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# Study on the Dynamic Behavior of Unequal Molal Overflow Distillation Columns with an Approach of Pseudo-Equal Molal Overflow

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## Abstract

A study is carried out to investigate the dynamic behavior of distillation columns with unequal molal overflow, both theoretically and experimentally. For the theoretical study, an approach is taken to transform the unequal molal overflow distillation system into a pseudo-equal molal one, which is then used to develop dynamic equations representing unequal molal overflow distillation columns. For the experimental study, the acetone-water binary system is chosen, and the transient response in temperature of a 11-plate bubble cap distillation column to step disturbances in the reflux rate is measured. Comparison of experimental results with theoretical predictions shows that the pseudo-equal molal overflow approach gives a reasonably satisfactroy prediction. which is superior to that made by the dynamic equations based on the as sumption of constant (or equal) molal overflow. The results of the present study therefore indicate the feasibility of extending the pseudo-equal molal overflow approach to multicomponent distillation systems.

## 1. Introduction

Much has been discussed in the literature about the dynamic behavior of distillation columns. In recent years, the advent of large, high speed computers has made it possible to solve a large set of system equations for distillation columns. However, the sheer magnitude of the computations and the complexity of the analysis involved have often hampered the practical use of better and more sophisticated models in the application of modern control principles. Various simplifying assumptions have been made in system-models to reduce the computational work and to make the problem more manageable. A common and important assumption among them is constant (or equal) molal overflow.

The great advantage of a constant molal overflow model over an unequal molal overflow one is that the energy balance equations no longer have to be considered in the analysis. This may be clearly seen from the fact that both the McCabe-Thiele and Panchon-Savarit methods give identical results for a binary distillation system which is truly constant molal overflow. The validity of dynamic models based on the constant molal overflow assumption has been investigated by several authors. Notable among them are Armstrong and Wilkinson (1), Baber and Gerster (2, 3), and Luyben et al. (4). It should be noted that the experimental systems in these studies were so chosen that they exhibit nearly constant molal overflow.

However, in many instances, unequal molal overflow prevails and it raises serious doubts about the validity of an equal molal overflow model

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*Dept. of Chem. Eng., pol. Inst. of Brooklyn describing such a system. Mickley, Gould and Schwartz (5) have noted an appreciable deviation between the frequency response predicted with the above assumption and the true response of an unequal molal overflow system. In these cases we have a net rate of condensation on a tray which is dependent on the vapor and liquid compositions. The flow dynamics of each tray is different because of this interaction and it has to be characterized by the enthalpy balance equations. Huckaba, May and Franke (6, 7) have considered such models, assuming a linear enthalpy-concentration relation. This work is supported by experimental analysis of the methanol-tertiary butyl alcohol system which exhibits an unequal molal overflow. The models proposed by Rosenbrock (8), and Williams, Harnett and Rose (9), take into account enthalpy balances and can be used to describe unequal molal overflow behavior. But, apart from the difficulty of obtaining the enthalpy-concentration relations, we encounter in the unequal molal overflow models a larger number of equations than in the constant molal overflow models.

It would therefore desirable to find a method, which, under reasonable assumptions, would permit one to treat the original unequal molal overflow system as an 'apparently' constant (or equal) molal overflow one. One such method was suggested earlier by Peters (10) and later by Robinson and Gilliland (11), and is referred to as the pseudo-equal molal overflow approach. The essence of this technique is to transform the composition and flow variables of a truly unequal molal overflow system into the pseudo-equal molal quantities, thus permitting one to deal with a new set of system equations, essentially of the same form as those of a truly constant molal overflow system. The advantages of using such transformed variables are as follows.

First, the interactions between the composition and flow variables are properly taken into account in the system equations instead of being neglected. This enhances the possibility of further simplifying the computations by linearizing the system equations about a steady-state. The severe limitations on the range of allowable perturbations, when using a constant molal overflow model to describe a truly unequal molal overflow system, have been mentioned by Mickley, Gould and Schwartz (5). These restrictions are attributed to the interaction of composition and flow variables.

Secondly, the dynamic models and controls developed for a truly constant molal overflow system would be directly applicable to the transformed pseudo-equal molal overflow system. It should be noted that the application of such a method to multicomponent distillation systems would be much more significant than the binary systems. This is because, in multicomponent systems, the enthalpy-concentration data may not be as readily available as in binary systems, and the number of system equations to be dealt with vastly increases as the number of components increases.

In the present study the pseudo-equal molal overflow approach has been taken to investigate the dynamic behavior of unequal molal overflow systems of binary components. The dynamic responses of tray compositions to disturbances in the reflux rate are obtained for the acetone-water system in order to evaluate the pseudo-equal molal overflow approach as opposed to the constant molal overflow.

## 2. Psuedo-Equal Molal Overflow Approach

An essential characteristic of a constant molal overflow is that the net molal rate of condensation on a tray is equal to zero. This is attributed to the fact that the molal heat of vaporization of the liquid mixture is independant of its composition, thus causing equal rates of mass transfer between vapor and liquid. It is implied here that the molal heats of vaporization are equal for all components, the non-ideal effects of heat of mixing being neglected. The enthalpy-concentration diagram in this case has a set of two parallel straight lines: the bubble-point line and the dew-point line.

