A Nonequilibrium Stage Model of Multicomponent Separation Processes

Part III: The Influence of Unequal Component-Efficiencies in Process Design Problems

The conventional equilibrium-stage model that uses a component-independent stage efficiency and a nonequilibrium-stage model, in which mass transfer rate equations are solved simultaneously with the stage conservation equations, are employed to solve four representative distillation design problems. There are large differences between the number of stages predicted by the two models for a specific separation of the more volatile component. The differences arise from two causes: the way in which the liquid phase resistances and equilibrium equations are used in the models, and the consequences of diffusional interaction effects. Neglect of the latter may lead to an underdesigned column; there is between a 9 and 15% difference in the stage requirements predicted by the nonequilibrium model with a rigorous mass transfer model and a nonequilibrium model which ignores interaction effects.

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SCOPE

In Part I of this series, a nonequilibrium-stage model of counter-current multicomponent separation processes was described. The motivation for developing the model was the observation that the equilibrium-stage model modified by the inclusion of a stage efficiency that has the same value for all components (the model presently used to simulate separation processes) is unable to accurately predict the composition profiles in processes separating multicomponent mixtures in which the various species exhibit differing facilities for mass transfer. In Part II, we used the model to simulate ternary distillation experiments carried out at total reflux in wetted-wall and bubble cap columns (Krishnamurthy and Taylor, 1985a,b). We also attempted, briefly, to compare the performance of our nonequilibrium-stage model with an equal-efficiency "equilibrium-stage" model (see Figure 12 of Part II) with a view to demonstrating the influence of diffusional interaction effects (which cause the mass transfer rate of a particular species to depend not only on its own concentration gradient, but also on the concentration gradients of all other species as well). Among other things, these effects may lead to component point efficiencies lying outside the range [0,1], the normal range of binary Murphree efficiencies. Although the model we developed in Part I followed the observed composition profiles much more closely than the equal-efficiency equilibrium-stage model, we felt that a comparison of composition profiles obtained under total reflux conditions was not the best way to illustrate differences between the predictions of the various models. It is true that at total reflux, the driving forces are as large as they will ever be and this might contribute to significant interaction effects; however, a comparison of composition profiles is not always appropriate for the following reasons. First, the experiments were carried out with a relatively small number of stages. Second, in our simulations of the total reflux experiments it was necessary to specify the flow rate and composition of the stream leaving the reboiler instead of specifying a feed stream at some intermediate stage. These two factors mean that the extrapolation of the results of the simultations in Part II to more realistic situations (where the column may have more than ten times the number of stages encountered in the experimental columns and would be operated with a nonzero feed rate and at a finite reflux ratio) may not be meaningful. We feel it is better to compare our nonequilibrium stage model to the efficiency-modified equilibrium-stage model in the kinds of calculations more commonly encountered in the literature on separation process modeling: operating (or simulation) problems and design calculations where the number of stages to effect a particular separation is to be determined. Such a comparison is the main objective of this paper.

Three nonideal ternary systems and a relatively ideal five component hydrocarbon system are selected for study:

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1. Methanol–isopropanol–water
2. Acetone–methanol–water
3. Ethanol-*t*-butanol–water
4. Methane–ethane–propane–butane–pentane.

The first three were selected because prior experimental work had indicated that the individual component efficiencies were quite different, and that diffusional interaction effects were important. Krishna et al. (1977) present the results of a series of experiments carried out with system 3; point efficiencies outside the range [0,1] were obtained (in one case a point efficiency of −27 was reported). In Part II of this series we presented the results of our simulations of Vogelpohl's experiments with systems 1 and 2 in a bubble-cap tray column; the calculated composition profiles were in good agreement with the experimentally measured profiles. Although efficiencies are not computed in our nonequilibrium-stage model, it is possible to back out values for the component efficiencies from the results of a simulation. For two of Vogelpohl's experiments the resulting component efficiency profiles are shown in Figures 10 and 11 (discussed below); there is considerable variation between the efficiencies of each component on a given stage and also from stage to stage for a given component (similar figures are presented by Vogelpohl, 1979).

System 1 was also used in a theoretical study made by Toor and Burchard (1960). To our knowledge, theirs is the only study similar to this one. For the single problem they considered, a model allowing for interaction effects led to a column requiring 117 stages; neglect of interaction effects suggested that only 84 stages were needed! Of necessity, Toor and Burchard made many approximations simply in order to be able to carry out their calculations; interaction effects were accounted for through component efficiency factors and a simplified model of multicomponent mass transfer (the best available at that time) was used. Among other things, we wanted to see how our nonequilibrium-stage model would fare on the problem posed by Toor and Burchard (1960).

Since the pioneering work of Toor and Burchard, there have been a number of developments. New and improved models of multicomponent mass transfer have been proposed, models which are, indeed, capable of explaining the strange behavior of the component efficiencies encountered in the experiments of Krishna et al. and of Vogelpohl (see Krishna and Standart, 1979, for a recent review of the field). We used a number of mass transfer models in our simulations of total reflux experiments described in Part II. We believe that this paper is the first to employ the more rigorous mass transfer models in separation process design and simulation calculations.

Design and operating problems are posed for each of the four systems and solved using four different process models:

I. An equilibrium-stage model with a stage efficiency of unity.
II. An equilibrium-stage model with the stage efficiency computed on each stage using the AIChE method.
III. The nonequilibrium-stage model with an interactive model of mass transfer.
IV. The nonequilibrium-stage model with each component given the same facility for mass transfer.

Model III is the only one which accounts for interaction effects; it is not however, the only one which predicts unequal component stage efficiencies. This is discussed further below.

CONCLUSIONS AND SIGNIFICANCE

The relative performance of the equilibrium-stage model that utilizes a constant component efficiency and the nonequilibrium model on the four problems studied here provides a basis for demonstrating the consequences for process design of neglecting the influence of the liquid phase resistance and diffusional interactions, a peculiarity of multicomponent mass transfer. The two models predict numbers of stages for a specified separation that are very different from each other in three of the four test problems. The differences are as much as 42 stages (53% with the equal-efficiency equilibrium-stage model used as a basis) and are at least 10 stages (30%) for all of the problems involving nonideal systems. These differences are due partly to diffusional interaction effects and partly to the manner in which the liquid phase resistances and equilibrium relations are handled. The two effects may be complementary or compensatory, depending on the specific mass transfer situation. By using two different formulations of the nonequilibrium model (one of which neglects diffusional interaction effects) it has been shown that diffusional interaction effects alone cause a difference of up to 14 stages (15% with the formulation which neglects diffusional interaction effects used as a basis).

The equilibrium-stage model is seen to underpredict severely the number of stages for a given separation, possibly explaining the large safety factors that are normally associated with industrial column designs based on this model. The nonequilibrium model is physically more realistic, and provides a rational approach to the design and simulation of multicomponent separation processes.

THE CALCULATIONS

Overview

There are two kinds of problems that one encounters in the literature on separation process modeling: operating problems (in which we determine the separation obtained from a column of specified configuration), and design problems (in which we determine the number of stages required to effect a specified separation). In the former we are able to compare composition profiles and the composition of the product streams directly. In the latter class of problems any differences between models manifest themselves in a rather more obvious and dramatic fashion.

Many ingenious algorithms have been devised for solving equilibrium-stage operating problems [see, e.g., King (1980, Ch. 10); Henley and Seader, (1981, Ch. 15)]. It is probably fair to say that a simultaneous solution of the model equations using Newton's method (or one of its relatives) is the most versatile approach to solving separation process problems. We also use a simultaneous correction procedure to solve the nonequilibrium-stage model equations (see Krishnamurthy and Taylor, 1985a, for further discussion). The traditional way to solve design problems is to alter the problem specification to that of an operating problem (i.e., specify the number of stages instead of the desired separa-

TABLE 1. COLUMN DIMENSIONS

Column diameter	0.3000 m
Active area	0.06008 m^2
Outlet weir height	0.0300 m
Average column width	0.2400 m
Distance traveled by liquid on a tray	0.2400 m

tion), solve a number of problems, and see which ones meet the design specifications. Specialized algorithms for solving equilibrium-stage design problems do exist (Ricker and Grens, 1974); the procedures are, however, a little involved and we have not attempted to incorporate their ideas into our computer programs. We have followed the traditional (time-consuming and very expensive) route to solving our design problems. A large number of problems have been solved and the precision of our solutions is within one stage per section.

