{N}_1 = -c_t B_{11}^{-1} \nabla x_1 \tag{14}$$

where B_{11} is calculated from the infinite dilution coefficients as follows:

$$B_{11} = \frac{x_2}{\text{Đ}^0_{12}} + \frac{x_3}{\text{Đ}^0_{13}} + \cdots + \frac{x_3}{\text{Đ}^0_{1n}} \tag{15}$$

(3) The last of the three coefficient matrices is $[\Gamma]$, the matrix of thermodynamic factors with elements

$$\Gamma_{ij} = x_i \frac{\partial \ln (\gamma_i x_i)}{\partial x_j} = \delta_{ij} + x_i \frac{\partial \ln \gamma_i}{\partial x_j}, \quad i,j = 1, 2, \ldots, n-1 \tag{16}$$

The elements Γ_{ij} can be calculated from the non-ideal solution model used to describe the vapour–liquid equilibrium data, for example the models of Wilson, NRTL and UNIQUAC could be used for this purpose[29]. In the absence of experimental data on the Wilson, NRTL or UNIQUAC parameters, the UNIFAC group contribution method could be used to provide estimates of Γ_{ij}[30].

For thermodynamically ideal systems the matrix $[\Gamma]$ degenerates to the identity matrix:

$$[\Gamma] = [\mathrm{I}] \quad \text{(thermodynamically ideal mixture)} \tag{17}$$

We see from the above that the interphase mass transfer process in multicomponent systems is characterized by three coefficient matrices: $[\beta]$, $[B]$ and $[\Gamma]$, reflecting, in turn, non-equimolar transfer behaviour, differences in constituent binary pair diffusivities Đ_{ij} and departures from thermodynamic ideality. For the triply special case of equimolar transfer in an ideal gas mixture made up of species of similar size and nature we see that the relations (6) degenerate to

$$\mathbf{N}_i = -c_t \text{Đ} \nabla x_i \quad \text{(very special case)} \tag{18}$$

which is the simplest form of Fick's law generalized to multicomponent mixtures. The thrust of the present communication is to analyse the many practical situations where the simple relation (18) is not adequate even for gross engineering design purposes. The general analysis will help to identify situations where departure from (18) can be expected to be serious.

The solution of the constitutive relations (6) together with equations of continuity

$$\frac{\partial x_i}{\partial t} = -\frac{1}{c_t} \nabla \cdot \mathbf{N}_i, \quad i = 1, 2, \ldots, n-1 \tag{19}$$

to obtain the composition profiles and fluxes N_i is a formidable problem. An exact solution is possible for steady-state diffusion of ideal gas mixtures across a "film"[31]. Krishna[32] has suggested a generalization of the ideal gas film model to other situations of practical interest. This is the latter approach we recommend and summary of the procedure for the estimation of the interfacial fluxes N_i is given below.

Firstly, it is assumed that for the hydrodynamic description of the particular phase under consideration, the diffusion equations can be solved for the corresponding situation in a *binary* mixture under the conditions of equimolar transfer, a few such solutions are discussed in the next section. For example, for diffusion in the liquid phase on a tray the penetration model solution for binary mass transfer is given by

$$k = 2D^{1/2}/(\pi t)^{1/2} \tag{20}$$

where k is time-averaged binary mass transfer coefficient and t is the vapour–liquid contact time. The binary solution (20) can be used to calculate the pair mass transfer coefficient k_{ij} in a multicomponent mixture, thus:

$$k_{ij} = 2\,\text{Đ}_{ij}^{1/2}/(\pi t)^{1/2}, \quad i,j = 1, 2, \ldots, n \tag{21}$$

where we use the Maxwell-Stefan pair diffusivity Đ_{ij} in place of the Fickian binary diffusivity in the binary solution (20).

Once the binary pair mass transfer coefficients have been estimated the next step is to calculate the matrix of inverted mass transfer coefficients $[\bar{R}]$ whose elements are given by

$$\bar{R}_{ii} = \frac{\bar{x}_i}{k_{in}} + \sum_{\substack{j=1 \\ j \neq i}}^{n} \frac{\bar{x}_j}{k_{ij}}, \quad i = 1, 2, \ldots, n-1 \tag{22}$$

$$\bar{R}_{ij} = -\bar{x}_i \left(\frac{1}{k_{ij}} - \frac{1}{k_{in}} \right), \quad i,j = 1, 2, \ldots, n-1 \quad (i \neq j) \tag{23}$$

where $\bar{x}_i$ denotes an average composition (say the arithmetic average) between the bulk fluid phase (x_i) and the interface (x_{ie}).

The interfacial fluxes N_i ($i = 1, 2, \ldots, n-1$) are then given by

$$(N) = c_t^l [\bar{\beta}^l][\bar{R}^l]^{-1}[\bar{\Gamma}^l](x - x_e) \tag{24}$$

where the superscript l is introduced to distinguish the liquid phase. The matrices $[\bar{\beta}]$ and $[\bar{\Gamma}]$ are evaluated using equations (7) and (16) at the average compositions $\bar{x}_i$. Equation (24) represents an approximate solution to the generalized Maxwell-Stefan equations and has proved to be of good accuracy for the problem of distillation mass transfer[33,34]. The use of the approximation (24) also avoids the trial-and-error solution required for the exact model[31].

Equation (24) describes the transfer process in the liquid phase (N_i is considered positive for transfer from bulk liquid phase to the vapour–liquid interface). Following an exactly parallel development for the vapour phase we may derive the following relationship

$$(N) = c_t^v [-\beta^{-v}][\bar{R}^v]^{-1}(y_e - y) \tag{24}$$

where y_i and y_{ie} denote the vapour phase compositions in the bulk and interface respectively. In deriving (24) we have taken $[\Gamma^v] = [I]$.

In distillation operations only the bulk phase compositions x_i and y_i are accessible via material balance relationships. We need to eliminate the unknown interfacial compositions x_{ie} and y_{ie}. To achieve this we proceed as follows.