On the other hand, an unequal molal overflow exhibits non-parallel lines (or curves) in the enthalpy-concentration diagram, due to the differences in the latent heats of individual components of the mixture.

We can make these lines parallel and straight by assigning a pseudo-molecular weight to each component-the true molecular weight of a component weighted by its true molal heat of vaporization-such that the heats of vaporization based on the pseudo-molecular weights are equal to one another.

As shown by Robinson and Gilliland (11), the enthalpy content of component $i$ in the vapor stream from $n^{\text{th}}$ plate may be written as,

$$V_n Y_{ni} \varDelta H_i = \hat{V}_n \hat{Y}_{ni} \, \varDelta H_r \tag{1}$$

where $V_n$ is the true vapor flow rate from the $n^{\text{th}}$ plate; $Y_{ni}$ is the true mole fraction of component $i$; $\varDelta H_i$ is the true molal heat of vaporization of component $i$; $\varDelta H_r$ is the pseudo-molal heat of vaporization for all components, usually equal to the true latent heat of a reference component; and $\hat{V}_n$, $\hat{Y}_{ni}$ denote pseudo-molal flow rate and composition, respectively. Defining the pseudo-molal weighting factor for componet $i$ as

$$r_i = \frac{\varDelta H_i}{\varDelta H_r}$$

Equation 1 may be rewritten as

$$\hat{V}_n \hat{Y}_{ni} = V_n Y_{ni} \, r_i \tag{2}$$

The constraint on pseudo-molal composition is

$$\sum_i \hat{Y}_{ni} = 1 \tag{3}$$

Similarly for the liquid stream, we have

$$\hat{L}_n \hat{X}_{ni} = L_n X_{ni} \, r_i \tag{4}$$

and

$$\sum_i \hat{X}_{ni} = 1 \tag{5}$$

The transformation of flow rates into corresponding pseudo-molal quantities is obtained by taking a summation of Equation 2 or 4 over all components and using appropriate constraints,

$$V_n \sum_i Y_{ni} \, r_i = \hat{V}_n \tag{6}$$

$$L_n \sum_i X_{ni} \, r_i = \hat{L}_n \tag{7}$$

Combining Equations 2 and 6, and Equations 4 and 7, we obtain the transformation of composition,

$$\hat{Y}_{ni} = \frac{Y_{ni} \, r_i}{\sum_i Y_{ni} \, r_i} \tag{8}$$

$$\hat{X}_{ni} = \frac{X_{ni} \, r_i}{\sum_i X_{ni} \, r_i} \tag{9}$$

A truly unequal molal overflow, when expressed in terms of the pseudo-equal molal quantities, exhibits an 'apparently' equal molal overflow. Unlike the assumption of constant molal overflow, the interaction between composition and flow variables is not ignored here. The enthalpy balances necessary to characterize it are incorporated in the definition of pseudo-molal quantities.

The transformation relation, specified by the weighting factor $r_i$, is constant over the entire column, when the variation in the heats of vaporization of individual components, and the heat of mixing, are negligible over the given range of temperature and pressure. If these effects are appreciably large, giving a sharply nonlinear enthalpy-concentration relation, we would formulate different transformations in different sections of the column, based on the correspondingly linearized segments of the enthalpy concentration relation. After transforming the true variables into the corresponding pseudo-molal quantities, we can compute the dynamic behavior of an unequal molal overflow system, using the simplifying assumption of constant molal overflow. The dynamic behavior of the orginal system is recovered later by using the inverse relationships of Equation 6 and 7, and Equations 8 and 9.

Let us now consider a binary distillation system. The pseudo-molal transformation of composition is

$$\hat{X}_{n1}=\frac{r_1 X_{n1}}{r_1 X_{n1}+X_{n2}} \tag{10}$$

Note that component 2 is taken to be the reference component, i. e., $r_2=1$. The inverse relationship of Equation 10 is obtained as

$$X_{n1}=\frac{\hat{X}_{n1}}{r_1+(1-r_1)\hat{X}_{n1}} \tag{11}$$

The inverse relationship of deviation variables may be obtained by expanding Equation 11 in a Taylor series

$$\begin{aligned}X_{n1}=\bar{X}_{n1}&+\left.\frac{dX_{n1}}{d\hat{X}_{n1}}\right|_{\hat{X}_{n1}=\bar{\hat{X}}_{n1}}(\hat{X}_{n1}-\bar{\hat{X}}_{n1})\\&+\frac{1}{2}\left.\frac{d^2X_{n1}}{d\hat{X}_{n1}^{\,2}}\right|_{\hat{X}_{n1}=\bar{\hat{X}}_{n1}}(\hat{X}_{n1}-\bar{\hat{X}}_{n1})^2+\end{aligned} \tag{12}$$

where the overbar indicates a steady state. Defining deviation variables as

$$x_{n1}=X_{n1}-\bar{X}_{n1},\quad \hat{x}_{n1}=\hat{X}_{n1}-\bar{\hat{X}}_{n1},$$

one may rewrite Equation 12 as

$$x_{n1}=r_1\left(\frac{\bar{X}_{n1}}{\bar{\hat{X}}_{n1}}\right)^2\hat{x}_{n1}-r_1(1-r_1)\left(\frac{\bar{X}_{n1}}{\bar{\hat{X}}_{n1}}\right)^3\hat{x}_{n1}^2+\cdots \tag{13}$$

and similarly for vapor compositions, we have

$$y_{n1}=r_1\left(\frac{\bar{Y}_{n1}}{\bar{\hat{Y}}_{n1}}\right)^2\hat{y}_{n1}-r_1(1-r_1)\left(\frac{\bar{Y}_{n1}}{\bar{\hat{Y}}_{n1}}\right)^3 y_{n1}^2+\cdots \tag{14}$$

