TERNARY MASS TRANSFER IN A WETTED-WALL COLUMN. SIGNIFICANCE OF DIFFUSIONAL INTERACTIONS. PART II. EQUIMOLAR DIFFUSION

By **R. KRISHNA** (MEMBER), **R. M. SALOMO** and **M. A. RAHMAN**

Department of Chemical Engineering, University of Manchester Institute of Science and Technology, Manchester, England

One important and distinguishing feature of mass transfer in systems with three or more species, *i.e.* multicomponent systems, is the necessity of taking diffusional interaction, or coupling, effects into account in the calculation of interfacial mass transfer rates. A consequence of diffusional interaction effects in multicomponent distillation in a continuous contact (packed, wetted-wall *etc.*) column is that the constituent pseudo-binary heights of transfer units HTU_i in either fluid phase (vapour and liquid) will be unequal to one other, and so will be the overall parameters.

The objectives of the present communication were: (1) to determine the significance of diffusional interactions inasmuch as these affect the component heights of transfer units, and (2) to test the predictive capability of published multicomponent mass transfer models.

Experimental measurements for distillation of the system ethanol (1)–tert butanol (2)–water (3) were carried out in a 0.0556 m internal diameter wetted-wall column with a test section of height 1.013 m. The distillation runs were performed at total reflux and the vapour and liquid compositions entering and leaving the column, together with the corresponding temperatures, were measured. The mass transfer process was found to be vapour phase controlled. The calculated values of the pseudo-binary numbers of transfer units, NTU_{oyi}, for the three components were found to be significantly different from one another in most of the experimental runs. The relative values of the NTU_{oyi} were found to depend on the ratio of the mass transfer driving forces $\Delta y_1/\Delta y_2$, as anticipated by multicomponent mass transfer model formulations. For measured conditions at the bottom of the wetted-wall column the compositions at the top of the column were calculated using binary mass transfer correlations and a multicomponent film model. The model predictions for those runs in which the gas phase was in turbulent flow gave top compositions which agreed with the measured compositions to within the constraints imposed by the accuracy of the vapour–liquid equilibrium data fit and of the accuracy of experimental composition measurement.

The study confirmed the significance of diffusional interactions for the system studied, a typical non-ideal mixture. Further, the applicability of predictive multicomponent mass transfer models was established, at least for vapour phase mass transfer controlled distillations.

INTRODUCTION

Our overall objective is to determine the significance of diffusional interaction effects in chemical engineering practice. In the first paper in this series[1] we considered mass transfer between a ternary vapour (gas) phase and a binary liquid phase in which we had the situation of Stefan diffusion in the vapour phase. In the present communication we consider mass transfer during distillation of a ternary mixture where we approach conditions of equimolar diffusion (mass transfer) in both vapour and liquid phases. In common with the previous communication[1], the contacting apparatus chosen for study is a wetted-wall colum. The conclusions reached in this study can be expected to be relevant in the design of continuous contact multicomponent distillation columns, *e.g.* packed columns. Many of the mass transfer equations discussed earlier[1] are also applicable to the distillation case under study; some of these relations will also be discussed in the present communication in the interests of completeness and clarity. As far as possible the same, or complementary, notation is used here. We have previously reviewed the theory of multicomponent mass transfer and its application to distillation [2, 3] and therefore no literature survey is presented here; also the present authors are unaware of any new publications in this area since the publication of our extensive review[2]. The work reported here forms part of a comprehensive experimental programme of research on separation processes initiated by the late Professor George Standart at the University of Manchester Institute of Science and Technology.

Before describing the experimental work performed, we discuss the underlying theory which will be used later to analyse the experimental results. Our experiments were chosen to check specific conclusions of this theory.

THEORETICAL ANALYSIS

Consider distillation of an *n*-component mixture at total reflux in a wetted-wall column, pictured schematically in Figure 1. The material balance for the *i*th component in the vapour phase can be written as[1–5]:

$$\frac{dG_i}{d\xi} = -N_i a A_c Z, \quad i = 1, 2, \cdots, n \tag{1}$$

where G_i is the molar flow rate of the component *i*; N_i is the molar flux (in a stationary coordinate reference frame), considered positive for transfer from vapour to liquid phase; a is the interfacial area for mass transfer per unit volume of the apparatus; Z is the total column height; ξ is the fractional distance measured from the bottom of the column ($\xi = 0$, bottom, subscript B; $\xi = 1$, top, subscript T). A_c is the cross-sectional area available for flow of phases.

We shall further assume that conditions of equimolar diffusion prevail during the distillation operation. The constraint of equimolar diffusion results in constant

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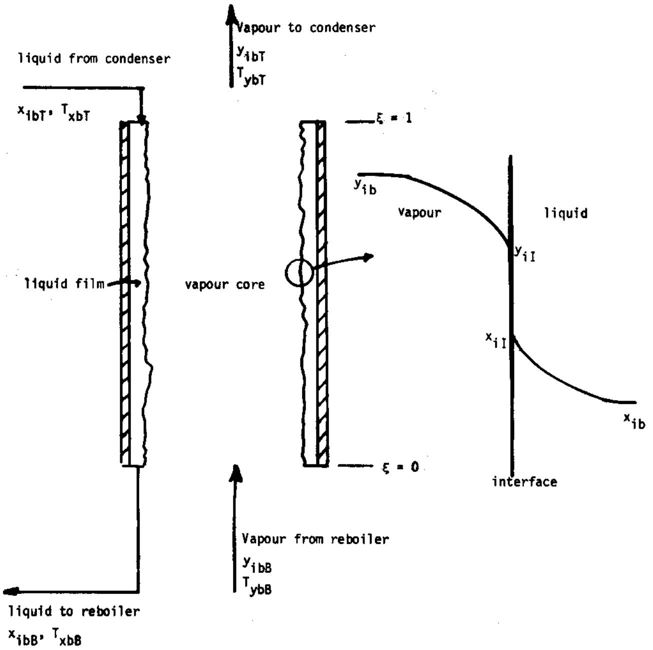

Figure 1. Schematic diagram of wetted-wall column together with sketch of composition profiles in the region of the interface.

molar flows of the gas and liquid phases and is valid for the case in which the molar latent heats of vaporization of the constituent species are equal (or nearly equal) to one another and there is no large temperature difference between the vapour and liquid phases[4]. Thus we have

$$N_t = \sum_{i=1}^{n} N_i = 0; \quad G_t = \sum_{i=1}^{n} G_i = \text{constant}$$
$$L_t = \sum_{i=1}^{n} L_i = \text{constant} \tag{2}$$

For total reflux conditions we have further

$$L_t = G_t; \quad y_{ib\xi} = x_{ib\xi}, \quad i = 1, 2, \ldots, n-1 \tag{3}$$

i.e. equality of vapour and liquid flows and bulk phase mole fractions at any position.