Firstly, the vapour–liquid equilibrium relationship requires to be linearized over the composition range of interest. We write

$$y_i^* = \sum_{j=1}^{n-1} \frac{\partial y_i^*}{\partial x_j} x_j + b_i, \quad i = 1, 2, \ldots, n-1 \tag{25}$$

From the definition of activity coefficients γ_i, we have

$$y_i^* = \gamma_i x_i p_i^0 / p_t, \quad i = 1, 2, \ldots, n \tag{26}$$

Differentiating equation (26) with respect to x_j we obtain after some manipulations

$$\frac{\partial y_i^*}{\partial x_j} = K_i^{eq} \bar{\Gamma}_{ij}^l, \quad i, j = 1, 2, \ldots, n-1 \tag{27}$$

where K_i^{eq} is the K-value:

$$K_i^{eq} = y_i^*/x_i = \gamma_i p_i^0/p_t, \quad i = 1, 2, \ldots, n-1 \tag{28}$$

It is interesting to note that the thermodynamic factors $\bar{\Gamma}_{ij}^l$, whose elements are given by equation (16) arise naturally in two entirely different contexts: description of non-ideal diffusion and of (linearized) vapour–liquid equilibrium.

Combining equations (25) and (27) we obtain the linearized vapour–liquid relationship in the usable form

$$(y^*) = [K^{eq}][\bar{\Gamma}^l](x) + (b) \tag{29}$$

where $[K^{eq}]$ is a diagonal matrix of equilibrium K-values. y_i^* is the composition in equilibrium with the bulk liquid phase of composition x_i. At the interface we have the equilibrium relationship

$$(y_e) = [K^{eq}][\bar{\Gamma}^l](x_e) + (b) \tag{30}$$

Equations (29) and (30) are required to eliminate the interface compositions and derive the addition of resistances formula for multicomponent systems. It is however necessary to proceed with more caution than with the corresponding binary mass transfer problem so as not to violate the rules of matrix algebra.

Equation (24) is re-written in the form

$$(x - x_e) = [\Gamma^l]^{-1}[\bar{R}^l][\bar{\beta}^l]^{-1}(N)/c_t^l \tag{31}$$

Pre-multiplying equation (31) by $[K^{eq}][\bar{\Gamma}^l]$ and introducing the equations (29) and (30) we obtain

$$(y^* - y_e) = [K^{eq}][\bar{\Gamma}^l][\bar{\Gamma}^l]^{-1}[\bar{R}^l][\bar{\beta}^l]^{-1}(N)/c_t^l \tag{32}$$

which relation can be further simplified because

$$[\bar{\Gamma}^l][\bar{\Gamma}^l]^{-1} = [I] \tag{32a}$$

It is interesting to note the cancellation of the matrix of thermodynamic factors$[\bar{\Gamma}^l]$. Any errors inherent in the linearization of $[\Gamma]$ by calculation at the average composition $\bar{x}_i$ are not critical because of the cancelling effect. This simplification only results if the approximation suggested by Krishna[32–34] is adopted. It is to be stressed here that the above simplification will not be obtained if the linearized theory of Toor[6,7] or Stewart and Prober[35] is adopted. The latter theories involve diagonalization of the matrix $[B]^{-1}[\Gamma]$ and require the calculation of $\partial y_i^*/\partial x_j$ using equation (27). Our recommended procedure given above requires evaluation of the equilibrium K-value, K_i^{eq}, for the composition range of interest, a much simpler task.

Introducing (32a) into equation (32) we get

$$(y^* - y_e) = [K^{eq}][\bar{R}^l][\bar{\beta}^l]^{-1}(N)/c_t^l \tag{33}$$

Writing equation (24) in the form

$$(y_e - y) = [\bar{R}^v][\bar{\beta}^v]^{-1}(N)/c_t^v \tag{34}$$

and adding equations (33) and (34) we obtain

$$(y^* - y) = \left[[\bar{R}^v] + \frac{c_t^v}{c_t^l}[K^{eq}][\bar{R}^l][\bar{\beta}^l]^{-1}[\bar{\beta}^v] \right][\bar{\beta}^v]^{-1}(N)/c_t^v \tag{35}$$

Let us now *define* the overall matrix of inverted vapour phase mass transfer coefficients $[\bar{R}^{ov}]$ by

$$[\bar{R}^{ov}] = [\bar{R}^v] + \frac{c_t^v}{c_t^l}[K^{eq}][\bar{R}^l][\bar{\beta}^l]^{-1}[\bar{\beta}]^v \tag{36}$$

With the definition (36) we can calculate the interfacial fluxes N_i from

$$(N) = c_t^v[\bar{\beta}^v][\bar{R}^{ov}]^{-1}(y^* - y) \tag{37}$$

Equations (36) and (37) are the working relations for the calculation of the fluxes N_i. We take up next the question of the estimation of the pair mass transfer coefficients K_{ij} required in the calculation of the matrices $[\bar{R}^l]$ and $[\bar{R}^v]$ using equations (22) and (23).

Tray Hydrodynamics and Estimation of Mass Transfer Coefficients

In order to estimate the pair mass transfer coefficients k_{ij} in both vapour and liquid phases, to allow calculation of $[R^{ov}]$, we first need to model the tray hydrodynamics. The vapour–liquid dispersion on the tray is described by a two-zone model. In Zone I, just above the tray floor, is the bubble formation zone and is represented by cylindrical gas jets issuing from the holes in the tray. Above this Zone I, is the bulk froth zone in which the vapour is dispersed in the form of rigid spherical bubbles in various size populations. Above this Zone II, will in practice be a splash zone but the interfacial area for mass transfer must be expected to be an order of magnitude lower than in Zones I and II and therefore excluded in the present treatment. We now consider the mass transfer processes in the two zones I and II, in turn.

Zone I: Formation Zone

At the level of attack in this paper we consider the liquid phase to be well mixed in the vertical direction and in Zone I, this liquid phase will be in contact with a gas jet in the form of a cylindrical jet. The transient diffusion equation for a binary mixture under conditions of equimolar transfer, can be solved analytically and the solution is available in Crank[36]. In the vapour phase the time-average mass transfer coefficient k_{ij}^v is given by

$$k_{ij}^v = -\frac{1}{a_I' t_I} \ln\left[\sum_{m=1}^{\infty} \frac{4}{j_m^2} \exp\left(-Fo_I \frac{Đ_{ij}}{Đ_{ref}} j_m^2 \right) \right] \tag{38}$$

where j_m represents the roots of the Bessel function $J_0(j_m) = 0$. The Fourier number Fo_I is defined by

$$Fo_I = \frac{4\,\text{Đ}_{ref} t_I}{d_I^2} \tag{39}$$

where d_I is the diameter of the cylindrical gas jet and t_I is the gas residence time:

$$t_I = \frac{h_I}{U_I} \tag{40}$$

h_I is the height of the formation zone and U_I represents the (absolute) velocity of the vapour in the jet.