It may be seen here that the assumptiion of constant molal overflow in a truly unequal molal overflow system is, mathematically a special case of the pseudo-equal molal overflow approach. Setting $r_1=1$ in the above equations, in addition to the prodefined value of $r_2=1$, makes the pseudo-molal compositions identical to the true molal compositions. The inverse relations in Equations 13 and 14 are then reduced to trivial cases: $x_{n1}=\hat{x}_{n1}$ and $y_{n1}=\hat{y}_{n2}$.

Analogous to compositions, we can establish the inverse relationship for flow variables of a binary system as

$$l_n=\frac{\hat{l}_n}{r_1\bar{X}_{n1}+\bar{X}_{n2}} \tag{15}$$

Using the transformed values of steady state flow rates (Equation 7) in the above equation, we get

$$\frac{l_n}{\bar{L}_n}=\frac{\hat{l}_n}{\bar{\hat{L}}_n} \tag{16}$$

Similarly, for vapor flow rates we have

$$\frac{v_n}{\bar{V}_n}=\frac{\hat{v}_n}{\bar{\hat{V}}_n} \tag{17}$$

It is clear that the pseudo-molal deviations of flow rates, normalized with respect to the corresponding steady states, would give the normalized flow deviations of the original system directly.

## 3. Dynamic Model

The dynamic model of the binary system used in the present work is a greatly simplified version of that suggested by J. E. Rijnsdorp (12). The basic assumptions made here are as follows:

(a) Constant (or equal) molal overflow. (Note that the pseudo-molal approach permits one to use this assumption to evaluate dynamic behavior of an

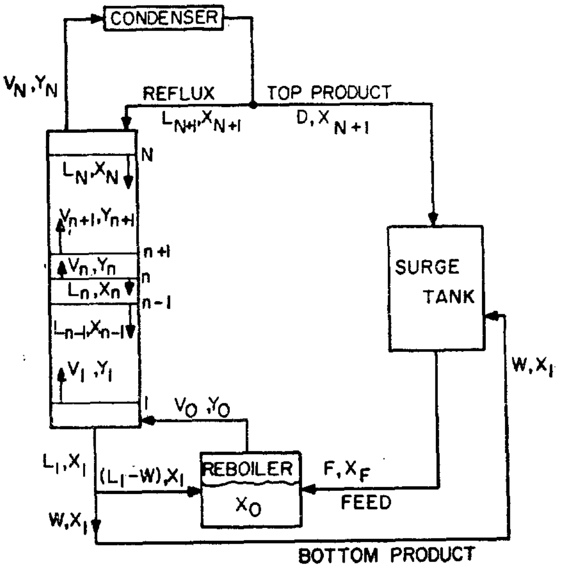


**Fig. 1** An $N$-tray distillation column with the rectification section only

unequal molal overflow system),

(b) Negligible vapor holdup,

(c) Linear vapor-liquid equilibrium,

(d) Constant pressure throughout the column,

(e) Delays in mass-transfer are neglected, i.e., equilibrium of vapor and liquid is attained instantaneously,

(f) Negligible heat losses and entrainment, and perfect mixing on each tray.

The dynamic equations are developed for an $N$-tray rectification section, as sketched in Figure 1.

### 3.1 Composition dynamics on a plate

Since there is no feed plate or side-stream draw-off, the overall material balance on the $n^{\text{th}}$ plate is

$$\frac{dM_n}{dt}=L_{n+1}-L_n+V_{n-1}-V_n \tag{18}$$

and the balance of component $i$ is

$$\begin{aligned}\frac{d(M_nX_{n,\,i})}{dt}&=L_{n+1}X_{n+1,\,i}-L_nX_{n,\,i}\\&\quad+V_{n-1}Y_{n-1,\,i}-V_nY_{n,\,i}\end{aligned} \tag{19}$$

In the following development, the subscript $i$, denoting the component $i$, is dropped, and the compositions are written as $X_n$ and $Y_n$. Multiplying Equation (18) by $X_n$ and subtracting it from Equation (19), we get,

$$\begin{aligned}M_n\frac{dX_n}{dt}&=L_{n+1}(X_{n+1}-X_n)\\&\quad+V_{n-1}(Y_{n-1}-Y_n)-V_n(Y_n-X_n)\end{aligned} \tag{20}$$

Considering small deviations about a steady state and noting that for a contant molal overflow: $\bar{L}_{n+1}=\bar{L}_n=\cdots=\bar{L}$, and $\bar{V}_{n-1}=\bar{V}_n=\cdots=\bar{V}$,
we get

$$\begin{aligned}\overline{M}_n\frac{dx_n}{dt}&=\bar{L}(x_{n+1}-x_n)+\bar{V}(y_{n-1}-y_n)\\&\quad+l_{n+1}(\bar{X}_{n+1}-\bar{X}_n)+v_{n-1}\bar{Y}_{n-1}-v_n\bar{Y}_n\end{aligned} \tag{21}$$