The interfacial mass transfer rate relations must properly be written in terms of the diffusion fluxes J_i, with respect to the molar average reference velocity[2]; for equimolar diffusion $J_i \equiv N_i$ and we may write the rate relations in terms of the overall driving forces $y_{ib} - y_i{}^* \equiv \Delta y_i$ as

$$(N) = [K_{oy}](\Delta y) = [K_{oy}](y_b - y^*) \tag{4}$$

where $[K_{oy}]$ is the matrix of overall mass transfer coefficients; $y_i{}^*$ is the composition in equilibrium with the bulk liquid phase x_{ib}. Combining equation (4) with (1) and (2) we obtain

$$\frac{d(y_b)}{d\xi} = -[NTU_{oy}](y_b - y^*) = -[NTU_{oy}](\Delta y) \tag{5}$$

where we have further defined a matrix of overall vapour phase number of transfer units:

$$[NTU_{oy}] \equiv \frac{[K_{oy}]\, aA_c Z}{G_t} \tag{6}$$

If both the partial matrices of coefficients $[k_y]$ and $[k_x]$ are defined in terms of the generalized Maxwell–Stefan diffusion coefficients, then Krishna[6] has shown that a simple addition of resistances formula results

$$[NTU_{oy}]^{-1} = [NTU_y]^{-1} + \lceil S_\rfloor [NTU_x]^{-1} \tag{7}$$

where $\lceil S \rfloor$ is the diagonal matrix of stripping factors

$$S_i \equiv K_{eqi}\, G_t/L_t, \quad i = 1, 2, \ldots., n \tag{8}$$

where K_{eqi} are the equilibrium K-values.

The procedure for estimating the elements of $[NTU_y]$ and $[NTU_x]$ from information on pure component and constituent binary pair transport properties is discussed in Appendix I.

The matrix $[NTU_{oy}]$ is generally non-diagonal (*i.e.* $NTU_{oy12} \neq 0$; $NTU_{oy21} \neq 0$), except for thermodynamically ideal systems made up of molecules of similar size (molecular weight), shape, polarizability, hydrogen bonding characteristics, *etc.*

Another way of writing the mass transfer rate relations (4) is to adopt a pseudo-binary formulation, *i.e.* in which the rate of transfer of component i is taken to be proportional to its own intrinsic driving force, thus:

$$N_i = \grave{K}_{oyi}(y_{ib} - y_i{}^*) = \grave{K}_{oyi}\,\Delta y_i, \quad i = 1, 2, \cdots, n \tag{9}$$

in which case the differential mass balance relations take the form:

$$\frac{dy_{ib}}{d\xi} = -N\grave{T}U_{oyi}\,\Delta y_i, \quad i = 1, 2, \cdots, n \tag{10}$$

where $N\grave{T}U_{oyi}$ are pseudo-binary overall number of vapour phase transfer units. We may combine equations (5) and (10) to relate the pseudo-binary $N\grave{T}U_{oyi}$ to the elements of $[NTU_{oy}]$, thus we obtain:

$$N\grave{T}U_{oy1} = NTU_{oy11} + NTU_{oy12}\frac{\Delta y_2}{\Delta y_1} \tag{11}$$

$$N\grave{T}U_{oy2} = NTU_{oy22} + NTU_{oy21}\frac{\Delta y_1}{\Delta y_2} \tag{12}$$

and

$$N\grave{T}U_{oy3} = \frac{\Upsilon\, N\grave{T}U_{oy1} + N\grave{T}U_{oy2}}{\Upsilon + 1} \tag{13}$$

where $\Upsilon = \Delta y_1/\Delta y_2$, is the ratio of mass transfer driving forces, which of course changes along the column; the relations (11) to (13) are therefore strictly applicable to a differential section of the column height.

It should be clear from equations (11) to (13), that the pseudo-binary numbers of transfer units $N\grave{T}U_{oyi}$ will not only depend on the system properties but also on the ratio of driving forces Υ, which further depends on the region of operation in the composition diagram. Consider $N\grave{T}U_{oy1}$; the cross-coefficient NTU_{oy12} is usually about 10 to 20% of the main coefficient $N\grave{T}U_{oy11}$ but this small cross-coefficient may be multiplied with a large ratio $1/\Upsilon$ to lead to significant contribution of the second term on the right hand side of equation (11). This latter contribution is due to diffusional interactions because for a system with similar values of the diffusion coefficients in either fluid phase, the coefficient NTU_{oy12} (as also NTU_{oy21}) will be zero and there will be no diffusional interactions. When

$\Upsilon = 0.1$, for example, the contributions of both terms on the right-hand side of equation (11) would be about equal, resulting in a significant contribution due to diffusional interactions. It should be borne in mind that Υ can be of either sign and have a large or small absolute value. Thus it is easy to see that the pseudo-binary numbers of transfer units can differ from one another to a significant extent. Krishna *et al*[3] performed experiments with the system ethanol (1)–tert butanol (2)–water (3) in a sieve tray column to illustrate the dramatic effects of diffusional interactions; in the experiments the Murphree point efficiency of tert butanol exhibited values greater than unity, and negative values. Negative point efficiencies are obtained when the diffusional interactional contribution acts in a 'direction' opposite to the main, or diagonal, contribution, and is of a larger magnitude than the main contribution. In a continuous contact distillation column here under consideration, the contributions due to diffusional interactions, *i.e.* $NTU_{oyij}\,\Delta y_j/\Delta y_i$, $i \neq j$, would lead to differences in the pseudo-binary heights of transfer units.

The above discussion serves to specify the objectives of the present communication, these are:

(1) To determine the significance of diffusional interactions during the distillation of a ternary mixture in a continuous-contact column (here a wetted-wall column); specifically to verify the dependencies of the pseudo-binary NTU_{oyi} on the ratio of driving forces Υ

(2) To test the accuracy of a multicomponent mass transfer model[6] for the prediction of the matrix $[NTU_{oy}]$.

The system chosen for experimental study was ethanol–tert butanol–water, used earlier in distillation experiments in a sieve tray column[3]. These experiments showed large diffusional interaction contributions and it is interesting to check whether such effects can also be detected in a different contacting apparatus, chosen in this study to be a wetted-wall colunn.

EXPERIMENTAL

The experimental unit used in the study was a 0.0556 m internal diameter wetted-wall column with a test section of height 1.013 m. The wetted-wall column was initially designed to study the influence of thermal diffusion effects in vapour–liquid mass transfer and to this end the column is equipped with a central heating rod of outer diameter 0.0254 m for the purposes of imposing a temperature gradient across the vapour–liquid interface. For the purposes of the work to be reported here, the central heating rod was not switched on and the distillation of the mixture ethanol–tert butanol–water was carried out adiabatically. Figure 2 shows a diagrammatic representation of the experimental unit, described in details in the theses of Tavana[19] (who studied thermal diffusion) and Salomo[17] and Rahman[18] (who both carried out ternary distillation runs). The experimental data reported in this paper are those obtained and reported in the thesis of Salomo[17]. We give below a brief description of the experimental unit and operating procedure; the interested reader will find further details elsewhere[17–19].