Problem Specifications

Despite the much larger number of equations to be solved for the nonequilibrium-stage model ($5c+1$ as opposed to $2C+1$ for the equilibrium-stage model), the number of degrees of freedom is the same in both cases. Thus, any specification made for an equilibrium-stage problem also applies to the corresponding nonequilibrium problem. The standard specification for operating problems includes the feed rate, its composition and thermal state, the number of stages, location of the feed stage(s), pressure and heat load on each stage (except for the condenser and reboiler), and two additional end specifications; in our case, we chose to specify the reflux ratio and the bottom product rate. The reflux ratio was determined by solving a number of problems and picking the ratio that gave a reasonable number of stages.

For design problems, the number of stages and location of the feed stages are unknown and so we must choose two (or more) other specifications. We chose to specify the desired purity in the distillate of the more volatile component, and the feed stage was located in order to minimize the total number of stages required.

If a constant efficiency (i.e., the same for all components on all stages) is chosen for the equilibrium-stage design, then the basis for the feed rate is irrelevant. However, when the efficiency is to be estimated using, for example, the AIChE method, then the feed rate must be specified in such a way as to insure the satisfactory operation of the column. The same is true of our nonequilibrium-stage model. We based our calculations on the column used by Vogelpohl (1979) and fixed the feed rate so as to lead to the same average F-factor found in his experiments. The dimensions of the column are given in Table 1. We also found that our hypothetical columns would be operating at about 75% of flooding; this is a reasonable figure.

The complete set of specifications is summarized in Table 2 (design problems) and Table 3 (operating problems).

For the methanol-isopropanol-water system, the specifications used here are, as far as possible, the same as those made by Toor and Burchard (1960). One small modification was made for consistency with our other examples. Toor and Burchard specified the composition of methanol in the reboiler, and the numerical procedure involved advancing from stage to stage from the reboiler, through the feed stage, until the desired composition of methanol was obtained in the distillate. The bottoms flow rate was not specified. In our calculations, the bottom product rate was specified, but in a way that made it possible to achieve the specified separation of the more volatile component in the distillate.

Hopkins and Fritsch (1955) describe an industrial process in which water is used as the solvent in the extractive distillation of an acetone-methanol crude. Two feed streams are employed in that process: a pure water feed near the top of the column, and an acetone-methanol crude feed at some intermediate location. Hence, in the example problems for this system, two feeds are specified in order that we may better represent the existing process.

The hydrocarbon separation is adapted from an example considered by Henley and Seader (1981, p. 484). It concerns the high-pressure separation of ethane from propane, the feed consisting of the first five members of the homologous series.

Equilibrium-Stage Calculations

A computer code was written to solve the equilibrium-stage model equations; the formulation due to Naphtali and Sandholm (1971) was adopted, with the model equations solved using the hybrid algorithm of Lucia and Macchietto (1983). The conventional equilibrium relations were modified by the incorporation of a Murphree efficiency factor. The component efficiencies are taken to be the same on a given stage but allowed to vary from stage to stage. The Murphree stage efficiency was determined using the AIChE method as described by King (1980, p. 621). The number of transfer units of both vapor and liquid phases was used

TABLE 2. SPECIFICATIONS FOR THE DESIGN PROBLEMS

Specification	Methanol–Isopropanol–Water	Acetone–Methanol–Water		Ethanol–t-Butanol–Water	Hydrocarbons C_1 to C_5
Pressure, MPa	0.1013	0.1013		0.1013	2.76
Reflux ratio	5.0	10.0		12.5	1.89
Feed rate, Kmol × 10^3/s	0.8333	0.2222(F1)	0.8889(F2)	0.3472	0.9583
Feed temp., K	347.0	340.0	334.5	352.25	313.56 (Vapor)
Feed composition					
Component 1	0.40	—	0.25	0.55	0.2000
2	0.20	—	0.75	0.20	0.4625
3	0.40	1.0	—	0.25	0.3000
4	—	—		—	0.0313
5	—	—		—	0.0062
Bottom product rate, Kmol/s × 10^3	0.5000	0.8889		0.1563	0.3236
Desired composition of component i in distillate	0.9800(1)	0.9500(1)		0.9000(1)	0.6900(2)
Condenser type	Total	Total		Total	Total
Reboiler	Equilbrium	Split-stream		Split-stream	Equilibrium

TABLE 3. SPECIFICATIONS FOR THE THE OPERATING PROBLEMS

System	No. of Stages	Feed Stage Location
1. Methanol–Isopropanol–Water	30	13
2. Acetone–Methanol –Water	80	13 (water feed) 68 (acetone–methanol
3. Ethanol-*t*-Butanol –Water	79	30
4. 5 Components hydrocarbon (C_1–C_5)	33	16

All other specifications as in Table 2.

in the determination of the overall number of transfer units for the vapor phase.

Except as noted below, physical properties of the mixture were used in the determination of the numbers of transfer units. The equilibrium ratio of the more volatile component was taken to represent the slope of the equilibrium curve (except for system 4, where K_2 was used); the binary diffusivity of the key components was also used. Weeping and entrainment are neglected in the present version of our nonequilibrium-stage model; we have, therefore, ignored these effects when estimating the stage efficiency from the AIChE method. We also note that the liquid phase was assumed to be completely mixed, consistent with our nonequilibrium-stage calculations.

Nonequilibrium-Stage Calculations

The nonequilibrium-stage model was described in detail in Part I (Krishnamurthy and Taylor, 1984a). The key feature of the model is that the conservation equations for each phase are solved simultaneously with equations that, it is hoped, accurately model the processes of interphase mass and energy transfer. The mass transfer rates in the vapor phase are calculated from the *c-1* dimensional matrix equation

$$(\mathcal{N}^V) = [k^V]\, a(\bar{y}^V - y^I) + \mathcal{N}_t(\bar{y}^V) \tag{1}$$

where $[k^V]$ is a square matrix of multicomponent mass transfer coefficients and is calculated from

$$[k^V]a = [\mathcal{B}^V]^{-1}a[\Xi^V] \tag{2}$$

$[\mathcal{B}^V]$ is a matrix of inverted *binary* mass transfer coefficients, $[\Xi^V]$ is a matrix that corrects $[\mathcal{B}^V]$ for the influence of finite rates of mass transfer. Expressions for $[\mathcal{B}^V]$ and $[\Xi^V]$, which depend on the choice of method, can be found in Part II.