Assumption of constant pressure throughout the column means that the deviations in vapor flow rate entering the column are transmitted instantaneously to all the plates. Hence we have

$$v_{n+1}=v_n=\cdots=v_0 \tag{22}$$

A steady-state material balance about $n^{\text{th}}$ plate yields

$$\bar{Y}_{n-1}-\bar{Y}_n=-\frac{\bar{L}}{\bar{V}}(\bar{X}_{n+1}-\bar{X}_n) \tag{23}$$

and the deviations of vapor composition are related to the deviations of liquid composition by

$$y_n=\epsilon_n\ x_n \tag{24}$$

Using Equations 22, 23 and 24 in Equation 21 gives

$$\begin{aligned}\frac{dx_n}{dt}&=\frac{E_{n-1}}{T_{x_n}}x_{n-1}-\frac{(1+E_n)}{T_{X_n}}x_n\\&\quad+\frac{1}{T_{X_n}}x_{n+1}+\left(\frac{l_{n+1}}{\bar{L}}-\frac{v_0}{\bar{V}}\right)\frac{(\bar{X}_{n+1}-\bar{X}_n)}{T_{X_n}}\end{aligned} \tag{25}$$

where

$$E_n=\epsilon_n\frac{\bar{V}}{\bar{L}};\ \ T_{X_n}=\frac{\overline{M}_n}{\bar{L}}$$

It should be noted that Equation 25 may be used to calculate the dynamic responses of both the constant molal and pseudo-equal molal overflow systems with coefficients $E_n$, $E_{n-1}$, $T_{X_n}$ for the former and $\hat{E}_n$, $\hat{E}_{n-1}$, $\hat{T}_{X_n}$ for the latter. In other words, only the numerical values of the coefficients associated with Equation 25 would be different in either case. Note further that the initial conditions of the variables: $x_n$ and $l_n$ also have to be converted into those for the pseudo-equal molal basis, i.e., $\hat{x}_n$ and $\hat{l}_n$.

Once the response of the deviations of pseudo-molal variables is obtained, the response of the original unequal molal overflow system is regenerated by use of Equations 13 and 15. The accuracy of this inversion may be improved by considering a larger number of terms in Equation 13. On the other hand, the constant molal overflow approach takes the computed response from Equation 25 directly. Thus the essence of the pseudo-equal molal approach lies in the transformed coefficients and the subsequent inversion.

### 3. 2 Top plate and condenser

We have no reflux accumulator, referring to Figure 1. Neglecting the delays in the condenser we can relate the deviation of reflux composition to that on the top ($N^{\text{th}}$) plate as

$$x_{N+1}=y_N=\epsilon_N x_N \tag{26}$$

Accordingly, Equation 25 is modified as

$$\begin{aligned}\frac{dx_N}{dt}&=\frac{E_{N-1}}{T_{XN}}x_{N-1}-\frac{(1+E_N-\epsilon_N)}{T_{XN}}x_N\\&+\left(\frac{l_{N+1}}{\bar{L}}-\frac{v_0}{\bar{V}}\right)\frac{(\bar{X}_{N+1}-\bar{X}_N)}{T_{XN}}\end{aligned} \tag{27}$$

### 3. 3 Reboiler

Here the feed enters the reboiler and the bottom product is withdrawn at a point between bottom plate and reboiler. The dynamic equation for the reboiler may be written as

$$\begin{aligned}\frac{dx_0}{dt}&=-\frac{\epsilon_0\bar{V}_0}{M_0}x_0+\frac{(\bar{L}_1-\bar{W})}{M_0}x_1+\frac{\bar{F}}{M_0}x_F\\&+\frac{(l_1-w)}{M_0}(\bar{X}_1-\bar{X}_0)-\frac{v_0}{M_0}(\bar{Y}_0-\bar{X}_0)\\&+\frac{f}{M_0}(\bar{X}_F-\bar{X}_0)\end{aligned} \tag{28}$$

where the subscript zero refers to the reboiler.

### 3. 4 Surge tank

The dynamics of feed composition in the surge tank is written as

$$\begin{aligned}\frac{dx_F}{dt}&=\frac{\bar{D}}{V_H}(x_{N+1}-x_F)+\frac{\bar{W}}{V_H}(x_1-x_F)\\&+\frac{d}{V_H}(\bar{X}_{N+1}-\bar{X}_F)+\frac{w}{V_H}(\bar{X}_1-\bar{X}_F)\end{aligned} \tag{29}$$

### 3. 3 Propogation of flow rates

In a model based on 'apparently' constant molal overflow, the pseudo-molal rates of evaporation and condensation on a given plate are equal and independent of composition. In other words, the pseudo-molal flow rates are independent of composition. Hence, the dynamic equation for liquid flow rate may be written as

$$\frac{dM_n}{dt}=L_{n+1}-L_n \tag{30}$$

which may be rewritten in terms of deviation variables:

$$T_1\frac{d(l_n/\bar{L})}{dt}=\frac{l_{n+1}}{\bar{L}}-\frac{l_n}{\bar{L}} \tag{31}$$

where $T_1=\left(\frac{\partial M_n}{\partial L_n}\right)_{\bar{M}n}$, which is the liquid cascade time constant.