A constant head tank provides process liquid to the column. The flow rate of this reflux is controlled by a needle valve below rotameter R_1 in Figure 2. The flow is measured by this rotameter and the liquid heated to the desired pre-established temperature by means of an electric heating tape wound round the flow line. The process liquid is then introduced as a uniform film at the top of the column through a porous ring, The interior surface of the column was specially treated to promote wetting of the column by the test mixture[19] and visual observations confirmed that wetting was indeed established[19]. After passing down the column, the process liquid is collected at the bottom of the test section in a collecting dish, passed through a cooler in order to have its flow rate metered by a rotameter R_3 at the temperature of calibration and returned to the reboiler.

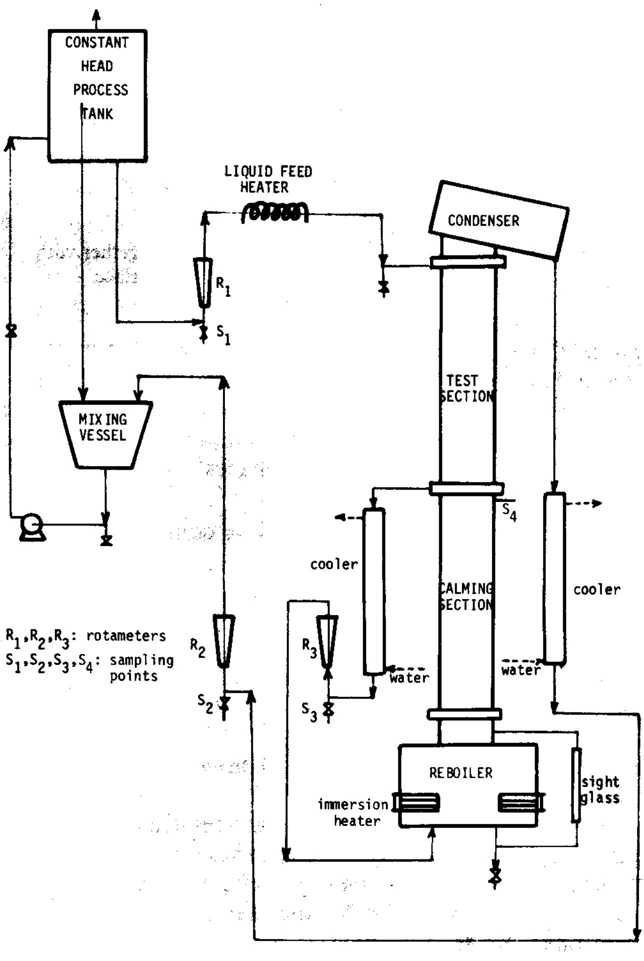

Figure 2. Diagram of experimental apparatus.

Saturated vapour produced in the reboiler is first passed through a calming section to minimize entrainment, then it proceeds to the test section where it contacts the falling liquid film. The outcoming vapour is condensed and cooled to permit flow measurement at rotameter R_2, before flowing into the mixing vessel which assists in keeping a constant reflux head. This is done by a process liquid circulating pump, fed by the mixing vessel, which raises liquid to the constant head tank. The overflow from this tank is returned to the mixing vessel.

Copper-constantan thermocouples were used to measure the following temperatures: (1) inlet temperature of liquid film (T_{bxT}), (2) outlet temperature of liquid film

Table 1. Experimental data and calculated values of pseudo-binary numbers of transfer units

Run No.	Bulk vapour compositions				Vapour phase driving forces				Ratios of $\Delta y_1/\Delta y_2$		Number of transfer units (pseudo-binary		
	Bottom		Top		Bottom		Top		Bottom	Top			
	y_{1b}	y_{2b}	y_{1b}	y_{2b}	$-\Delta y_1$	$-\Delta y_2$	$-\Delta y_1$	$-\Delta y_2$	$\Delta y_1/\Delta y_2$	$\Delta y_1/\Delta y_2$	$N\grave{T}U_{oy1}$	$N\grave{T}U_{oy2}$	$N\grave{T}U_{oy3}$
1	0.1617	0.2105	0.2115	0.2907	0.0617	0.1372	0.362	0.0676	0.4494	0.5359	1.054	0.825	0.899
2	0.0538	0.0413	0.1466	0.1980	0.1215	0.2359	0.0647	0.1553	0.5152	0.4166	1.033	0.733	0.821
3	0.1981	0.3196	0.2224	0.3570	0.0289	0.0168	0.0215	0.0337	0.4676	0.6373	0.975	0.813	0.868
4	0.2025	0.3167	0.2223	0.3518	0.0296	0.0608	0.0224	0.0359	0.4872	0.6241	0.769	0.747	0.754
5	0.2708	0.2524	0.3018	0.2835	0.0464	0.0528	0.0338	0.0290	0.8774	1.1676	0.783	0.789	0.785
6	0.2687	0.2451	0.3019	0.2783	0.0492	0.0564	0.0353	0.0307	0.8725	1.1498	0.797	0.792	0.793
7	0.2505	0.2184	0.2929	0.2587	0.0615	0.0749	0.0423	0.0409	0.8217	1.0330	0.831	0.723	0.744
8	0.2313	0.1875	0.2831	0.2408	0.0781	0.0959	0.0496	0.0512	0.8143	0.9700	0.832	0.755	0.790
9	0.2078	0.1648	0.2690	0.2284	0.0916	0.1175	0.0559	0.0620	0.7793	0.9019	0.854	0.738	0.790
10	0.1862	0.1405	0.2555	0.2128	0.1070	0.1385	0.0639	0.0740	0.7723	0.8628	0.836	0.706	0.764
11	0.1359	0.0868	0.2344	0.1897	0.1426	0.1801	0.0768	0.0933	0.7918	0.8227	0.934	0.770	0.842
12	0.1557	0.3845	0.1696	0.4179	0.0163	0.0535	0.0127	0.0314	0.3053	0.4056	0.965	0.811	0.849
13	0.1502	0.3900	0.1620	0.4207	0.0154	0.0537	0.0123	0.0336	0.2867	0.3647	0.859	0.720	0.753
14	0.1467	0.3938	0.1585	0.4256	0.0148	0.0537	0.0117	0.0330	0.2752	0.3529	0.899	0.752	0.786
15	0.1401	0.3935	0.1534	0.4268	0.0145	0.0573	0.0114	0.0349	0.2527	0.3271	1.035	0.742	0.806
16	0.1341	0.3667	0.1482	0.4125	0.0175	0.0746	0.0127	0.0439	0.2351	0.2994	0.946	0.796	0.827
17	0.1137	0.2744	0.1423	0.3598	0.0320	0.1423	0.0191	0.0734	0.2251	0.2599	1.161	0.830	0.894
18	0.0645	0.1125	0.1234	0.2906	0.0713	0.2773	0.0299	0.1250	0.2571	0.2391	1.283	0.924	0.993
19	0.4068	0.2184	0.4338	0.2224	0.0395	0.0135	0.0333	0.0057	2.9210	5.8576	0.744	0.447	0.681
20	0.3571	0.1946	0.3893	0.2177	0.0590	0.0345	0.0430	0.0187	1.7088	2.3055	0.644	0.901	0.727
21	0.3429	0.1933	0.3779	0.2172	0.0623	0.0400	0.0453	0.0222	1.5591	2.0379	0.659	0.795	0.707

(T_{bxB}), (3) temperature of vapour entering test section (T_{byB}), (4) temperature of vapour leaving test section (T_{byT}), (5) wall temperature at bottom of test section and (T_{wB}), and (6) wall temperature at top of test section (T_{wT}).