We have used a reference diffusivity Đ_{ref} in the definition of the Fourier number because as we shall see later this number describes the hydrodynamic influence on the mass transfer in the gas phase in a convenient manner. The parameter a_I' represents the interfacial area *per unit volume of (dispersed) gas* and is given by

$$a_I' = 4/d_I. \tag{41}$$

Specification of the diameter of the gas jet, d_I, the height of the formation zone, h_I, and the absolute vapour velocity of the vapour through the jet, U_I, serves to describe the vapour phase mass transfer completely.

Let us now turn to the liquid phase transfer process in the surrounding (well-mixed) liquid phase. In this case the penetration model applies and the time averaged mass transfer coefficient k_{ij}^l is given by equation (21) with the contact time t_I as given by equation (40).

Zone II. Bulk Froth Zone

Actually this zone will contain bubbles of a range of sizes. In our model we shall assume that the bubble size distributions can be represented by discrete populations, each population having bubbles of uniform size and assumed to be rigid spherical bodies. Consider a bubble of diameter $d_{II,k}$ in the kth population. The transient diffusion equation for equimolar binary mass transfer can be solved for this bubble and the time averaged mass transfer coefficient k_{ij}^v, in the vapour phase, is given by (36)

$$k_{ij}^v = -\frac{1}{a_{II,k}' t_{II,k}} \times \ln\left[\frac{6}{\pi^2}\sum_{m=1}^{\infty}\frac{1}{m^2}\exp\left(-\pi^2 m^2 Fo_{II,k}\frac{\text{Đ}_{ij}}{\text{Đ}_{ref}}\right)\right] \tag{42}$$

where the Fourier number $Fo_{II,k}$ for the kth bubble size population in Zone II is

$$Fo_{II,k} = \frac{4\,\text{Đ}_{ref} t_{II,k}}{d_{II,k}^2} \tag{43}$$

The gas residence time $t_{II,k}$ is calculable from the height of the bulk froth zone h_{II} and the bubble rise velocity $U_{II,k}$

$$t_{II,k} = \frac{h_{II}}{U_{II,k}}. \tag{44}$$

Specification of the bubble diameter, $d_{II,k}$, the bubble rise velocity, $U_{II,k}$, and the height of the bulk froth zone, h_{II}, serves to describe the hydrodynamics of the kth bubble size population, after equations (42)–(44) are supplemented with the following expression for the interfacial area per unit volume of (dispersed) gas:

$$a_{II,k}' = \frac{6}{d_{II,k}} \tag{45}$$

As for the case of Zone I, the liquid phase transfer coefficient is adequately described by the penetration model, with the time averaged mass transfer coefficient given by equation (21) using the contact time $t_{II,k}$ as calculated from equation (44).

Material Balance Relations and Calculation of Point Efficiencies

Having established the interfacial mass transfer rate relations and chosen a hydrodynamic model to allow the calculation of the transfer coefficients in either fluid phase, it now remains to combine the derived relations with the material balance equations. We consider the mass transfer process within the vertical slice pictured in Figure 1. The bulk liquid phase is considered to be well mixed within this slice. If G_i represents the molar flow of component i in the vapour phase, the material balance relationship can be written for plug flow of the vapour phase as

$$\frac{dG_i}{dh} = N_i a A, \quad i = 1, 2, \ldots, n \tag{46}$$

where h represents the distance above the tray floor, a is the interfacial area per unit volume of froth and A is the active tray bubbling area. Introducing the superficial vapour velocity, U_s, based on the active bubbling area, we may rewrite equation (46) as

$$\frac{d(c_t^v U_s y_i)}{dh} = N_i a, \quad i = 1, 2, \ldots, n \tag{47}$$

Only $n - 1$ of the equations (47) are independent and further analysis is conveniently carried out if we express (47) in $n - 1$ dimensional matrix notation and combine

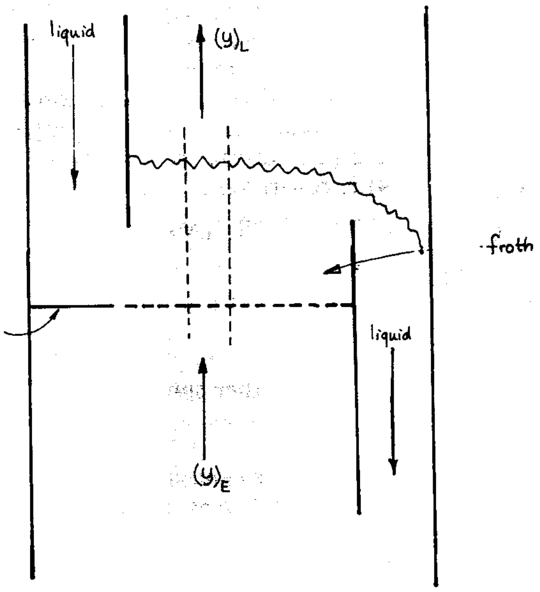

Figure 1. Schematic diagram of distillation tray. $(y)_E$ is the vector of compositions of vapour entering the vertical slice; $(y)_L$ is vector of compositions of vapour leaving the vertical slice. The liquid is assumed to be well mixed within the slice considered.

with the rate relations (37) to obtain

$$\frac{\mathrm{d}(U_s y)}{\mathrm{d}h} = [\beta^{\mathrm{v}}][\bar{R}^{\mathrm{ov}}]^{-1}(y^* - y)a \tag{48}$$

which differential equation has to be integrated along the dispersion height to yield the composition of the vapour leaving the zone. For Zone I, the boundary conditions are

$$h = 0, \quad (y) = (y)_{\mathrm{E}};\ (y^* - y) = (y^* - y)_{\mathrm{E}} \tag{49}$$

$$h = h_{\mathrm{I}}, \quad (y) = (y)_{\mathrm{I}};(y^* - y) = (y^* - y)_{\mathrm{I}} \tag{50}$$

where $(y)_{\mathrm{E}}$ represents the vector of entering vapour phase compositions; (y^*) is the composition in equilibrium with the bulk liquid phase composition (x) and $(y)_{\mathrm{I}}$ is the composition of the vapour phase leaving Zone I and entering the bulk froth Zone II. The mass transfer resistance matrix in Zone I is $[R_{\mathrm{I}}^{\mathrm{ov}}]$ and is to be calculated from equations (36) and (38)–(41), using the following expression for the interfacial area per unit volume of dispersion:

$$a = a_{\mathrm{I}}' \varepsilon_{\mathrm{I}} \tag{51}$$

where ε_{I} represents the hold-up of the vapour phase in Zone I. In the general case numerical integration of the differential equation (48) will be required.