Our simulations of the total reflux experiments with the systems considered in this work have shown that the experiments were largely vapor-phase controlled. The liquid phase offered less than 10% of the total resistance. However, there are situations where the liquid phase resistance may be somewhat more important; extractive distillation and high-purity separations are two that come to mind. It is, therefore, necessary to take the resistance offered by the liquid phase into account. An approximate analytical solution of the generalized Maxwell-Stefan equations (which represent diffusion in the liquid phase) has been given by Krishna (1977) and used in our design calculations. An expression for the

TABLE 4. RESULTS OF DESIGN CALCULATIONS

System/Quantity	Component	Method I Equilibrium Stage $\eta_j = 1.0$	II Equilibrium Stage η_j from AIChE method	III Nonequilibrium Stage Interactive	IV Nonequilibrium Stage Equal diffusivity
1. Methanol–Isopropanol–Water					
No. of stages		22	30	41	38
Feed Stage		10	13	16	17
Distillate	1	0.9813	0.9804	0.9815	0.9802
Composition	2	0.0135	0.0134	0.0157	0.0164
	3	0.0052	0.0062	0.0028	0.0034
2. Acetone–Methanol–Water					
No. of stages		53	80	105	91
Feed location		11	13	11	11
Acetone-Methanol feed		46	68	85	82
Distillate	1	0.9508	0.9500	0.9500	0.9500
Composition	2	0.0394	0.0360	0.0310	0.0305
	3	0.0098	0.0140	0.0190	0.0195
3. Ethanol-*t*-Butanol-water					
No. of stages		54	79	121	111
Feed location		27	30	53	48
Distillate	1	0.9000	0.9006	0.9004	0.9000
Composition	2	0.0397	0.0378	0.0454	0.0465
	3	0.0603	0.0617	0.0542	0.0535
4. Hydrocarbon (C_1–C_5)					
No. of stages		19	33	31	32
Feed stage		9	16	15	16
Distillate	1	0.3020	0.3020	0.3020	0.3020
Composition	2	0.6900	0.6901	0.6900	0.6900
	3	0.0080	0.0079	0.0080	0.0080
	4	—	—	—	—
	5	—	—	—	—

TABLE 5. PREDICTED DISTILLATE COMPOSITIONS FOR THE OPERATING PROBLEMS

Problem	Component	Method II	Method III
i	1	0.9804	0.9552
	2	0.0133	0.0373
	3	0.0063	0.0075
ii	1	0.9500	0.9330
	2	0.0360	0.0529
	3	0.0140	0.0141
iii	1	0.9006	0.8569
	2	0.0377	0.0732
	3	0.0617	0.0699
iv	1	0.3020	0.3020
	2	0.6901	0.6916
	3	0.0079	0.0064
	4	—	—
	5	—	—

liquid phase mass transfer rates based on this approximate solution takes a form similar to Eq. 1 for the vapor phase.

$$(\mathcal{N}^L) = [k^L]a(x^I - \bar{x}^L) + \mathcal{N}_t^L(\bar{x}^L) \tag{3}$$

with $[k^L]$, the matrix of multicomponent liquid phase mass transfer coefficients calculated from

$$[k^L]a = [\mathcal{B}^L]^{-1}a[\Gamma^L][\Xi^L] \tag{4}$$

$[\Xi^L]$ is a matrix of finite flux correction factors given by

$$[\Xi^L] = [\theta^L]\,\{\exp[\theta^L]\}\,\{\exp[\theta^L] - [I]\}^{-1} \tag{5}$$

$$\text{and } [\theta^L] = [\Gamma^L]^{-1}\,[\Phi^L] \tag{6}$$

$[\mathcal{B}^L]$ and $[\Phi^L]$ are defined by expressions similar to those that define $[\mathcal{B}^V]$ and $[\Phi^V]$ for the vapor phase (see Part II). $[\Gamma^L]$ is the matrix of thermodynamic factors with elements given by

$$\Gamma_{ik} = \delta_{ik} + \frac{x_i^L}{x_k^L}\frac{\partial \ln \gamma_i^L}{\partial \ln x_k^L} \qquad i,k = i,2\ldots c-1 \tag{7}$$

The elements of $[\Gamma^L]$ were determined by numerical differentiation of the activity coefficient model. In the present calculations, the matrix $[\Gamma^L]$ is strongly diagonally dominant and could reasonably well be approximated by the identity matrix. Interaction effects such as reverse diffusion arise through the presence of nondiagonal entries in the matrices $[k^V]$ and $[k^L]$.

The binary mass transfer coefficients required in the calculation of $[\mathcal{B}^V]$ and $[\mathcal{B}^L]$ are obtained by a modification of the AIChE correlations of Numbers of Transfer Units. For the vapor phase, we have

$$k_{ik}^V a = \frac{(0.776 + 4.567W - 0.2377F_f + 87.319L_F)G}{(\mu_m/\rho_m \mathcal{D}_{ik})^{0.5}} \tag{10}$$

and for the liquid phase,

$$k_{ik}^L a = (4.124 \times 10^8 D_{ik})^{0.5}\,(0.21313F + 0.15)t_L L \tag{11}$$

where t_L, the average liquid contact time is given by

$$t_L = \frac{1.2002\,Z_C Z_L}{L_F} \tag{12}$$

Z_C, the liquid hold-up on tray, is calculated from

$$Z_C = 0.0254\,(1.65 + 7.4803W + 80.478L_F - 0.5328F_f) \tag{13}$$

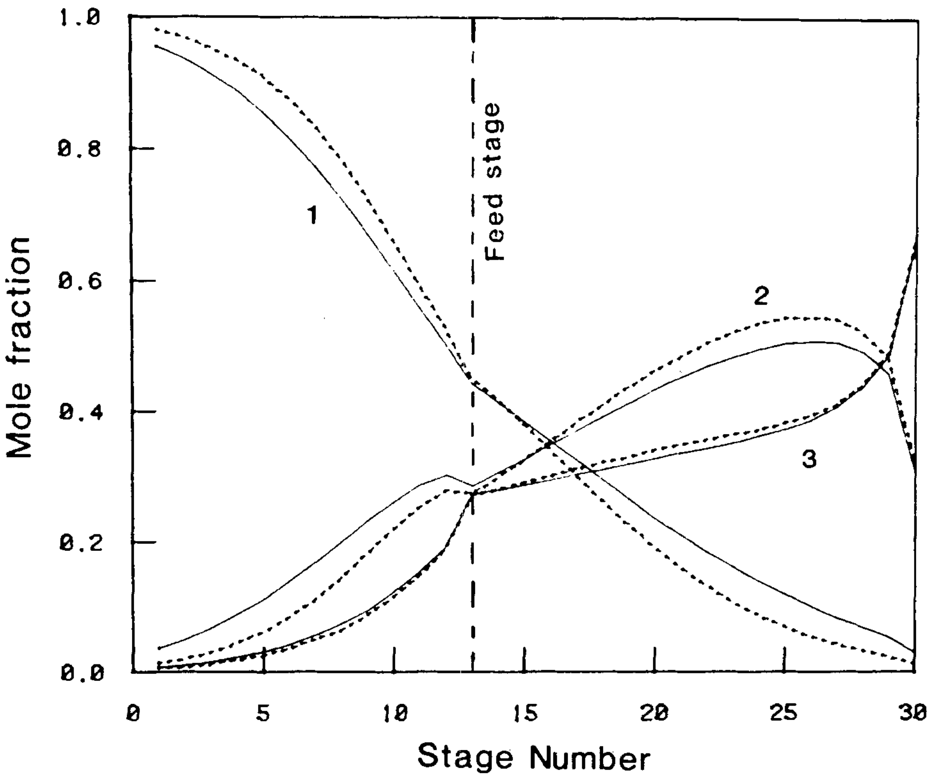

Figure 1. Composition profiles for methanol (1), isopropanol (2), and water (3) system. — Nonequilibrium model (interactive, method III). ---- Equilibrium-stage model (method II).