After considerable care to ensure that steady-state operation was achieved samples of both vapour and liquid were taken at the top and bottom of the test section and these were analysed by means of a gas chromatograph (Model 900, Perkin Elmer Ltd). The mole fractions of mixtures of unknown composition could be determined with an accuracy of ± 0.002; see El-Yafi *et al*[16] and Salomo[17] for further details on error analysis. The top and bottom liquid and vapour compositions measured agreed with the total reflux constraint $y_{ib\xi} = x_{ib\xi}$ to within the limits of the accuracy of the composition determination in all but one (Run 1) of the 21 runs obtained by Salomo[17]. Therefore arithmetic average values of the top compositions and bottom compositions were used in further analysis; these are reported in Table 1.

The vapour–liquid equilibrium data, required in analysing the mass transfer behaviour of the system, was also measured independently in our laboratories at Manchester with the same gas chromatograph used in the composition determinations. The VLE data have been reported elsewhere[16] and the correlation of the activity coefficients used in the present communication is summarized in Appendix II. The accuracy of the fit of the experimental vapour–liquid equilibrium data in terms of average deviations from measured mole fractions are:

ethanol: 0.00277; tert butanol: 0.00168; water: 0.00381.

EXPERIMENTAL RESULTS AND DISCUSSION

With the correlated equilibrium data, the driving forces Δy_i at the top and bottom of the column, together with the ratio $\Delta y_1/\Delta y_2$ can be calculated and these are given in Table 1 for the 21 runs. Also presented in Table 1 are the values of the pseudo-binary numbers of overall vapour phase transfer units calculated from the three components in the mixture according to the integrals (compare with equation 10):

$$N\grave{T}U_{oyi} = -\int_{y_{ibB}}^{y_{ibT}} \frac{dy_{ib}}{y_{ib} - y_i^*}, \quad i = 1, 2, 3 \tag{14}$$

The integrations were performed numerically with the assumption of linear variation of y_{ib} along the column from bottom (subscript B, $\xi = 0$) to top (subscript T, $\xi = 1$).

Various other details with respect to measured temperatures and flows are available elsewhere[17] and are not given here.

A cursory examination of the $N\grave{T}U_{oyi}$ values for the three components shows that for most of the runs these values are significantly different from one another, pointing qualitatively to significant diffusional interaction effects. Another feature of the values of the pseudo-binary numbers of transfer units is the wide range of values obtained for components 1 and 2:

$$0.640 < N\grave{T}U_{oy1} < 1.283; \quad 0.447 < N\grave{T}U_{oy2} < 0.924 \tag{15}$$

The relative values of $N\grave{T}U_{oy1}$ and $N\grave{T}U_{oy2}$ appears at first sight at Table 1 to be dependent on the ratio of driving forces $\Upsilon = \Delta y_1/\Delta y_2$, as anticipated by the multicomponent mass transfer model formulation; see equations (11) to (13). To check whether the trends obtained experimentally correspond to those anticipated by coupled mass transfer models, we need to predict the values of the elements of $[NTU_{oy}]$; the procedure for estimating these elements is outlined in Appendix I and illustrated in particular for Run 21. The estimation procedure is applicable for turbulent flow of the gas phase. Turbulent flow conditions were maintained in all but three of the runs reported in Table 1; the exceptional cases are Run 2 ($Re_g = 2070$), Run 11 ($Re_g = 2051$) and Run 18 ($Re_g = 1983$). These three runs were all performed in the water rich region and are excluded from the analysis given below.

For all the runs, excluding 2, 11 and 18, the mass transfer process was estimated to be vapour phase controlled; this is a happy circumstance because of the many uncertainties in the estimation of the diffusion coefficients in the liquid phase and the corresponding mass transfer coefficients; the gas phase parameters are however more reliably estimated. It was assumed in the quantitative analysis that $[NTU_{oy}] = [NTU_y]$ and the addition of resistances formula (7) was not used; see Appendix I for a discussion on this point. Table 2 gives the estimated values of the matrix $[NTU_{oy}]$ for the runs in which we have turbulent vapour flow; these values correspond to conditions prevailing at the bottom of the column.

Examination of Table 2 shows that the matrix $[NTU_{oy}]$ is typically:

$$[NTU_{oy}] \simeq \begin{bmatrix} 0.7 & 0.1 \\ 0.1 & 0.7 \end{bmatrix} \tag{16}$$

We may therefore draw the following conclusions on the basis of equations (11) to (13):

(1) When $\Upsilon \simeq 1$, then we must expect $N\grave{T}U_{oy1} \simeq N\grave{T}U_{oy2} \simeq N\grave{T}U_{oy3}$. This is experimentally found to be the case for Runs 5 and 6 (see Table 1).

(2) When $\Upsilon| < 1$, then $N\grave{T}U_{oy1} > N\grave{T}U_{oy3} > N\grave{T}U_{oy2}$. This is experimentally verified for the Runs 1, 3, 4, 7 to 17.

(3) When $\Upsilon > 1$, then $N\grave{T}U_{oy1} < N\grave{T}U_{oy3} < N\grave{T}U_{oy2}$. This is experimentally verified for the Runs 20 and 21.

Run 19, however, does not seem follow the expectation (3) above; this may be due to the small value of Δy_2 at the top of the column (-0.0057) and the consequent sensitivity of $N\grave{T}U_{oy2}$ to even a small error in the determination of the driving force Δy_2. In other words, it may be that the observed trend $N\grave{T}U_{oy1} > N\grave{T}U_{oy3} > N\grave{T}U_{oy2}$ is not significant.