In the above equation, normalized flow variables are used so that a transformation of flow rates into pseudo-molal quantities is not required, as indicated by Equation 16. It would also circumvent an experimental error in the flows measured at steady states, introduced by a change in rotameter calibration with different densities of liquid streams at different steady stsates.

## 4. Experimental work

In the present study, column dynamics is obtained for a binary system since it is easier to handle, both theoretically and experimentally. The dynamics of the experimental system is then compared with those calculated with pseudo-equal molal and equal molal approaches.

The acetone-water system is chosen for the following reasons:

(a) The difference in molal heats of vaporization of acetone and water guarantees an unequal molal overflow.

(b) Enthalpy-concentration lines for this system are only weakly nonlinear, i. e., the heat of mixing is indeed small and can be neglected. This satisfies the assumptions set forth earlier in presenting the pseudo-equal molal approach.

(c) The vapor-liquid equilibrum exhibits reasonably linear segments, over which the experimental column may be operated. This is not essential for the verificaton of the pseudo-equal molal approach, but it provides an additional simplification for the calculation of theoretical response.

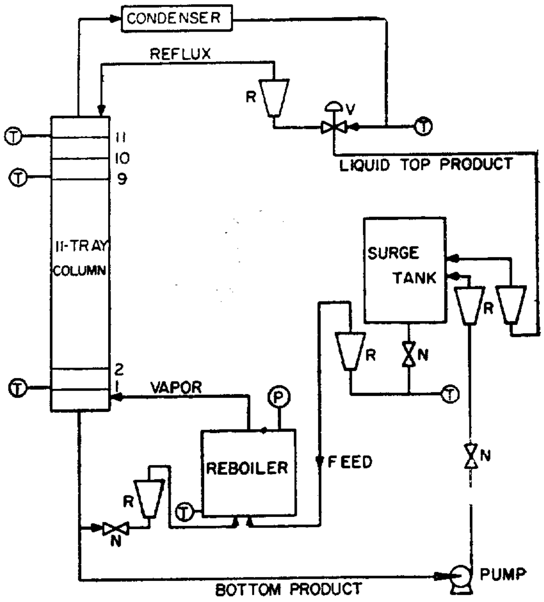
Figure 2 shows a schematic of the distillation column, together with the measurement devices installed in it. As may be seen, there are no sidestream drawoffs or feed plates provided in the column. The feed enters into the reboiler, with the column being operated as a rectifier. Details of the column speccifications are given in Table 1.

**Table 1. Specifications of Distillation Column**

| | |
|---|---|
| **Column** | |
| No. of plates: 11 | Single crossflow type |
| Column I. D.: 9 in. | Plate spacing: 6 in. |
| No. of bubble cap per tray =3 | pitch: $3\frac{1}{2}$in. triangular |
| Cap dia=$2\frac{1}{4}$ in. | cap height=$1\frac{1}{2}$ in. |
| slot width=1/8 in. | slot height=9/16 in. |
| Riser height=1 in. | Riser diam. =$1\frac{1}{4}$ in. |
| Circular Weir diam. | Weir height=$1\frac{1}{4}$ in. |
| =$1\frac{1}{4}$ in. | downcomer clearence=3/8 in. |
| **Reboiler** | |
| Diam. =24 in. | Length=22 in. |
| Electrical Heaters | total rates capacity=20 kw. |

The reflux accumulator is avoided to minimize reflux delays. A three-way diverting valve, coupled with an electropneumatic transducer, is used as a reflux divider. Products from the column are sent to the surge tank and are mixed there to serve as feed. Holdup in the surge tank is maintained large enough to dampen the dynamic changes in the total composition of the product streams. Liquid flow rates are measured for product streams, reflux, and feed. Thermocouples are installed at the top, bottom and 9th plate, and at the locations shown in Figure 2.

Temperature measurement is the most critical in this experiment. Liquid compositions are estimated from temperatures. Due to the peculiar nature of the acetone-water boiling point diagram, large changes in composition would produce a relatively small change in temperature. For this reason, the thermocouples are connected to an "Acromag" Transmitter to amplify the electrical signal and pick up any small variations of temperature. This circuit provides a resolution power of about $\pm 0.1$°F.



N—Needle Valve P—Pressure Gauge
R—Rotameter T—Thermocouple
V—3-WAY Diverting Valve

Fig. 2 Schematic diagram of the experimental system

The system was first operated at a steady state, with a desired reflux ratio. The steady state holdup in the surge tank was maintained large enough to ensure about 80-90 minutes delay in the flow line. Hence the system could be approximated as an open flow one, since the transient response takes about 20 minutes. With some trial and error, the cooling water rate was adjusted to restrict the condensate subcooling to within 5°C. The vapor and trapped air were purged from time to time to maintain a constant pressure in the system.

The liquid flow rates from and to the column were measured directly, and the vapor generation rate was estimated from the electrical heat input into the reboiler. Assuming the liquid on every plate to be at boiling point, compositions on the top, $9^{th}$ plate, bottom plate, and reboiler were determined from the respective temperature readings. The entrie steady-state composition profile in the column was calculated, estimating the plate efficiency values to give a proper fit at measured points.