The composition of the vapour entering the kth bubble size population in Zone II is given by

$$h = h_{\mathrm{I}}, \quad (y) = (y)_{\mathrm{I}}, \quad k = 1, 2, \ldots, B \tag{52}$$

We need to set up the differential equation for each of the individual bubble size populations as follows

$$\frac{\mathrm{d}(U_{\mathrm{II,k}} y_{\mathrm{II,k}})}{\mathrm{d}h} = [\beta^{\mathrm{v}}_{\mathrm{II,k}}][\bar{R}^{\mathrm{ov}}_{\mathrm{II,k}}]^{-1}(y^* - y)_{\mathrm{II,k}} a'_{\mathrm{II,k}} \tag{53}$$

which requires to be integrated between the entering condition (52) and the condition at the exit of the kth population zone II:

$$h = h_{\mathrm{II}}, \quad (y) = (y_{\mathrm{II,k}})_{\mathrm{L}}. \tag{54}$$

The composition of component i in the vapour mixture exiting zone II is the weighted average of the individual populations

$$y_{\mathrm{iL}} = \sum_{k=1}^{B} f_{\mathrm{k}} y_{\mathrm{i,II,k,L}}, \quad i = 1, 2, \ldots, n \tag{55}$$

where f_{k} is the fraction of the total vapour entering Zone II which passes up the froth via the kth bubble size population. This fraction f_{k} is given by

$$f_{\mathrm{k}} = \frac{U_{\mathrm{II,k}} \varepsilon_{\mathrm{II,k}}}{U_{\mathrm{s}}} \tag{56}$$

where $\varepsilon_{\mathrm{II,k}}$ is the gas hold-up of kth population in Zone II. It is clear from equation (56) that the major portion of the gas will be transported through the dispersion by the fast rising bubble populations, leading to gas channelling and a deleterious effect on the tray efficiency[11,15]

Once the exiting vapour compositions y_{iL}, leaving Zone II, are calculated the Murphree point efficiencies of the individual components can be determined

$$E_{\mathrm{i}}^{\mathrm{ov}} = 1 - \frac{(y_{\mathrm{i}}^* - y_{\mathrm{i}})_{\mathrm{L}}}{(y_{\mathrm{i}}^* - y_{\mathrm{i}})_{\mathrm{E}}}, \quad i = 1, 2, \ldots, n \tag{57}$$

In the general case of non-equimolar transfer the differential equations (48) and (53) have to be solved numerically, but a convenient analytic relationship can be derived for the case of equimolar transfer with the further assumption of constant $[R^{\mathrm{ov}}]$ in each of the two zones. The analytical solution can be best expressed in the form

$$(y^* - y)_{\mathrm{L}} = [Q](y^* - y)_{\mathrm{E}} \tag{58}$$

where the $n - 1 \times n - 1$ dimensional square matrix $[Q]$ is constructed from the individual zone contributions:

$$[Q] = \sum_{k=1}^{B} f_{\mathrm{k}}[Q_{\mathrm{II,k}}][Q_{\mathrm{I}}]. \tag{59}$$

The Zone I contribution is given by

$$[Q_{\mathrm{I}}] = \exp\left[-[\bar{R}_{\mathrm{I}}^{\mathrm{ov}}]^{-1} a_{\mathrm{I}}' t_{\mathrm{I}}\right]. \tag{60}$$

The contribution of the kth population in Zone II is

$$[Q_{\mathrm{II,k}}] = \exp\left[-[\bar{R}^{\mathrm{ov}}_{\mathrm{II,k}}]^{-1} a'_{\mathrm{II,k}} t_{\mathrm{II,k}}\right]. \tag{61}$$

The matrix exponentials in equations (60) and (61) can be evaluated by the use of Sylvester's theorem[2]. Due to differences in the pair mass transfer coefficients k_{ij}, in either fluid phase, the matrices $[\bar{R}^{\mathrm{ov}}]$ will have non-zero off-diagonal elements and as a consequence the matrix $[Q]$ will have non-zero off-diagonal elements. The consequence of these off-diagonal elements can best be appreciated by considering the simple example of a ternary system and writing equation (58) in the form

$$\Delta y_{1\mathrm{L}} = Q_{11}\,\Delta y_{1\mathrm{E}} + Q_{12}\,\Delta y_{2\mathrm{E}} \tag{62}$$

$$\Delta y_{2\mathrm{L}} = Q_{21}\,\Delta y_{1\mathrm{E}} + Q_{22}\,\Delta y_{2\mathrm{E}} \tag{63}$$

The Murphree point efficiency for components 1 and 2 are then expressible in the form

$$E_1^{\mathrm{ov}} = 1 - Q_{11} - Q_{12}\frac{\Delta y_{2\mathrm{E}}}{\Delta y_{1\mathrm{E}}} \tag{64}$$

$$E_2^{\mathrm{ov}} = 1 - Q_{22} - Q_{21}\frac{\Delta y_{1\mathrm{E}}}{\Delta y_{2\mathrm{E}}}. \tag{65}$$

The point efficiency of component 3 is related to E_1^{ov} and E_2^{ov}:

$$E_3^{\mathrm{ov}} = \frac{\Delta y_{1\mathrm{E}} E_1^{\mathrm{ov}} + \Delta y_{2\mathrm{E}} E_2^{\mathrm{ov}}}{\Delta y_{1\mathrm{E}} + \Delta y_{2\mathrm{E}}}. \tag{66}$$

For mixtures made up of components of similar size and nature, the matrix $[R^{\mathrm{ov}}]$ will reduce to the form of a scalar times the identity matrix (cf. discussions following equation (17)). In such cases the matrix $[Q]$ will also reduce to the form Q [I] and it follows from equations (64)–(66) that $E_1^{\mathrm{ov}} = E_2^{\mathrm{ov}} = E_3^{\mathrm{ov}}$. In the general case with non-zero off-diagonal elements in $[Q]$, the component efficiencies $E_{\mathrm{i}}^{\mathrm{ov}}$ will be different from one another. It is also interesting to note the direct influence of the ratio $\Delta y_{1\mathrm{E}}/\Delta y_{2\mathrm{E}}$ on the values of the component efficiencies. The ratio $\Delta y_{1\mathrm{E}}/\Delta y_{2\mathrm{E}}$ is determined by the operating conditions and the vapour–liquid equilibrium relationship; the ratio can be large or small, positive or negative. Let us examine some of the interesting possibilities. Suppose Q_{12} and Q_{21} are both negative in sign (this is the case for the system ethanol–tert butanol–water to be analysed later); the coefficients Q_{11} and Q_{22} will always be of positive sign. For large positive values of $\Delta y_{1\mathrm{E}}/$