Let us further illustrate the importance of diffusional interaction phenomena by considering the specific example of Run 17. From Table 2 we note that the elements of $[NTU_{oy}]$ calculated at the bottom of the column are

$$[NTU_{oy}] = \begin{bmatrix} 0.6567 & 0.0509 \\ 0.1068 & 0.6687 \end{bmatrix} \tag{17}$$

Further the column matrix of driving forces at the bottom

Table 2. Estimations of the elements of $[NTU_{oy}]$ using multicomponent mass transfer model. Also given are deviations of predicted top vapour compositions for the three components from the experimentally determined values

	Elements of matrix $[NTU_{oy}]$				Deviation i = (predicted y_{iT}) − (experimental y_{iT})		
Run No.	NTU_{oy11}	NTU_{oy12}	NTU_{oy21}	NTU_{oy22}	dev 1	dev 2	dev 3
1	0.6844	0.0765	0.0873	0.6505	−0.00776	−0.00752	0.01527
3	0.7056	0.0863	0.1120	0.6935	−0.00226	−0.00118	0.00343
4	0.7016	0.0875	0.1100	0.6867	0.00260	0.00028	−0.00288
5	0.7326	0.1195	0.0892	0.6653	0.00318	−0.00095	−0.00223
6	0.7393	0.1203	0.0882	0.6693	0.00318	−0.00102	−0.00217
7	0.7149	0.1122	0.0803	0.6438	0.00100	0·00045	−0.00145
8	0.6985	0.1058	0.0726	0.6240	0.00087	−0.00317	0.00230
9	0.6838	0.0979	0.0680	0.6108	−0.00148	−0.00378	0.00526
10	0.6631	0.0903	0.0622	0.5909	−0.00242	−0.00394	0.00636
12	0.7016	0.0676	0.1336	0.7302	−0.00080	−0,00041	0.00121
13	0.6892	0.0642	0.1334	0.7216	0.00043	0.00211	−0.00254
14	0.6882	0.0627	0.1346	0.7233	−0.00003	0.00106	−0.00103
15	0.6859	0.0599	0.1351	0.7238	−0.00173	0.00170	0.00003
16	0.6774	0.0575	0.1279	0.7090	−0.00038	0.00169	0.00207
17	0.6567	0.0509	0.1068	0.6687	−0.00601	−0.00841	0.01442
19	0.8099	0.1812	0.0753	0.6725	0.00334	0.00434	−0.00768
20	0.7534	0.1553	0.0670	0.6308	0.01004	−0.00386	−0.00618
21	0.7444	0.1492	0.0670	0.6271	0.00915	−0.00189	−0.00726

of the column are given in Table 1 as

$$(\Delta y) = -\begin{pmatrix} 0.0320 \\ 0.1423 \end{pmatrix} \tag{18}$$

If we apply the differential equation (5) to a small increment of the column we obtain the change in the composition dy_1 of component 1 up the column as

$$\begin{aligned} \frac{\mathrm{d}y_1}{\mathrm{d}\xi} &= (0.6567)(0.0320)+(0.0509)(0.1423) \\ &= 0.0210+0.0072 = 0.0282 \end{aligned} \tag{18}$$

The contribution of the term

$NTU_{oy12}\,\Delta y_2$ is $(0.0072/0.0282) = 25\%$

of the total change $\mathrm{d}y_1/\mathrm{d}\xi$ despite the fact that the ratio $NTU_{oy12}/NTU_{oy11} = (0.0509/0.6567)$ is only about 8%. In other words, we should not ignore the presence of cross-coefficients in the matrix $[NTU_{oy}]$ just because they happen to be a small percentage of the main coefficients; these small cross-coefficients may be multiplied by a (relatively) large driving force to given an enhanced diffusional interaction effect. In the case considered above, diffusional coupling enhances the separation of component 1 by 25%. The overall effect is that the measured pseudo-binary numbers of transfer units show that $N\hat{T}U_{oy1} > N\hat{T}U_{oy3} > N\hat{T}U_{oy2}$.

The conclusion to be drawn from the qualitative analysis so far of the experimental results is that the relative trends in the values of the pseudo-binary $N\hat{T}U_{oyi}$'s are explainable in terms of a non-diagonal matrix of overall number of transfer units $[NTU_{oy}]$. A more stringent test would be to use the multicomponent mass transfer model to predict the composition profiles in the column.

For experimentally determined compositions of the vapour and liquid at the bottom of the column (recall that $x_{ibB} = y_{ibB}$ at total reflux), the differential equations (5) were integrated along the length of the column to predict the compositions at the top ($\xi = 1$). A finite difference approximation was used in the integration procedure with ten equal increments, *i.e.* $\Delta\xi = 0.1$; constant values of $[NTU_{oy}]$ and y_i^* were used within each increment. Table 2 gives the deviations in the compositions of the three components at the top of the column (deviation i = (predicted y_{iT}) − (experimental y_{iT})).

A cursory examination of the deviations of the three components from experimental values shows for each component there are both positive and negative deviations; there appears to be no bias in the predicted values of NTU_{oyij}, *i.e.* these coefficients are neither on the high or low side. The average absolute deviations for the three component are

ethanol	0.00315
tert butanol	0.00265
water	0.00465

Bearing in mind that the composition measurements are accurate to within ±0.002 and that the average deviations for the vapour–liquid equilibrium data fitting are, respectively, 0.00277, 0.00168 and 0.00381, it may be concluded that the predictions of the top vapour compositions using the multicomponent mass transfer model are within the accuracy of the VLE fit and accuracy of the composition measurements.

One aspect ignored in the analysis presented above is the influence of Marangoni instabilities. Since the transfer process is gas film controlled, the influence of Marangoni instabilities will be to alter the interfacial area available for transfer; such effects will alter the individual numbers of transfer units $N\hat{T}U_{oyi}$ to the same extent and will not alter the conclusion reached regarding the significance of diffusional interactions leading to differences in individual $N\hat{T}U_{oyi}$'s. It is not known to what extent they would alter the conclusion reached regarding the accuracy of multicomponent transfer models.

CONCLUSIONS

The following conclusions may be drawn from the experimental study and analysis in the foregoing:

(1) For the system ethanol (1)–tert butanol (2)–water (3), diffusional interactions are present to a significant extent; these interaction, or coupling, effects manifest themselves in the fact that the experimentally determined pseudo-binary numbers of transfer units $N\grave{T}U_{oyi}$ (or equivalently the pseudo-binary heights of transfer units $H\grave{T}U_{oyi}$) are significantly different from one another. The relative trends in the values of the $N\grave{T}U_{oyi}$'s can be predicted by utilising a matrix of overall number of transfer units $[NTU_{oy}]$, which includes non-diagonal elements. These non-diagonal elements NTU_{oyij} $(i \neq j)$ are essential in the interpretation of the measured data; without these coefficients, the observed dependence of the values of $N\grave{T}U_{oyi}$ on the ratio of driving forces Υ cannot be explained.

(2) The multicomponent mass transfer model used for estimating the elements of $[NTU_{oy}]$ predicts the outlet compositions to within the constraints set by the accuracy of the vapour–liquid equilibrium data fit and by the accuracy of the experimental composition determination. It appears therefore that the suggested model can be used in the design of multicomponent distillation columns provided the mass transfer is vapour phase controlled. There is dearth of experimental multicomponent distillation data for systems with mass transfer controlled by the liquid phase. It is recommended that such studies be initiated so that the published models[4, 6] can be tested, and, if proven satisfactory, be incorporated into standard design procedures.

(3) A final conclusion to be drawn from the study is the unsuitability of pseudo-binary parameters, such as $N\grave{T}U_{oyi}$, to describe system behaviour because of their odd dependence on the system driving forces, and hence on the operating conditions. These coefficients would defy simple correlation with system thermodynamic and transport properties. This conclusion agrees with the conclusions of our previous experimental study[3] in which it was shown that the Murphree point efficiency, $\grave{E}_{oyi}$, which is also a pseudo-binary parameter, showed very odd driving force dependencies. These efficiencies displayed values ranging from $-\infty$ to $+\infty$, with little or no change in the system hydrodynamics. In common with the $N\grave{T}U_{oyi}$ these pseudo-binary efficiencies would defy a simple correlation with system properties.