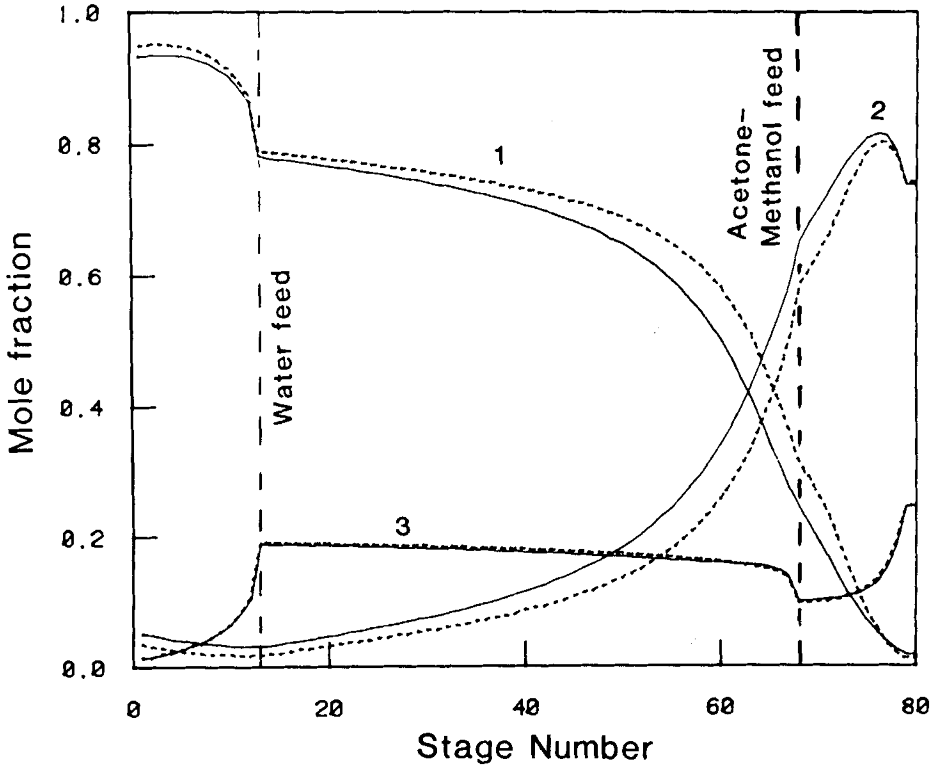

Figure 2. Composition profiles for acetone (1), methanol (2), and water (3) system. — Nonequilibrium model (interactive, method III). ---- Equilibrium-stage model (method II).

(All other symbols and their units are defined in the notation.)

The energy transfer rates in the two phases are calculated using expressions discussed in Part II. The heat transfer coefficients have been estimated through the use of an analogy between heat and mass transfer. The Chilton-Colburn analogy is used for the vapor phase, and an analogy that assumes a penetration-type mechanism is used for the liquid phase. However, it should be noted that in all examples considered, the temperature driving forces on any stage are extremely small (less than 0.5 K) and the actual value of the heat transfer coefficients has no bearing on the results of the design calculations.

Physical Properties

The binary diffusion coefficients for the vapor phase have been estimated using the correlation of Fuller et al. (Reid et al., 1977, p. 554). For the liquid phase, the binary diffusion coefficients at infinite dilution have been obtained using the Wilke-Chang correlation (Reid et al., 1977) and the concentration dependence has been accounted for through a Vignes-type relationship (Reid et al., 1977, p. 585).

Mixture properties such as viscosity and thermal conductivity were obtained from methods suggested by Reid et al.

K-values and enthalpies have been computed from the UNIQUAC method using the programs of Anderson (Prausnitz et al., 1981) for the nonideal problems, and the Chao-Seader correlation and Edmister's method (Henley and Seader, 1981, Chs. 4 and 5) respectively, for the hydrocarbon system. The binary interaction parameters required by the UNIQUAC model were found in the compilation by Gmehling and Onken (1977, pp. 628, 575).

RESULTS

Four different methods, listed below, have been used to solve the problems specified in Tables 2 and 3:

I. The equilibrium-stage model with the stage efficiency set to unity on all stages. This model gives the number of ideal stages required to obtain the separations specified in Table 2. A design based on a constant overall efficiency can be obtained directly from this result.

II. The equilibrium-stage model with the efficiency calculated on every stage using the AIChE method as discussed above.

III. The nonequilibrium-stage model with the vapor phase mass transfer rates calculated using the method of Krishna and Standart (1976) (see Part II for further discussion) and the liquid phase mass transfer rates calculated using the method of Krishna (1977), also as discussed above.

IV. The nonequilibrium-stage model with each species given the same facility for mass transfer by using an average diffusivity, the same for all binary pairs, in the calculation of the $k_{ij}{}^V$ and $k_{ij}{}^L$ and by setting $[\Gamma]$ to the identity matrix. The matrices $[k^V]$ and $[k^L]$ then become diagonal and interaction effects cannot occur.

A summary of the more important results of our design calculations (number of stages, location of feed stages and distillate composition) are given in Table 4. The results of our operating problem calculations (distillate composition)—those that differ from the results in Table 4—are given in Table 5. Composition profiles predicted by models II and III are shown in Figure 1 (methanol-isopropranol-water), Figure 2 (acetone-methanol-water), Figure 3 (ethanol-*t*-butanol–water), and Figure 4 (hydrocarbon system). Component efficiency profiles (backed out from the results of a simulation in the case of the nonequilibrium models) are shown in Figure 5 (methanol-isopropanol-water), Figure 6 (acetone-methanol-water), Figure 7 (ethanol-*t*-butanol–water) and Figure 8 (hydrocarbon system).

It is obvious from the results in Table 4 that the number of stages predicted by the equilibrium and nonequilibrium models

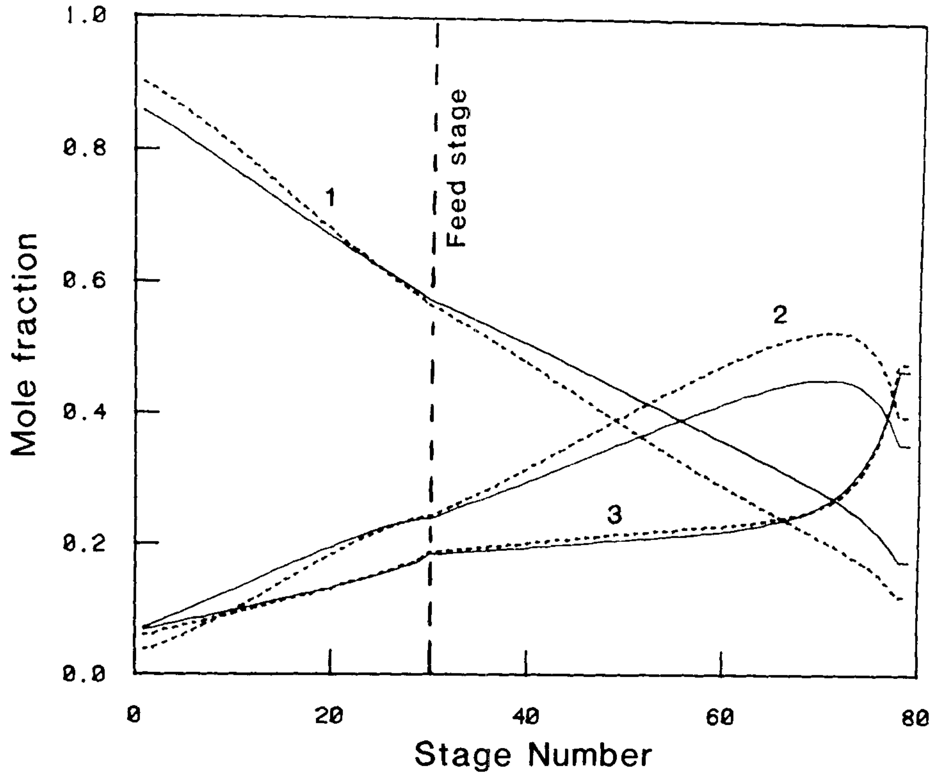

Figure 3. Composition profiles for ethanol (1), *t*-butanol (2), and water (3) system. — Nonequilibrium model (interactive, method III). ---- Equilibrium-stage model (method II).