A step disturbance was introduced in the reflux rate and the change in temperature at any one of the top, $9^{th}$ and bottom plates were read on a slow speed recorder.

## 5. Results and Discussion

Figure 3 shows the enthalpy-concentration diagram for acetone-water mixture (Eduljee et al., (13)). Here the molal heats of vaporization were obtained by extrapolation of the linear segments of the diagram as:

$$\Delta H_{acetone}=7200 \text{ cal/gmole}; \Delta H_{water}=9650 \text{ cal/g mole}.$$

Water is taken to be the reference component. Hence the pseudo-equal molal weighting factors used in transformations were

$$r_{water}=1; \quad r_{acetone}=0.745.$$

Using the composition transformations (quations 8 and 9), the vapor-liquid equilibrium was replotted in terms of pseudo-equal molal quantities, as in Figure 4. The equilibrium relation was approximated by four linear segments, and straight lines were fitted by the least squares method. These results are given in Table 2.

Experiments were carried out for a wide range of perturbations in the reflux rate, varying up to 42 percent of the initial rate. Table 3 lists, for a few such typical runs, the steady state flow rates and temperatures at the top, $9^{th}$ and bottom plates. There are necessary to generate the initial steady state composition profile and the model coefficients.

**Table 2. Approximated Equilibrium Curves**

| True Equilibrium | | Pseudo-molal Equilibrium | |
|---|---|---|---|
| (1) $Y=15.93X$; | $X\leq 0.04285$ | $\hat{Y}=18.23\hat{X}$; | $\hat{X}\leq 0.034$ |
| (2) $Y=0.829X+0.65$; | $0.04285<X\leq 0.1857$ | $\hat{Y}=1.154\hat{X}+0.584$; | $0.034<\hat{X}\leq 0.1588$ |
| (3) $Y=0.1342X+0.7854$; | $0.1857<X\leq 0.7857$ | $\hat{Y}=0.1625\hat{X}+0.7416$; | $0.1588<\hat{X}\leq 0.7886$ |
| (4) $Y=0.557X+0.443$; | $0.7857<X\leq 1.0$ | $\hat{Y}=0.616\hat{X}+0.384$; | $0.7886<\hat{X}\leq 1.0$ |

**Table 3. Experimental Runs for the Acetone-Water Distillation System**

| | Run Number | | | | | | |
|---|---|---|---|---|---|---|---|
| | P1 | P2 | P3 | T1 | T2 | B1 | B2 |
| Reboiler holdup, $M_0$, (Kg moles) | 2.916 | 2.73 | 2.92 | 2.93 | 2.56 | 3.12 | 2.95 |
| Surge tank holdup, $V_H$, (ft$^3$) | 2.1 | 2.1 | 3.0 | 2.1 | 2.1 | 2.1 | 2.1 |
| Boil-up rate, $V_0$, (Kg moles/min) | 0.0231 | 0.0231 | 0.0231 | 0.231 | 0.0231 | 0.0231 | 0.231 |
| Top product rate, $\bar{D}$, (gpm) | 0.21 | 0.21 | 0.21 | 0.19 | 0.16 | 0.19 | 0.16 |
| Reflux rate, $\bar{L}_{N+1}$, (gpm) | 0.21 | 0.22 | 0.21 | 0.21 | 0.18 | 0.22 | 0.21 |
| Temp. of liquid, (°C): | | | | | | | |
| top plate | 58.0 | 59.0 | 57.9 | 58.7 | 60.5 | 57.9 | 58.8 |
| $9^{th}$ plate | 60.2 | 62.0 | 60.9 | 74.0 | 85.2 | 60.9 | 75.0 |
| bottom plate | 79.5 | 82.2 | 79.7 | 85.0 | 87.3 | 83.0 | 84.1 |
| reboiler | 79.8 | 82.9 | 79.9 | 88.5 | 88.1 | 85.9 | 85.2 |
| refluxs tream | 51.8 | 53.1 | 52.0 | 52.3 | 52.7 | 51.5 | 52.9 |
| Average plate efficiency (percent) | 80.0 | 80.0 | 80.0 | 85.0 | 85.0 | 80.0 | 85.0 |
| Disturbance in reflux rate $\frac{l_{N+1}}{\bar{L}_{N+1}}$ | 0.15 | 0.25 | 0.428 | 0.262 | 0.143 | 0.419 | 0.143 |
| Secondary disturbance in feed rate $\frac{f}{F}$ | −0.013 | −0.09 | −0.12 | −0.073 | −0.028 | −0.25 | −0.079 |