Finally, it may be remarked that with the evidence presented in this communication together with the previous one[1], the validity of predictive mass transfer models for multicomponent systems have been established for both Stefan diffusion and equimolar diffusion. Further experimental investigations should be carried out for conditions for which neither of the two constraints hold; specifically it would be interesting to look at reacting systems for which coupling effects can be expected to be very large[2].

APPENDIX I

Estimation of the Matrix of Overall Number of Transfer units $[NTU_{oy}]$

In order to calculate the number of overall vapour phase transfer units $[NTU_{oy}]$ it is first required to estimate the values of the matrices $[NTU_y]$, $[NTU_x]$ and $[S]$. We consider these in turn. The model used for the determination of the partial vapour and liquid phase transfer units is the one given by Krishna[6] and below we present only an outline of the final procedure; the reader is referred to the original reference for derivations and background. The calculations are illustrated by considering Run 21 in detail.

Estimation of $[NTU_y]$

(1) The binary pair diffusivities of 1–2, 1–3 and 2–3 are first estimated at the temperature prevailing in the vapour phase. In most of the experimental runs the vapour temperature was around 80 °C. At this temperature the pair diffusivities for ethanol (1)–tert butanol (2)–water (3) are estimated from the method of Fuller, Schettler and Giddings[7] as

$$\mathscr{D}_{12} = 7.99\ \text{mm}^2\ \text{s}^{-1}; \quad \mathscr{D}_{13} = 21.4\ \text{mm}^2\ \text{s}^{-1}; \quad \mathscr{D}_{23} = 16.5\ \text{mm}^2\ \text{s}^{-1}$$

The above values were used for all runs because the binary pair diffusivities are composition independent.

(2) The next step is to estimate the gas phase viscosity. We use the formula for the mixture viscosity:

$$\mu_g = \frac{\sum_{i=1}^{3} y_i M_i^{\frac{1}{2}} \mu_{gi}}{\sum_{i=1}^{3} y_i M_i^{\frac{1}{2}}} \tag{I.1}$$

The pure component viscosities μ_{gi} were estimated at 80 °C to be $\mu_{gi} = 9.7\ \mu\text{Pa s}$; $\mu_{g2} = 8.9\ \mu\text{Pa s}$; $\mu_{g3} = 11.0\ \mu\text{Pa s}$. For each run the mixture viscosity was estimated at the arithmetic average of the top and bottom compositions. For Run 21, for example, the mixture viscosity was calculated to be 9.85 μPa s.

(3) The molar gas density at a temperature of 80 °C and at the arithmetic averaged composition between top and bottom of the column can be calculated using the ideal gas law. The gas phase Reynolds number can then be calculated using the equivalent diameter of the wetted-wall column. Thus with $d_{eq} = 0.044$ m; $G_t = 51.9\ \text{mmol s}^{-1}$ (Run 21) we calculate the gas phase Reynolds number: $Re_g = 3859$.

(4) The cross-sectional area available for flow is $A_c = \pi(d_2{}^2 - d_1{}^2)/4$ where d_2 the inner diameter of the wetted-wall column = 0.0556 m and d_1 the outer diameter of the central heating rod (unused in the experiments) = 0.0254 m. The equivalent diameter for flow of the phases (vapour and liquid) is $(d_2{}^2 - d_1{}^2)/d_2 = 0.044\ \text{m} = d_{eq}$. The interfacial area per unit volume of column is given by $a = 4/d_{eq}$. The total length of the test section $Z = 1.013$ m.

(5) The number of partial vapour phase transfer units of the binary pairs 1–2, 1–3 and 2–3 can be estimated by using the usual correlation for the Sherwood number:

$$Sh_g = 0.023 Re_g{}^{0.83} Sc^{0.44} \tag{I.2}$$

and we obtain for the pair $i-j$

$$\mathcal{NTU}_{yij} = 0.023 Re_g^{0.83}\, Sc_{ij}^{0.44} \frac{\text{Đ}_{yij}\, a A_c Z}{d_{eq}\, G_t/c_{tg}} \tag{I.3}$$

For Run 21 these values are calculated to be

$$\mathcal{NTU}_{y12} = 0.4855; \quad \mathcal{NTU}_{y13} = 0.8429; \quad \mathcal{NTU}_{y23} = 0.7286 \tag{I.4}$$

These values are, on the basis of assumptions made, constant along the length of the column.

(6) The multicomponent film model of Krishna[4, 6] or that of Toor[8] and Stewart and Prober[9] can be used to calculate the elements of the matrix $[NTU_y]$ from the knowledge of binary pair $\mathcal{NTU}_{yij}$. Both these procedures lead to almost identical values of $[NTU_y]$ and only the calculation procedure of Krishna[4, 6] are given here. This procedure simplifies considerably for the assumption of equimolar diffusion and for vanishingly small fluxes[6]; we may ignore the matrix of correction factors for finite-fluxes[6]. The elements of $[NTU_y]$ are calculated from the following relation:

$$NTU_{yij} = \frac{\mathcal{NTU}_{yj3}[y_i(\mathcal{NTU}_{y\,3-j,3} - \mathcal{NTU}_{y12}) + \delta_{ij}\mathcal{NTU}_{y12}]}{y_1 \mathcal{NTU}_{y23} + y_2 \mathcal{NTU}_{y13} + y_3 \mathcal{NTU}_{y12}} \qquad i,j = 1,2 \tag{I.5}$$

where δ_{ij} is the Kronecker delta. The mole fractions y_i in equation (I.5) are evaluated at the average between the bulk phase mole fraction and the interfacial mole fraction. These are not constant along the column and in the model used to predict the top compositions, the elements NTU_{yij} are evaluated afresh for every increment along the column; they are assumed constant within the increment. For Run 21 the values at the bottom of the column are: $NTU_{y11} = 0.7444$; $NTU_{y12} = 0.1492$; $NTU_{y21} = 0.0670$; $NTU_{y22} = 0.6271$. At the top of the column the corresponding values are: $NTU_{y11} = 0.7411$; $NTU_{y12} = 0.1592$; $NTU_{y21} = 0.0692$; $NTU_{y22} = 0.6203$. Notice that there is little difference between the values at the top and bottom of the column and an assumption of constant $[NTU_y]$ along the column would also be a good approximation; this assumption was however not used in the calculations.

Estimation of $[NTU_x]$

The estimation procedure for $[NTU_x]$ follows the simplified interphase model of Krishna[6]. A step-by-step procedure is outlined below.