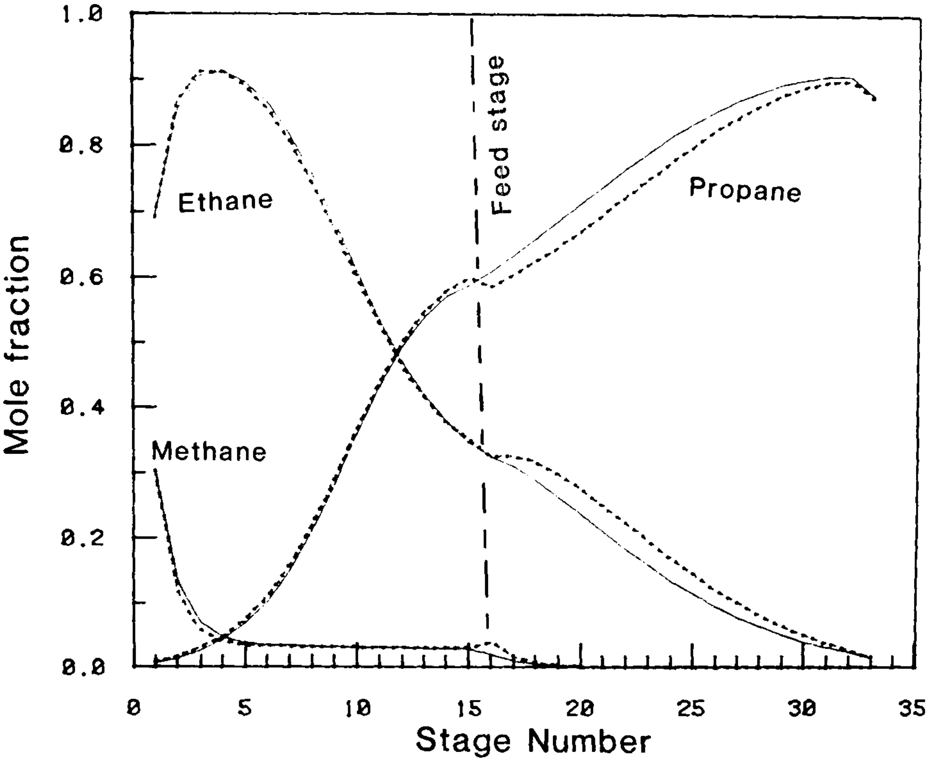

Figure 4. Composition profiles for the five-component hydrocarbon system. — Nonequilibrium model (interactive, method III). ---- Equilibrium-stage model (method II)

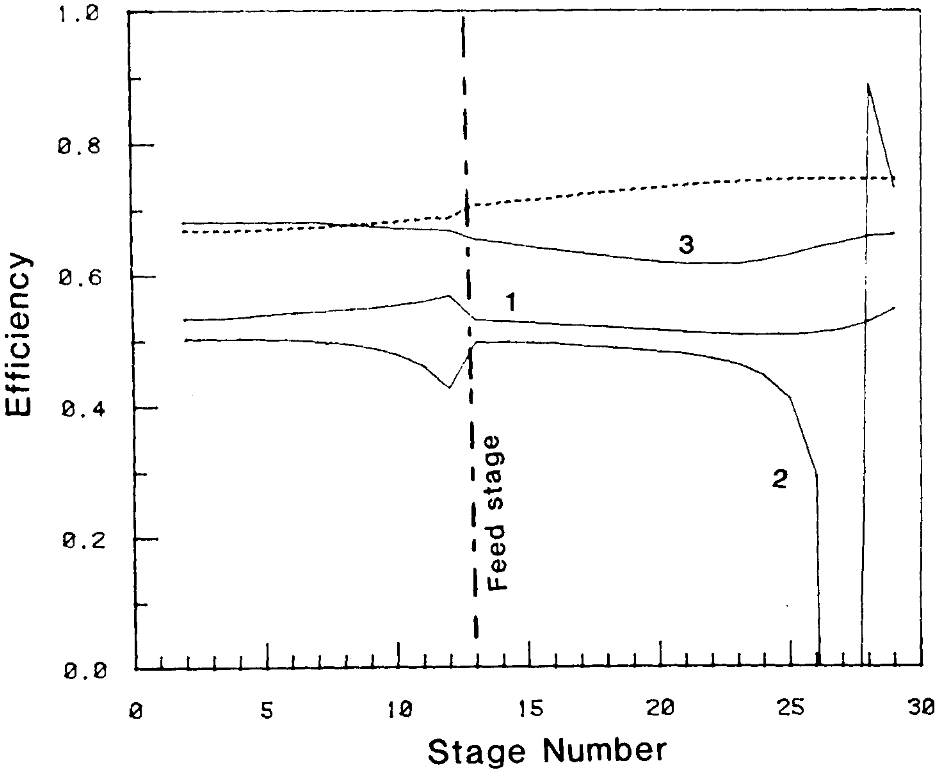

Figure 5. Efficiency profiles for methanol (1), isopropanol (2), and water (3) system. — Component efficiencies predicted by nonequilibrium model. ---- Stage efficiency based on components 1 and 3, predicted by the equilibrium model.

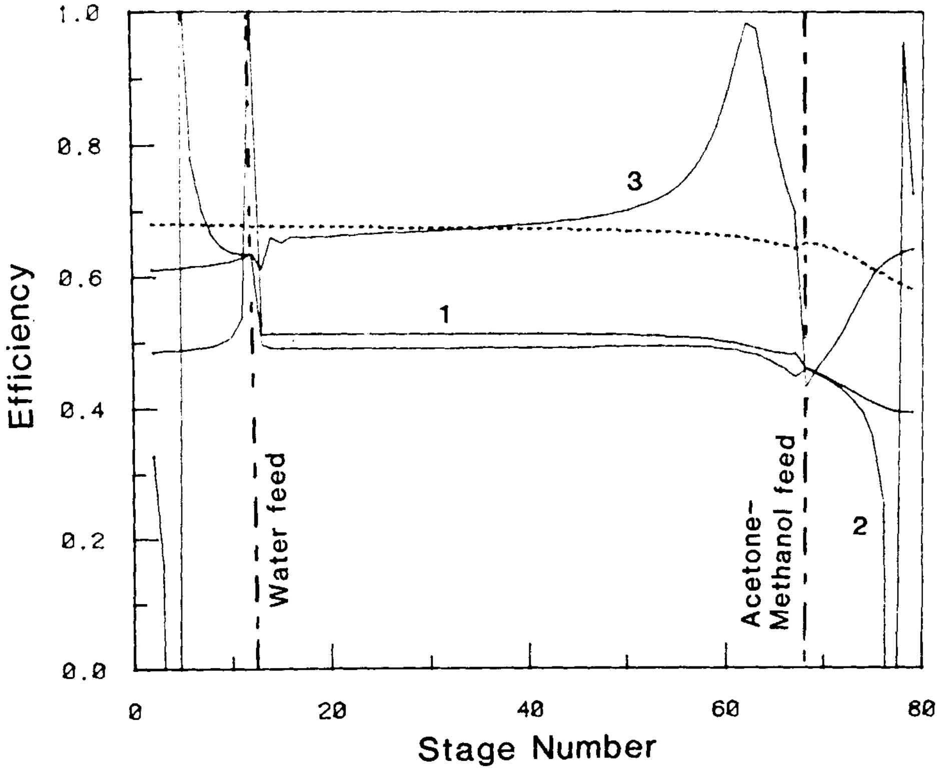

Figure 6. Efficiency profiles for acetone (1), methanol (2), and water (3) system. — Component efficiencies predicted by nonequilibrium model. ---- Stage efficiency based on components 1 and 3, predicted by the equilibrium model.