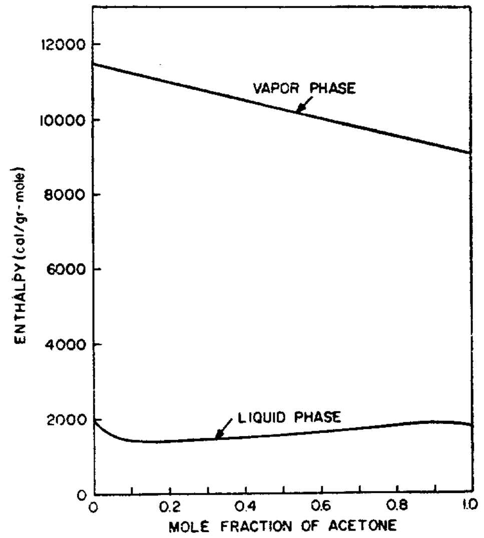


**Fig. 3** Enthalpy-concentration diagram for the acetone-water binary system

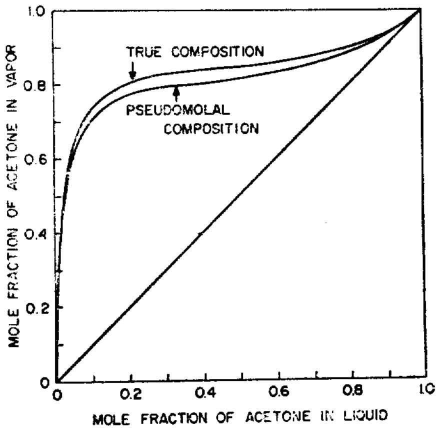


**Fig. 4** Vapor-liquid equilibrium for the acetone-water binary system

No bottom product is withdrawn in any of these runs.

A secondary distrbance in the input feed rate was observed, as the pressure-change associated with a reflux perturbation was transmitted to the surge tank (feed tank). This secondary distrubance was approximately of the form of a step change and was considered as an additional input perturbation, occurring simultaneously with the primary perturbation in the reflux rate. The time lag between these two inputs was only a few seconds and can be safely neglected in the computation of the transient. Also, the pressure deviations were observed to be less than $\pm\frac{1}{2}$ psi. and their effect on the heats of vaporization and the vapor-liquid equilibrium was considered insignficant.

Figure 5 compares the responses observed at the 9th plate, with those predicted by the equal (constant) molal and the pseudo-equal molal approaches. It may be seen that up to 20 percent change in the reflux rate, the predictions of the pseudo-molal approach fit the experimental results closely. For a large perturbation, the pseudo-molal response deviates from the true one. However, it provides a better approximation of the real system than the equal molal overflow. In this case, we have probably exceeded the validity range of the linearized model.

The responses at the top plate are shown in Figure 6, and those at the bottom plate in Figure 7. The computed responses involve some inaccuracies. For the top plate, the entering reflux is subcooled about 5°C at the initial steady state. The deviation from equilibrium of the vapor and liquid phases on this plate is accounted for by an efficiency factor, which

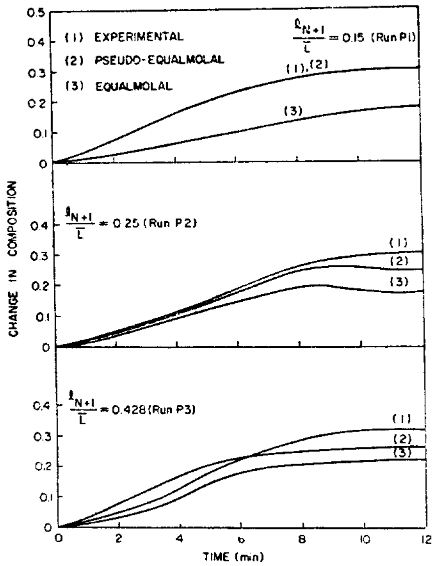


**Fig. 5** Transient responses at 9th plate to a step change in the reflux rate (Runs P1, P2 and P3).

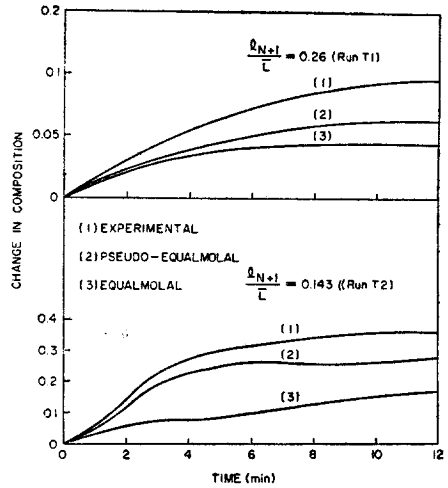


**Fig. 6** Transient responses at top plate to a step change in the reflux rate (Runs T1 and T2).

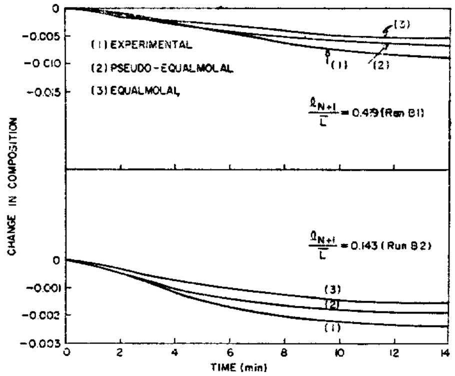


**Fig. 7** Transient responses at bottom plate to a step change in the reflux rate (Runs B1 and B2).

is subject to change as the subcooling changes during the transient. The variation of the efficiency of the top plate is not precisely known and it is assumed to be constant throughout the transient. The subcooling would also affect the internal reflux rate, but this effect would be small because the subcooling is small and hence it can be neglected.