(1) The first step is to evaluate the generalized Maxwell–Stefan diffusion coefficients of the binary pairs at the bulk liquid composition in the increment under consideration. The GMS diffusion coefficients Đ_{ij} are composition dependent and one logical procedure to evaluate Đ_{ij} in the *multicomponent* mixture is to use the Vignes-type formula developed for non-ideal *binary* mixtures[10]. Thus the coefficient Đ_{ij} is given in terms of the infinite values at either end of the concentration range:

$$\text{Đ}_{ij} = (\text{Đ}_{ij}{}^{0})^{x_j/(x_i+x_j)}(\text{Đ}_{ji}{}^{0})^{x_i/(x_i+x_j)} \tag{I.6}$$

where $\text{Đ}_{ij}{}^{0}$ is the diffusion coefficient for the pair $i-j$ in which i is infinitely dilute. The compositions x_i are taken as the bulk liquid compositions, which in turn are equal to the bulk vapour composition for total reflux conditions.

The infinite dilution coefficients $\text{Đ}_{ij}{}^{0}$ can be estimated using the correlations of Wilke and Chang[11], Olander[12], Othmer and Thakar[13] and Schiebel[14]. For the system ethanol (1)–tert butanol (2)–water (3) these are estimated as (units $\mu m^2\ s^{-1}$):

$$\text{Đ}_{12}{}^{0} = 4080; \quad \text{Đ}_{21}{}^{0} = 2600; \quad \text{Đ}_{13}{}^{0} = 3711; \quad \text{Đ}_{31}{}^{0} = 4064$$
$$\text{Đ}_{23}{}^{0} = 2652; \quad \text{Đ}_{32}{}^{0} = 3143 \tag{I.7}$$

For Run 21, the Đ_{ij} calculated at the arithmetic average composition between the top and bottom of the column are (units $\mu m^2\ s^{-1}$):

$$\text{Đ}_{12} = 3062 = \text{Đ}_{21}; \quad \text{Đ}_{13} = 3865 = \text{Đ}_{31}; \quad \text{Đ}_{23} = 2801 = \text{Đ}_{32} \tag{I.8}$$

(2) The liquid film Reynolds number $Re_l = 4\Gamma/\mu_l$ and $\delta = (3\mu_l\Gamma/\rho_l{}^2 g)^{1/3}$ is the film thickness. For Run 21, $\delta = 0.12$ mm and $Re_l = 86$. In all the 21 runs the Reynolds number was calculated to be about 100 or less. Therefore the liquid phase Sherwood number $Sh_l = 3.41$, as shown in, for example, Treybal[15]. The liquid phase partial numbers of transfer units can therefore be calculated as follows:

$$\mathcal{NTU}_{xij} = 3.41 \frac{\text{Đ}_{ij}}{\delta} \frac{a A_c Z}{L_t/c_{tl}} \tag{I.9}$$

where L_t is the molar liquid flow rate and c_{tl} is the molar concentration of the liquid phase.

For Run 21, equation (I.9) leads to the following values of the liquid phase $\mathcal{NTU}_{xij}$:

$$\mathcal{NTU}_{x12} = 7.17; \quad \mathcal{NTU}_{x13} = 9.05; \quad \mathcal{NTU}_{x23} = 6.56 \tag{I.10}$$

(3) From the values of the binary pair liquid phase numbers of transfer units calculated from equation (I.9), the matrix $[NTU_x]$ can be calculated from an equation exactly analogous to equation (I.5). Specifically, for Run 21 at the bottom of the column we have the elements given by $NTU_{x11} = 8.5545$; $NTU_{x12} = 0.6285$; $NTU_{x21} = -0.1608$; $NTU_{x22} = 6.7607$. At the top of the column the corresponding values are $NTU_{x11} = 8.5289$; $NTU_{x12} = 0.6823$; $NTU_{x21} = -0.1692$; $NTU_{x22} = 6.7783$. The composition changes along the column in most of the experimental runs are small and the matrix $[NTU_x]$ remains practically constant.

Estimation of the Diagonal Matrix of Stripping Factors $\lceil S \rfloor$

For total reflux we have $G_t = L_t$ and therefore the elements of $\lceil S \rfloor$ are given by $S_i = K_{eqi} = \gamma_i x_i p_i{}^0/p_t$ where γ_i is the activity coefficient of component i in the liquid mixture of mole fraction x_i; $p_i{}^0$ is the pure component vapour pressure of component i; p_t is the total system pressure. The vapour pressure data used are from El-Yafi *et al*[16], which reference also gives the vapour–liquid equilibrium data for the system ethanol (1) – tert butanol (2) – water (3). The correlation of the activity coefficients for this system is summarised in Appendix II. The stripping factors are calculated at the bottom of the column for Run 21 to be $S_1 = 1.1816$; $S_2 = 1.2067$. At the top of the column, the corresponding values are $S_1 = 1.1191$; $S_2 = 1.1002$.

Estimation of overall matrix $[NTU_{oy}]$

Using the addition of resistances formula it is possible to calculate the overall matrix $[NTU_{oy}]$. It can be seen from the values of the elements for $[NTU_y]$ and $[NTU_x]$ calculated for Run 21, which is typical for all the other runs, that the overall mass transfer process is vapour phase mass transfer controlled. In view of the many uncertainties in the precise estimation of the liquid phase diffusion coefficients $Đ_{ij}$ and of the liquid phase mass transfer coefficient according to equation (I9), it was decided to assume that $[NTU_{oy}] = [NTU_y]$ instead of calculating the overall parameters from the addition of resistances formula.

APPENDIX II

Correlation of Vapour–liquid Equilibrium Data for Ethanol–tert butanol–water

In view of the necessity of obtaining the maximum possible accuracy in the correlation of the vapour–liquid equilibrium data, these data were measured in the Separations Processes Laboratory at the University of Manchester under the supervision of Dr D. M. T. Newsham. The data have been reported separately elsewhere[16]. For completeness of presentation, the final correlation of the activity coefficients summarised below. Further details are also available in the thesis of Salomo[17].

The extended Black equation was used to fit the activity coefficients. The equation is of the form:

$$\ln\gamma_i = \frac{A_{ij}\left(\frac{A_{ji}}{A_{ij}}x_j\right)^2 + A_{ik}\left(\frac{A_{ki}}{A_{ik}}x_k\right)^2 + \left(A_{ij}+A_{ik}-A_{kj}\frac{A_{ik}}{A_{ki}}\right)\frac{A_{ji}A_{ki}}{A_{ij}A_{ik}}x_j x_k}{\left(x_i+\frac{A_{ji}}{A_{ij}}x_j+\frac{A_{ki}}{A_{ik}}x_k\right)^2}$$

$$+\sum_j C_{ij}x_j(x_i-x_j)(3x_i-x_j)-\tfrac{3}{2}\sum_j\sum_k C_{jk}x_j x_k(x_j-x_k)^2$$

$$+\sum_j D_{ij}x_j(x_i-x_j)^3(3x_i+1)-2\sum_j\sum_k D_{jk}x_j x_k(x_j-x_k)^3$$

$$i = 1, 2, 3 \qquad \text{(II.1)}$$

The constants in the above equation have been determined to be

$$A_{21} = -0.11520 \qquad A_{13} = 1.57210 \qquad A_{23} = 2.8102$$
$$A_{31} = 0.91370 \qquad A_{32} = 1.1614$$
$$C_{12} = C_{21} = -0.1425 \qquad D_{12} = -D_{21} = -0.3147$$
$$C_{13} = C_{31} = -0.1231 \qquad D_{13} = -D_{31} = 0.2115$$
$$C_{23} = C_{32} = 0.1909 \qquad D_{23} = -D_{32} = 0.5183$$