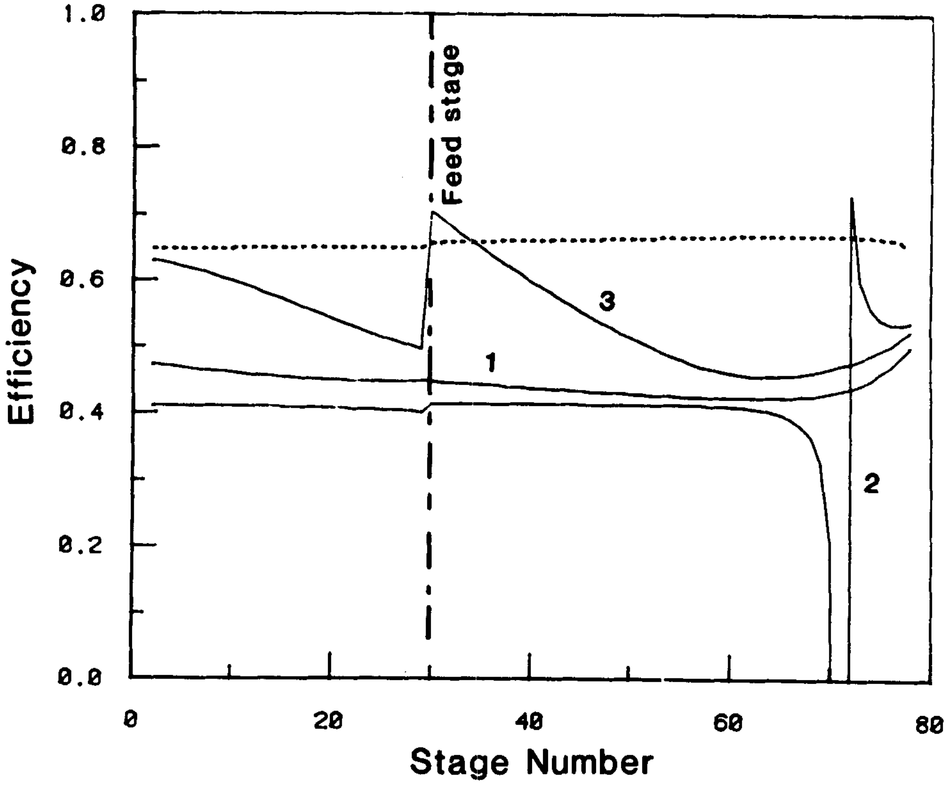

Figure 7. Efficiency profiles for ethanol (1), *t*-butanol (2), and water (3) system. — Component efficiency predicted by nonequilibrium model. ---- Stage efficiency based on components 1 and 3, predicted by the equilibrium model.

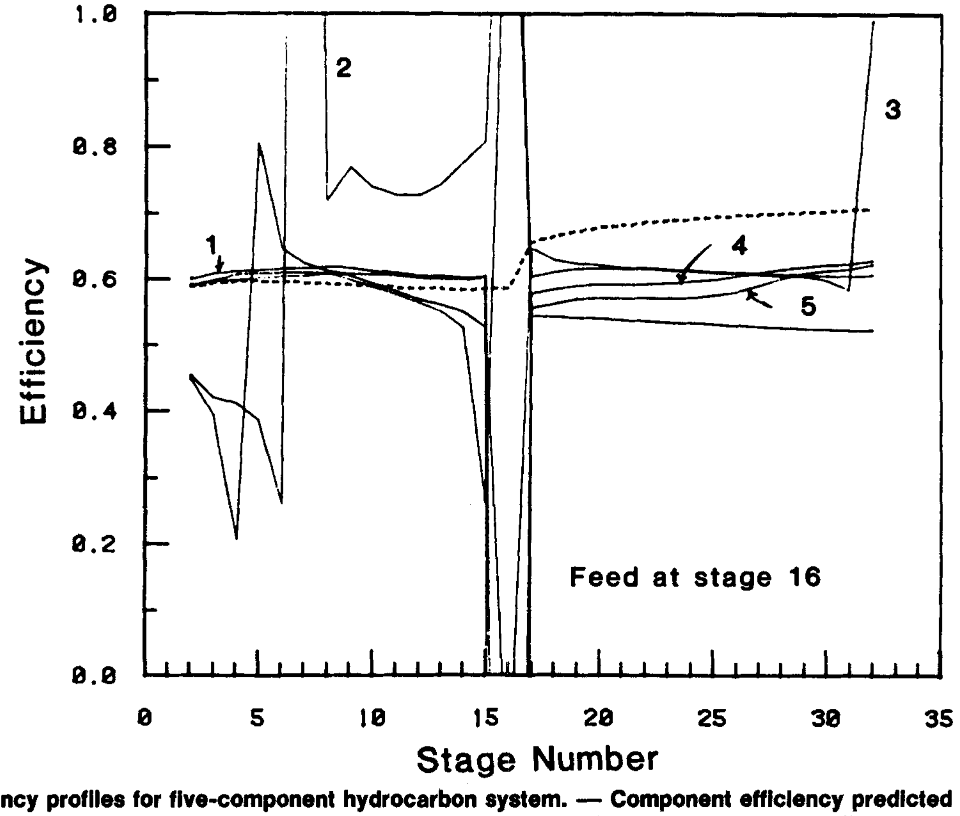

Figure 8. Efficiency profiles for five-component hydrocarbon system. — Component efficiency predicted by nonequilibrium model. ---- Stage efficiency based on components 1 and 5, predicted by the equilibrium model.

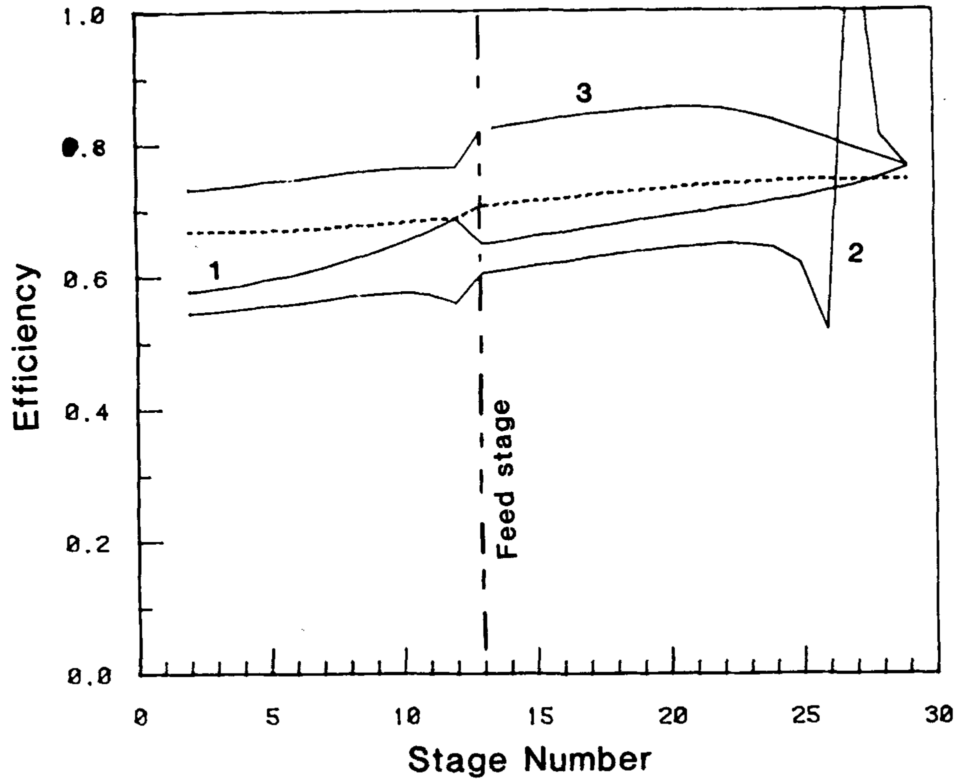

Figure 9. Efficiency profiles for assumed vapor phase controlled distillation of methanol (1), isopropanol (2), and water (3) system. — Component efficiencies predicted by nonequilibrium model. ---- Stage efficiency based on key components, predicted by the equilibrium model.

(methods II and III) are considerably different in at least three out of the four examples. The smallest difference is found for system 4 involving the distillation of the hydrocarbon mixture; a difference of only two stages or 5%. We find the largest difference of 42 stages (53%) for system 3 (ethanol–*t*-butanol–water system). (Model II is used as the basis for these percentage difference calculations.) There are a number of factors that give rise to these differences: the more important among them are diffusional interaction effects and the manner in which the liquid phase resistance and the equilibrium relations are handled in the models.

In the discussion which follows we focus attention first on the influence of the liquid phase, and second on the influence of diffusional interaction effects. Finally, we address the validity of the assumption, implicit in many models of multicomponent distillation, of equimolar overflow.