Δy_{2E}, the efficiency of component 2, E_2^{ov}, could attain values exceeding unity, i.e. greater than 100%. On the other hand for large negative values of $\Delta y_{1E}/\Delta y_{2E}$, E_2^{ov} could assume very small values and under sufficiently extreme conditions negative values could be obtained. The unboundedness of component efficiencies in multicomponent systems is in sharp contrast to the corresponding behaviour of binary mixtures for which the component point efficiency (equal for both components) must lie between 0 and 1.

In order to demonstrate the utility of the above model we carry out some calculations for the point efficiencies for the system ethanol (1)–tert butanol (2)–water (3). The composition of the vapour entering the tray is taken to be $y_{1E} = 0.5558$, $y_{2E} = 0.1353$. The composition of the vapour in equilibrium with the bulk liquid phase leaving the tray is ($y_1^* = 0.6040$, $y_2^* = 0.1335$. The ratio $\Delta y_{1E}/\Delta y_{2E}$ is calculated to be -26.8 and from the discussion following equation (66) we should expect the efficiency of tert butanol to be very small, even negative.

We assume that the tray operates in bubbling regime; the molecular diffusivities in the vapour and liquid phases are estimated as shown in an earlier communication[9].

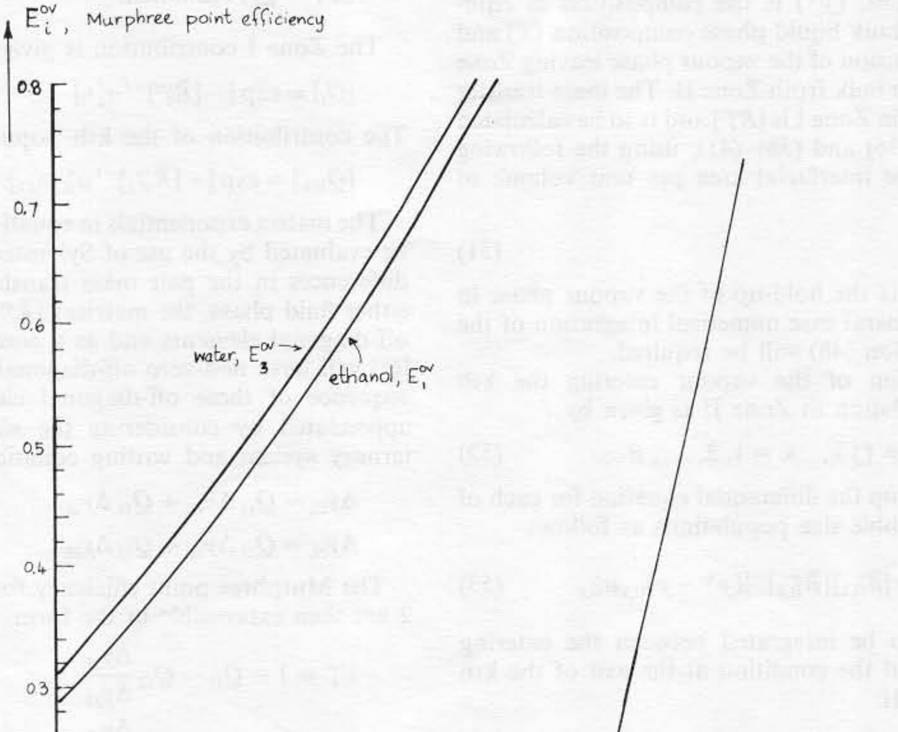

Figure 2. Murphree point efficiencies for the system ethanol (1)–tert butanol (2)–water (3) as a function of the Fourier number Fo_{II} in the bulk froth zone. The chosen conditions correspond to Run M46 of Krishna et al[2]. Mass transfer process is assumed to be gas phase controlled. $D_{ref} = 20\ \text{mm}^2\ \text{s}^{-1}$.