We have further the conditions:

$$A_{ii} = C_{ii} = D_{ii} = 0 \qquad \text{(II.2)}$$

and A_{12} is calculated from the Van Laar assumption

$$A_{12} = A_{21}\frac{A_{13}}{A_{31}}\frac{A_{32}}{A_{23}} \qquad \text{(II.2)}$$

The above set of constants and correlation fitted the measured vapour–liquid equilibrium data with the following average deviations in mole fractions:

ethanol:	0.00277
tert butanol:	0.00168
water:	0.00381

The accuracy of measurement of component mole fraction was ±0.002 for both the measurement of VLE and for the determination of the compositions at the top and bottom of the wetted-wall column.

SYMBOLS USED

a	interfacial area per unit volume of column volume available for flow of phases; $a = 4/d_{eq}$ (m^2 m^{-3})
A_c	column cross-sectional area; $A_c = \pi(d_2{}^2 - d_1{}^2)/4$ (m^2)
A_{ij}	constants used in vapour–liquid equilibrium data fit (see Appendix II)
c_{tg}	total molar gas concentration (kmol m^{-3})
c_{tl}	total molar liquid concentration (kmol m^{-3})
C_{ij}	constants in vapour–liquid equilibrium data fit (see Appendix II)
d_1	outer diameter of central heating rod; $d_2 = 0.0254$ (m)
d_2	inside diameter of wetted-wall column; $d_1 = 0.0556$ (m)
d_{eq}	hydraulic diameter; $d_{eq} = (d_2{}^2 - d_1{}^2)/d_2 = 0.044$ (m)
D_{ij}	constants used in vapour–liquid equilibrium data for (see Appendix II)
$\mathscr{D}_{ij}$	diffusivity of binary gas pair $i-j$ (m^2 s^{-1})
$Đ_{ij}$	generalised Maxwell–Stefan diffusion coefficient of pair $i-j$ in liquid phase (m^2 s^{-1})
$Đ_{ij}{}^0$	generalised Maxwell–Stefan diffusion coefficient of pair $i-j$ in liquid phase in which i is infinitely dilute (m^2 s^{-1})
$\grave{E}_{oyi}$	Murphree point efficiency of component i
g	gravitational acceleration; $g = 9.81$ (m s^{-2})
G_i	molar flow rate of component i in vapour phase (kmol s^{-1})
G_t	total mixture molar flow rate of vapour phase (kmol s^{-1})
$H\grave{T}U_{oyi}$	pseudo-binary overall vapour phase height of transfer unit of component i; $H\grave{T}U_{oyi} = Z/N\grave{T}U_{oyi}$ (m)
$H\grave{T}U_i$	pseudo-binary height of transfer unit (m)
J_i	molar diffusion flux of component relative to the molar average mixture velocity; $J_i \equiv N_i - y_i N_t$ (kmol m^{-2} s^{-1})
$[k_y]$	partial vapour phase mass transfer coefficient matrix (kmol m^{-2} s^{-1})
$[k_x]$	partial liquid phase mass transfer coefficient matrix (kmol m^{-2} s^{-1})
$[K_{oy}]$	overall vapour phase mass transfer coefficent matrix (kmol m^{-2} s^{-1})

$\check{K}_{oyi}$	pseudo-binary overall vapour phase mass transfer coefficient for component i (kmol m^{-2} s^{-1})
K_{eqi}	equilibrium K-value)
L_i	molar flow rate of component i in liquid phase (kmol s^{-1})
L_t	total mixture molar flow rate of liquid phase (kmol s^{-1})
M_i	molecular weight of component i (kg $kmol^{-1}$)
n	number of components in mixture; $n = 3$ for ternary
N_i	interfacial molar flux of component i with respect to a stationary coordinate reference frame (kmol m^{-2} s^{-1})
N_t	total mixture interfacial molar flux; $N_t = 0$ for equimolar mass transfer (kmol m^{-2} s^{-1})
$[NTU_x]$	partial liquid phase number of transfer units matrix
$[NTU_y]$	partial vapour phase number of transfer units matrix
$[NTU_{oy}]$	overall number of vapour phase transfer units matrix
$N\check{T}U_{oyi}$	pseudo-binary number of transfer units (overall vapour phase) of component i
$\mathcal{NTU}_{xij}$	partial liquid phase number of transfer units for binary pair $i-j$
$\mathcal{NTU}_{yij}$	partial vapour phase number of transfer units for binary pair $i-j$
p_i^0	vapour pressure of component i (N m^{-2})
p_t	total system pressure; $p_t = 1.01325 \times 10^5$ (N m^{-2})
Re	Reynolds number
$\ulcorner S \lrcorner$	diagonal matrix of stripping factors
Sc	Schmidt number
Sh	Sherwood number
T	temperature (°C)
x_i	mole fraction of component i in liquid phase
y_i	mole fraction of component i in vapour phase
y_i^*	mole fraction of component i in vapour phase in equilibrium with bulk liquid phase
Δy_i	driving force (overall vapour phase); $\Delta y_i \equiv y_{ib} - y_i^*$
Z	total length of test section; $Z = 1.013$ (m)

Greek letters

γ_i	activity coefficient of component i in solution
Γ	mass flow rate of liquid per unit perimeter of column (kg m^{-1} s^{-1})
δ	thickness of liquid film (m)
δ_{ij}	Kronecker delta
μ	viscosity (Pa s)
ξ	dimensionless distance measured from bottom of column
ρ	mixture mass density (kg m^{-3})
Υ	ratio of driving forces; $\Upsilon \equiv \Delta y_1/\Delta y_2$

Matrix notation

( )	$n-1$ dimensional column matrix
[ ]	$n-1 \times n-1$ dimensional square matrix
$\ulcorner\ \lrcorner$	$n-1$ dimensional diagonal matrix

Subscripts

b	refers to bulk fluid phase (vapour or liquid)
B	refers to bottom of column
g	refers to gas (vapour) phase
i, j, k	indices
l	refers to liquid phase
n	referring to component n
o	overall parameter or coefficient
T	refers to top of column
x	refers to liquid phase
y	refers to vapour phase
ξ	refers to position ξ from bottom of column
1, 2, 3	refers to components 1, 2 and 3

Superscript

$\check{\ }$	refers to pseudo-binary parameter

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ADDRESS

Correspondence concerning this paper should be addressed to Dr R. Krishna at his present address: Koninklijke/Shell-Laboratorium, Amsterdam, Badhuisweg 3, 1031 CM Amsterdam, The Netherlands.

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