DISCUSSION

One might expect that the stage efficiency calculated from the AIChE method would lie somewhere between the component efficiencies of the key components, backed out from the results of the nonequilibrium model. This, however, appears to be true only for one out of the four problems, the hydrocarbon example, as seen in Figure 8 (even for this case, it applies only in the rectifying zone). For all the other systems, the stage efficiency lies well above the band formed by the component efficiencies (Figures 5, 6 and 7). The reason for this is an appreciable liquid phase resistance that is better recognized and accounted for by the nonequilibrium model.

The equilibrium-stage model accounts for the liquid phase resistance by including it in the calculation of the overall number of transfer units. The equilibrium ratios (K-values) are computed using the composition of the streams leaving the stage. This is satisfactory only if the percent contribution of the liquid phase resistance to the overall resistance is very small. Although distillation is controlled by the vapor phase in several instances, this is not always the case. If the driving forces for mass transfer are small (as they are in extractive and azeotropic distillation and high-purity separations, for example), then the liquid phase resistance may assume greater importance. In the nonequilibrium model, the liquid phase resistances are accounted for more accurately by allowing the compositions at the interface and in the bulk liquid to be different. K-values are computed using the interface composition. Even a small driving force can shift the interface equilibrium considerably. This has the effect of reducing mass transfer rates and lowering efficiencies. To further illustrate this point, the operating problem involving the methanol-isopropanol-water system is solved a second time using the nonequilibrium model, but this time neglecting the liquid phase resistance. The component efficiencies that result are plotted in Figure 9, and in this case the stage efficiency lies in the band formed by the efficiencies of the key components.

If there is an appreciable resistance in the liquid phase, then the nonequilibrium model will generally require a greater number of stages for a given separation when compared to the equilibrium model. (Only if a sparingly soluble component is present in appreciable amounts over the column and its large equilibrium ratio is used in the calculation of the number of overall gas phase transfer units, will the equilibrium model overpredict the liquid phase resistance.) For an operating problem, with a specified number of stages, the composition of the more volatile component predicted by the nonequilibrium model will trail that pre-

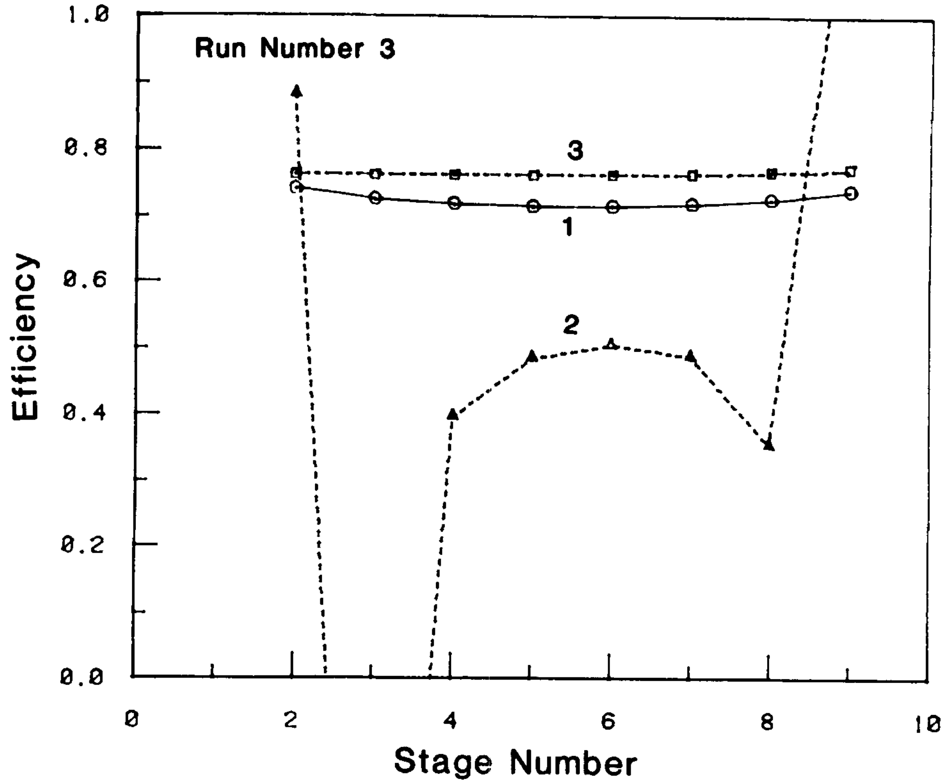

Figure 10. Component efficiencies in the distillation of acetone (1), methanol (2), and water (3); system at total reflux (experiments of Vogelpohl, 1979).

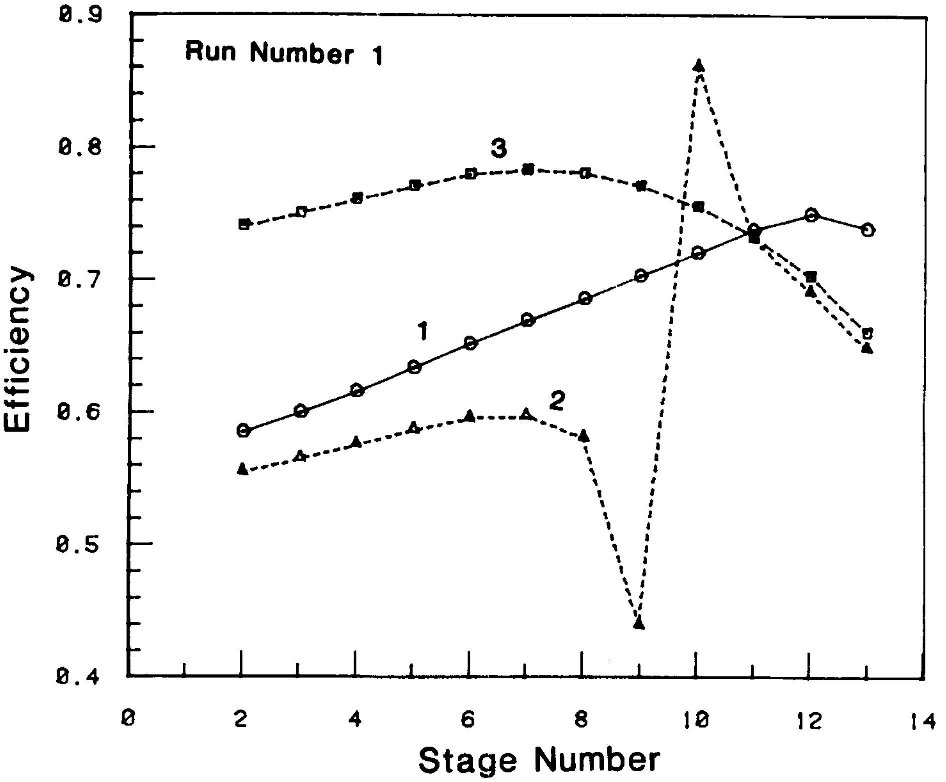

Figure 11. Component efficiencies in the distillation of methanol (1), isopropanol (2), and water (3); system at total reflux (experiments of Vogelpohl, 1979).