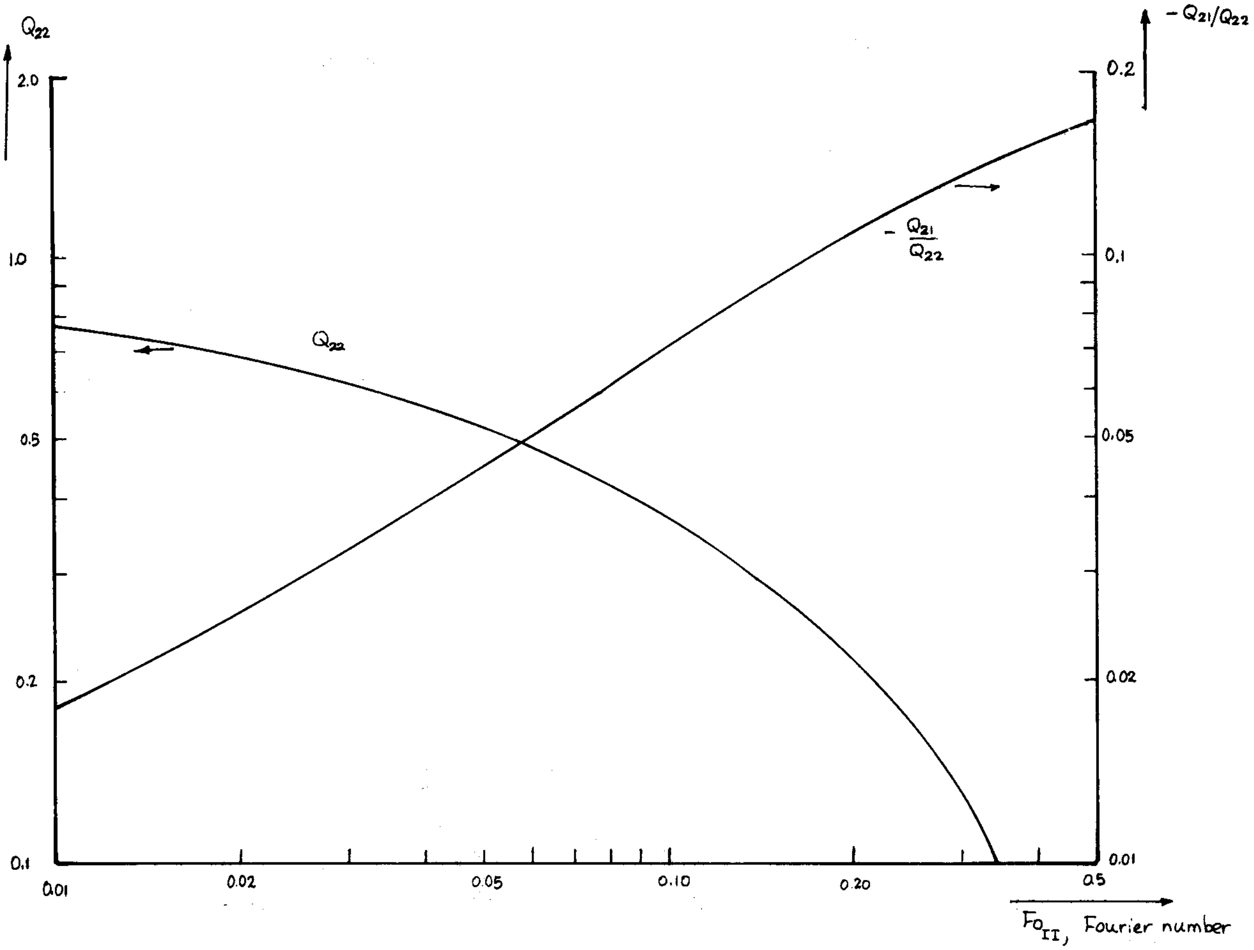

Figure 3. Variation of $-Q_{21}/Q_{22}$ and Q_{22} (elements of matrix $[Q]$) as function of the Fourier number Fo_{II} in the bulk froth zone. The chosen conditions correspond to Run M46 of [2]. The mass transfer process is assumed to be gas phase controlled. $Ð_{ref} = 20\,mm^2\,s^{-1}$.

The molar latent heats of vaporization of the three species are found to be $\lambda_1 = 38.7$ kJ/mol, $\lambda_2 = 39$ kJ/mol, $\lambda_3 = 40.6$ kJ/mol. These values are so close to each other that the bootstrap matrices $[\beta^v]$ and $[\beta^l]$ could be approximated by the identity matrix [I]. In the calculations to be presented the assumption of equimolar transfer was therefore adopted and the analytic relations (58)–(61) were used in the determination of the point efficiencies E_i^{ov}.

It is anticipated that most of the transfer process takes place in the bulk froth zone. Before attempting to use the complete two zone model, we shall first demonstrate some interesting features concerning the influence of the bubble sizes on the values of the component efficiencies. To do this we initially assume that the formation zone is of negligible importance and that the bulk froth zone consists of uniformly sized spherical bubbles. Further, anticipating the results to be presented later, we assume that the mass transfer process is completely controlled by the resistance in the vapour phase, i.e. $[\bar{R}^{ov}] = [\bar{R}^v]$. With the above set of assumptions, examination of the equations (42) and (61), shows that the component efficiencies are unique functions of Fo_{II}. Figure 2 shows the variation of E_i^{ov} with Fo_{II}. The components ethanol (1) and water (2) behave "normally" and the component efficiencies of these species increases with increasing Fo_{II}. The component tert butanol (2) on the other hand shows a completely different behaviour. As Fo_{II} is *increased* from 0.01 to 0.03, the efficiency E_2^{ov} *decreases* to a value of -0.15. Increase in Fo_{II} beyond 0.03 increases E_2^{ov} till at $Fo_{II} = 0.135$, the value of $E_2^{ov} = 0$. Beyond $Fo_{II} = 0.135$ the value of E_2^{ov} is positive and further increase in the Fourier number results in "normal" behaviour for tert butanol. At large values of Fo_{II}, equilibrium is attained and all the component efficiency values reach unity values. We see that even with the simplified model we are able to rationalize the observed negative E_2^{ov}. The decrease in E_2^{ov} between Fo_{II} of 0.01 and 0.03, however, deserves special comment and explanation. For small values of Fo_{II}, the mass transfer coefficient k_{ij}^v shows a square root dependence on the diffusivity. With increasing Fo_{II}, the dependence of k_{ij}^v on $Ð_{ij}$ approaches the linear (or "film model") limit. In other words, an increase in Fo_{II} results in an increasing dependence of the transfer coefficients on the pair $Ð_{ij}$; the differences in the pair $Ð_{ij}$ therefore become increasingly important and the off-diagonal elements Q_{12}, Q_{21} should show a corresponding increase, relative to the main diagonal elements Q_{11} and Q_{22}. Examination of equation (65) shows that an increase in the magnitude of Q_{21}, relative to Q_{22}, should decrease E_2^{ov}; this is in fact observed in Figure 2. To quantify the above explanation we plot $-Q_{21}/Q_{22}$ vs Fo_{II} in Figure 3 and note the increase in this ratio with increasing Fo_{II}. We are thus able to explain the behaviour exhibited below $Fo_{II} = 0.03$, for tert butanol. Why does E_2^{ov} *increase* beyond $Fo_{II} = 0.03$? The answer to this