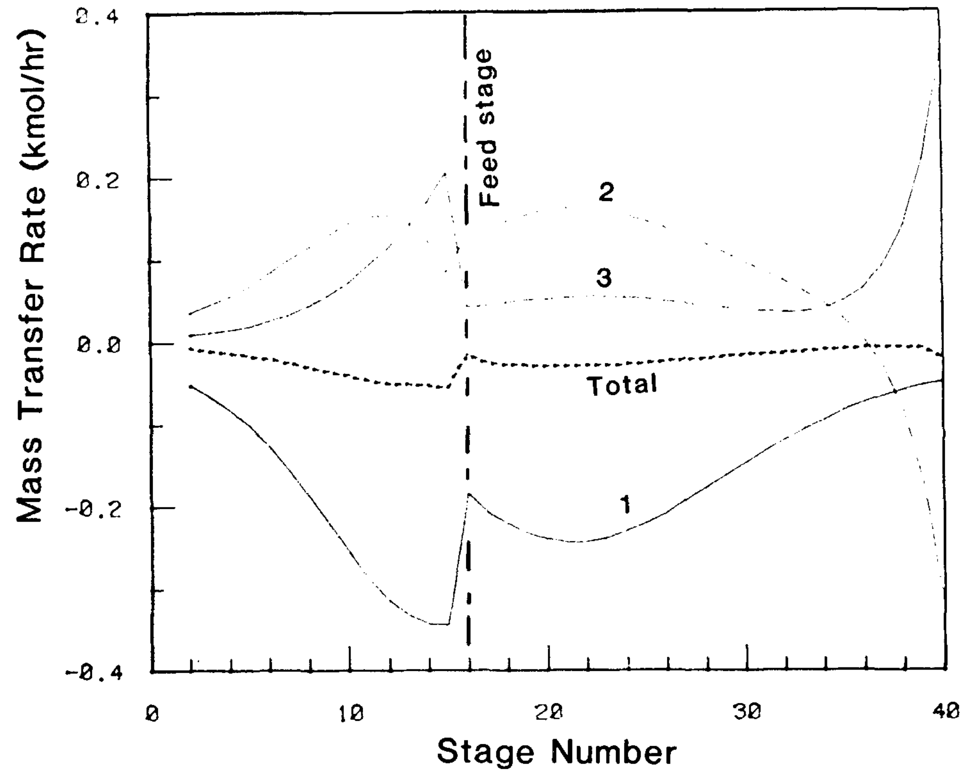

Figure 12. Transfer rate profiles for methanol (1), isopropanol (2), and water (3) system. — Component transfer rate. ---- Total transfer rate.

dicted by the equilibrium model in the rectifying section and will overpredict in the stripping section. We observe this to be the case in three examples (see Table 5 and Figures 1–3). For the hydrocarbon problem, the composition profiles predicted by the two models are almost identical in the upper part of the column, while below the feed stage the trend is opposite to what is stated above. The liquid phase resistance is less important in this system.

The influence of the diffusional interaction effects is much more complex and it cannot be determined a priori whether the neglect of these effects will lead to overprediction or underprediction of the number of stages for a given separation. Interaction effects can cause the component efficiencies to be widely different as shown in the efficiency plots (Figures 5–8). Notice that for the hydrocarbon system where the components are of similar nature, the component efficiencies are much closer to each other. The large deviations between values of the component efficiencies on some stages are due to the presence of a feed or a stage on which one of the intermediate components goes through a maximum in its composition profile. Diffusional interaction effects are more important on these stages, as the driving force of the intermediate component changes sign. Component efficiencies outside the (0,1) interval occur at the stage where this happens.

Because of the complicated manner in which diffusional interactions affect each component, the transfer rates predicted by the model that takes them into consideration may be greater than or less than the corresponding rate predicted using a constant component efficiency. If the transfer rate of the more volatile component is lower, then diffusional interaction effects complement the effect due to liquid phase resistances; if greater, the two effects may be compensatory. The variation in the magnitude of the diffusional interactions from stage to stage may cause the two effects to be complementary over some stages and compensatory over other stages. The observed difference in the final results of the two models (II and III) is a cumulative sum of the net effect on all stages.

In the operating problems we found a maximum difference in compositions predicted by methods II and III on any stage to be about 7 mol% and, for the top stage (considering the terminal composition that is used as a specification), to be about 4 mol% (Table 5). These seemingly small discrepancies may translate into a difference of more than 50% in terms of stages for a given separation, as we noted earlier. Discrepancies in compositions may be of greater importance when side stream products of a desired purity are required.

In order to isolate the effects of diffusional interactions on process design from other effects, it is best to compare the results of methods III and IV. In method IV, all binary pair mass transfer coefficients are set to an average value and, hence, diffusional interactions are neglected in this formulation of the nonequilibrium model. All other effects—liquid phase resistance, for example—are handled in a similar manner by both methods. The results of the design problems (Table 4) indicate a maximum difference of about 15% (method IV is the basis here) in number of stages required (acetone-methanol-water system, problem 2). The differences for the other nonideal systems are around 10%. Not surprisingly, there is a negligible difference of only one stage for system 4; interaction effects are virtually nonexistent for this system. An analysis of the results of the equal diffisivity formulation of the nonequilibrium model (method IV) leads to another interesting observation. For a vapor-phase controlled distillation, the component efficiencies must all be equal and, indeed, this is found to be the case. However, if the liquid phase resistance is taken into account, the component efficiencies (Murphree vapor efficiency) backed out from the results of a simulation need not be equal. The reason for this is that the liquid phase resistance shifts the interface equilibrium, with the result that the thermodynamic limit for the vapor is the interface composition and not the vapor composition in equilibrium with the bulk liquid (as it would be if there were no liquid phase resistance). Widely different component efficiencies observed on several stages and efficiencies outside the range (0,1) are also found to be due to the different volatilities of the various species. An implication of this finding is that caution must be exercised in interpreting experimental results. Unless negligible liquid phase resistance and minimal liquid mixing effects are insured, measured efficiencies outside the range (0,1) cannot be attributed to diffusional interactions alone.

Figures 5–8 illustrate the gross fluctuations in the component efficiencies. It must be remembered that these results are predicted by our nonequilibrium model. However, it should also be recognized that such behavior has been observed experimentally; Figures 10 and 11 show the component efficiency plots for two experiments conducted by Vogelpohl (1979) with the systems acetone-methanol-water and methanol-isopropanol-water. Vogelpohl presents similar figures to illustrate that component efficiencies may indeed be widely different and unbounded. Note that it is probably safe to assume vapor-phase control in these experiments (Vogelpohl, 1979; Krishnamurthy and Taylor, 1984b).

An approximation sometimes considered in the analysis of multicomponent distillation (Toor and Burchard, 1960; Dribika and Sandall, 1979) is to assume equimolar overflow; this assumption eliminates the need to use the energy balance at the interface. In order to test the validity of this assumption, the component and total transfer rate profiles for the methanol-isopropanol-water system are shown in Figure 12. It is seen that the total transfer rate is close to zero over the entire column. The discrepancy from the equimolar countertransfer condition is very small over the entire column; the largest departures from $N_t = 0$ occur only around the feed stage or where the intermediate component goes through a maximum in its composition profile. This has been found to be the case for the other systems as well. We do not conclude from these results that the assumption of equimolar overflow is necessarily a good one; simply that it would be a good assumption for the examples discussed in this paper.

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NOTATION

a = interfacial area, m^2
$[\mathcal{B}]$ = matrix of inverse mass transfer coefficients, m^{2}s/kmol
c = number of components
D = liquid phase binary diffusion coefficient, m^2/s
$\mathcal{D}$ = vapor phase binary diffusion coefficient, m^2/s
F_f = F-factor, product of gas flow rate per unit bubbling area and square root of gas density, kg$^{1/2}$·m$^{-1/2}$·s^{-1}
G = vapor flow rate, kmol/s
$[I]$ = identity matrix
$\mathscr{k}$ = binary mass transfer coefficient, kmol/m^2·s
k = multicomponent mass transfer coefficient, kmol/m^2·s
K = equilibrium ratio
L = liquid flow rate, kmol/s
L_F = volumetric liquid flow rate per unit average liquid-flow-path width, m^2/s
$\mathcal{N}$ = mass transfer rate, kmol/s
t_L = average liquid contact time, s
W = weir height, m
x = liquid phase composition
y = vapor phase composition
Z_C = liquid hold-up on tray, m
Z_L = average liquid-flow-path width, m

Greek Letters

γ = activity coefficients
$[\Gamma]$ = matrix of thermodynamic factors
δ = Kronecker delta
η = efficiency
ρ = density, kmol/m^3
μ = viscosity, kmol/ms
$[\theta]$ = liquid phase rate factor matrix, defined in Eq. 6
$[\Phi]$ = vapor phase rate factor matrix
$[\Xi]$ = matrix of finite flux correction factors

Subscripts

i,k = component number
t = total
m = mixture property

Superscripts

I = interface
L = liquid phase
V = vapor phase

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