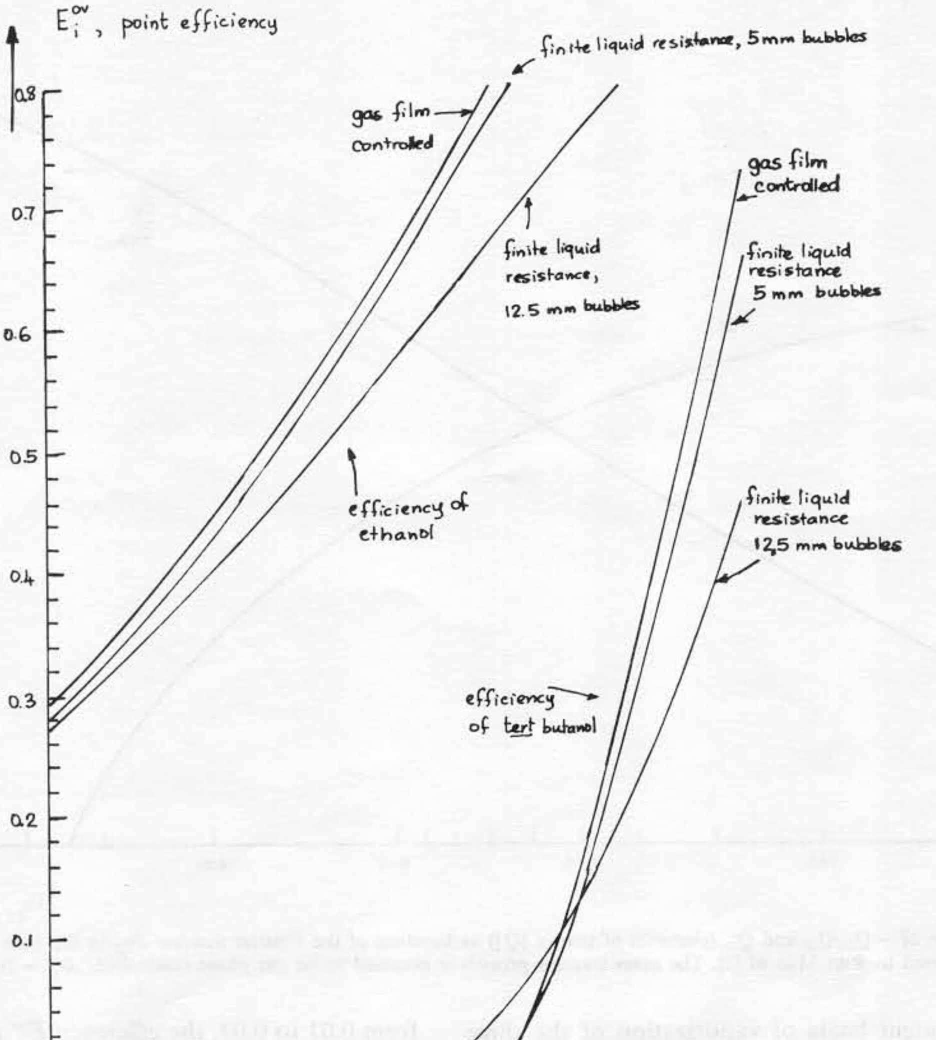

Figure 4. Influence of liquid phase mass transfer resistance on component efficiencies E_i^{ov}. Simulation of Run M46. $Ð_{ref} = 20\ mm^2\ s^{-1}$.

question is also to be found in Figure 3. As Fo_{II} is increased beyond 0.03, though $-Q_{21}/Q_{22}$ increases, there is a simultaneous decrease in Q_{22}. By a detailed examination of the values of Q_{22} and $-Q_{21}/Q_{22}$ it is found that the increase in $-Q_{21}/Q_{22}$ is slower than the corresponding decrease in Q_{22}. The efficiency E_2^{ov} therefore increases beyond $Fo_{II} = 0.03$. At $Fo_{II} = 0.135$ the efficiency $E_2^{ov} = 0$, a manifestation of the phenomenon of *diffusion barrier*[4,8]. Below $Fo_{II} = 0.135$, tert butanol may be said to exhibit the phenomenon of *reverse diffusion*[4,8]. For increasing values of Fo_{II}, the matrix $[Q]$ tends to the null matrix [0] and all the efficiencies will tend to unity; differences in component efficiencies become insignificant. Summarizing the conclusions of Figure 2, the influence of Fo_{II} on E_2^{ov} is characterized by two regimes; in the first regime, $0.01 < Fo_{II} < 0.03$, coupling effects increase in importance and the value of E_2^{ov} becomes increasingly negative. Beyond $Fo_{II} = 0.03$, the influence of coupling gradually decreases and tert butanol tends to exhibit "normal", binary-like behaviour.

Let us now examine two typical bubble size populations: (1) small bubbles of 5 mm diameter with a rise velocity of $0.3\ m\ s^{-1}$ and (2) large bubbles of 12.5 mm diameter with a rise velocity of $1.5\ m\ s^{-1}$. For a dispersion height $h_{II} = 75$ mm (estimated value for the experimental conditions), the corresponding Fourier numbers (taking the reference diffusivity value $Đ_{\text{ref}} = 20\ \text{mm}^2\ \text{s}^{-1}$) are 0.8 and 0.026 respectively. From Figure 2 it can be seen that the coupling effects will be minimal in a system consisting of small 5 mm bubbles, while for the 12.5 mm bubble size dispersion a negative efficiency will be experienced. To the knowledge of the author, this influence of bubble hydrodynamics has not thus far been appreciated in the chemical engineering literature. In actual practice there will be a bubble size distribution and the contributions of the individual bubble populations have to be weighted with the factors given by equation (56). The fast-rising bubble population will dominate the mass transfer characteristics of the system; typically this population transports 90% of the vapour mixture across the tray[11,15]. The small bubble population (say in the 2–5 mm range) do not contribute to the gas hold-up (and interfacial area) on the tray but this contribution is not wholly effective because this population transports only about 10% of the vapour mixture across the tray. This concept of "passive" and "active" gas hold-ups is also applicable to the description of bubble columns operating in the churn-turbulent regime[18,37] and the two-phase theory of fluidized beds[16] can be used to model such systems.

In the foregoing analysis we had assumed that the transfer process was completely controlled by the resistance in the vapour phase. Let us now examine the influence of the liquid side resistance on the component efficiencies, still considering only Zone II with uniform bubble sizes. The liquid phase mass transfer coefficient is calculated using equation (21). Since the contact time t_{II} is dependent on the rise velocity of the bubbles (cf. equation (44)), the liquid resistance is dependent on the particular bubble population assumed. Figure 4 summarises the results of the calculations for E_1^{ov} and E_2^{ov} for the small and large bubbles, 5 and 12.5 mm respectively. The influence of liquid resistance on the efficiency of ethanol, E_1^{ov}, follows our normal expectation; there is a slight resistance offered by 5 mm bubbles and a somewhat larger one offered by 12.5 mm bubbles. In both cases the efficiency E_1^{ov} is lowered due to the additional resistance considered. The situation is quite different when we consider the effect on tert butanol; for $Fo_{II} < 0.15$, the influence of the liquid resistance is to increase the efficiency of tert butanol. This un-binary like effect is due to the fact that in this particular Fourier regime, coupling effects reduce E_2^{ov} to low, negative, values and the effect of the liquid of the consideration of an additional mass transfer resistance in the liquid phase is to reduce the coupling effect (there are smaller differences in the pair $Đ_{ij}^{l}$ in the liquid phase than in the corresponding vapour phase $Đ_{ij}^{v}$). The net result of reduced coupling, quantified by a smaller $-Q_{21}/Q_{22}$, is to *increase* E_2^{ov}. Beyond $Fo_{II} = 0.2$, tert butanol exhibits "normal" behaviour and the liquid resistance serves to reduce the component efficiency.

Concluding Remarks

We have developed a model for the calculation of point efficiencies in multicomponent distillation from basic froth properties and diffusivity data on the binary pairs in the mixture. Some interesting differences between the transfer behaviour of multicomponent systems and a simple binary system have been underlined; such differences have hitherto not been mentioned in the chemical engineering literature. In the discussions we have pointed out the strong influence of the froth hydrodynamics on the extent of diffusional coupling exhibited by the system. We strongly believe that multicomponent distillation efficiencies can only be reasonably predicted on the basis of a proper hydrodynamic picture of the tray behaviour; in this connection we would suggest that "black box" type mass transfer models are unlikely to be adequate.

Though the model development has catered for non-equimolar transfer possibilities, caused by differences in component molar latent heats of vaporization, this aspect of the model has not been tested against experimental data; the system studied: ethanol–tert butanol–water displays equimolar transfer behaviour. Our previous calculations[20,21] have indicated that non-equimolar contributions could be important in some cases.

McEwan and Darton[1] state in their survey article "There is an extensive theoretical and academic literature on multi-component efficiency, and the gap between this and practicable design methods is one which urgently needs bridging." With the present publication, we have tried to bridge this "gap" and hope that the encouraging results obtained will spur the further development of the models and incorporation into routine design procedures for industrial columns.

SYMBOLS USED

a	interfacial area per unit volume of froth $[\text{m}^2\ \text{m}^{-3}]$
a'	interfacial area per unit volume of dispersed gas $[\text{m}^2\ \text{m}^{-3}]$
A	active bubbling area of tray $[\text{m}^2]$
b_i	"intercepts" in the linearized vapour–liquid equilibrium relationship [—]
B	number of bubble size populations [—]
$[B]$	inverted matrix of diffusion coefficients with elements B_{ij} given by equations (9) and (10) $[\text{m}^{-2}\ \text{s}]$
c_t	mixture molar density $[\text{kmol m}^{-3}]$
d	diameter of gas jet of spherical bubble [m]
$Đ_{ij}$	Maxwell-Stefan diffusion coefficient of pair i–j in multicomponent mixture $[\text{m}^2\ \text{s}^{-1}]$
$Đ_{\text{ref}}$	reference value of Maxwell-Stefan diffusivity; taken as $20\ \text{mm}^2\ \text{s}^{-1}$ in the calculations for the system ethanol–tert butanol–water $[\text{m}^2\ \text{s}^{-1}]$
E_i^{ov}	Murphree point efficiency (vapour phase) for component i [—]
f_k	fraction of vapour entering bulk froth free zone which is transported by the kth bubble size population [—]
Fo	Fourier number [—]
G_i	molar flow rate of component i in the vapour phase $[\text{kmol s} - 1]$
h	distance parameter measured from tray floor [m]
h_I	height of formation zone [m]
h_{II}	height of bulk froth zone [m]
$\bar{H}_i$	partial molar enthalpy of component i $[\text{J kmol}^{-1}]$
$[I]$	identity matrix with elements δ_{ik} [—]
j_m	roots of $J_0(j_m) = 0$ [—]
$J_0(\ )$	zero order Bessel function
k_{ij}	mass transfer coefficient of pair i–j in multicomponent mixture $[\text{m s}^{-1}]$
$[K^{eq}]$	Diagonal matrix of equilibrium K-values [—]
n	number of components in multicomponent mixture [—]
N_i	molar flux of component i across vapour–liquid interface $[\text{kmol m}^{-2}\ \text{s}^{-1}]$

N_t	mixture molar flux across vapour–liquid interface [kmol m^{-2} s^{-1}]
P_i^0	vapour pressure of component i [Pa]
P_t	total system pressure [Pa]
$[Q]$	matrix defined by equations (59)–(61) [—]
R	gas constant [8314.4 J kmol^{-1} K^{-1}]
$[R]$	matrix of inverted mass transfer coefficients [m^{-1} s]
t	contact time between vapour and liquid phases [s]
T	absolute temperature [K]
U_s	superficial vapour velocity based on active bubbling area [m s^{-1}]
U_I	absolute velocity of gas in jet in Zone I [m s^{-1}]
$U_{II,k}$	bubble rise velocity of kth population in Zone II [m s^{-1}]
x_i	mole fraction of component i in bulk liquid [—]
x_{ie}	mole fraction of component i at the interface in the liquid phase [—]
y_i	mole fraction of component i in bulk vapour [—]
y_{ie}	mole fraction of component i at the interface in the vapour phase [—]
y_i^*	vapour composition in equilibrium with the bulk liquid phase [—]
y_{iE}	composition of vapour entering tray [—]
y_{iL}	composition of vapour leaving tray [—]
Δy_{iE}	composition driving force $= y_i^* - y_{iE}$ [—]
Δy_{iL}	composition driving force $= y_i^* - y_{iL}$ [—]

Greek Letters

$[\beta]$	bootstrap matrix with elements given by equation (7) [—]
γ_i	activity coefficient of component i in liquid phase [—]
$[\Gamma]$	matrix of thermodynamic factors defined by equation (16) [—]
δ_{ik}	Kronecker delta [—]
ε	gas hold-up, i.e. fraction of dispersion occupied by gas [—]
λ_i	molar latent heat of vaporization of component i [J kmol^{-1}]
μ_i	molar chemical potential of species i [J kmol^{-1}]

Matrix Notation

( )	$n-1$ dimensional column matrix
[ ]	$n-1 \times n-1$ dimensional square matrix
$[\ ]^{-1}$	inverted matrix

Subscripts

I	referring to Zone I
II	referring to Zone II
II,k	referring to the kth bubble population in Zone II
e	referring to the interface
E	entering vapour mixture
L	vapour mixture leaving tray
n	nth component
T,p	gradient evaluated at constant temperature and pressure
t	referring to total mixture

Superscripts

l	liquid phase
v	vapour phase
ov	overall vapour phase parameter
0	infinite dilution parameter
—	overbar refers to composition averaged property
*	equilibrium value

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