Considering the bottom plate, nearly all the plates in the lower half of the column lie in a pinch zone. Any small errors in the estimation of the steady state profile and the model coefficients would be magnified in the dynamics, because of the extreme sensitivity of vapor compositions to small changes in liquid composition in this region, i. e., the slope of the equilibrium line is high in this range of composition.

However, these responses are useful for establishing the trend of the differences between the equal molal and the pseudo-equal molal approaches. The responses of the 9th plate (Figure 5) are the most reliable among the three. The temperature on this plate is closer to the boiling point because the effect of subcooling is attenuated by the vapor-liquid contact on the two plates above. Also this plate is away from the pinch, thus ensuring that there is a sufficiently large mass transfer-driving force to absorb the errors in the estimation of the steady state profile.

In evaluating the model, it is not necessary to especially consider the change in the molal vapor generation rate with a dynamic change in the reboiler composition. For the pseudo-equal molal approach, water is taken to be the reference compoent. This makes the pseudo-molal heat of vaporization of the mixture equal to that of water, independently of the composition. Correspondingly, in the equal molal overflow approach, the vapor generation rate is based on the heat of vaporization of water, independently of composition. Such an assumption is implicit in equal molal overflow, and it holds for the real system used here because the acetone composition in the reboiler never exceeds 3 mole percent.

The responses predicted by the equal molal overflow approach are smaller in magnitude than the true responses, as they are based on the component having the higher boiling point. Calculations based on the heat of vaporization of acetone would produce results correspondingly larger in magnitude than the true ones.

The steady state composition profile is generated for both the approaches from the knowledge of the reflux ratio and temperatures (compositions) at different points of the column. The plate efficiencies are estimated so as to give a proper fit of the compositions at the measured points. Assuming constant efficiencies throughout the transient, an effective equilibrium relation-corrected for steady state efficiencies-is used for calculating the dynamic responses.

The aforementioned model is a set of linear ordinary differential equations. The coefficients of the flow equations are constant, whereas those of the composition equations depend on the slope of the equilibrium line and would vary in 'steps' with time, depending upon the linear segment of the equilibrium line in effect at that plate at that time. This initial value problem is solved by the Adams-Modified Predictor-Corrector technique, with the fourth order Runge-Kutta scheme to obtain a starting solution. The IBM Scientific Subroutine Package provides a Fortran routine to solve a system of linear differential equations with time varying coefficients. This routine was slightly modified here to suit the present model.

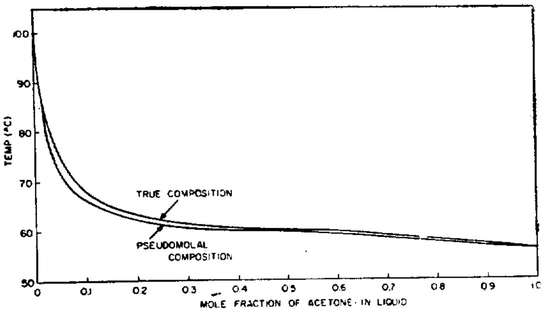
The response of the original system can be obtained from the pseudo-equal molal quantities by the use of Equation 13, which would regenerate the unequal molal overflow nature of the system. An alternative method-simpler and feasible for binary system-was used here in order to obtain a temperature response, using the boiling temperature-pseudo-equal molal composition relation-shown in Figure 8. The compositions of the original system are recovered by an inverse interpolation with the normal boiling point-real composition curve. In effect, such a method would account for the entire right-hand side of Equation 13, eliminating truncation errors.

Finally, the cascade time constant $T_l$ in Equation 31 is obtained from the correlation for flow over a circular weir (McCabe and Smith, (14)). Note that the time constant $T_l$ is a function of the weir and plate specifications, and the steady state volumetric flow rates. Hence it would remain unchanged in both equal molal and pseudo-equal molal approaches.

## 6. Conclusions

The dynamic response of an unequal molal overflow system, predicted by a linearized constant molal overflow model, is observed to deviate appreciably from the true response. These differences can be attributed to the interaction of flow and composition variables, which needs to be characterized by enthalpy balances. An unequal molal overflow system can be transformed into one with an 'apparently' constant (or equal) molal or the pseudo-equal molal overflow, under certain assumptions such as linear enthalpy-concentration relations. Such an approach does not ignore the interaction of flow and composition variables-a characteristic of unequal molal overflow. Dynamic models and controls, available for constant molal overflow cases, which have computational simplicity, can be used directly for the transformed system.

This study demonstrates the usefulness of the pseudo-equal molal approach for studying the dynamic behavior of a truly unequal molal overflow system. Although the experimental verification, carried out here, is for a binary system, the concept of pseudo-equal molal overflow can be readily extended to more complex, multicomponent systems where the subsequent simplification in computation and analysis can be very significant.



Feg. 8 Boiling temperature-liquid composition relation for the acetone-water binary system

## Nomenclature

$A$=Plate area

$D$=Top product withdrawl rate, moles/min

$d=D-\overline{D}$, deviation variable

$E_n=\epsilon_n\frac{\bar{V}}{\bar{L}}$, a parameter of $n^{th}$ plate

$F$=Feed rate, moles/min

$F=F-$, $\bar{F}$deviation variable

$\Delta H_i$=Molal heat of vaporization of component $i$

$\Delta H_r$=Molal heat of vaporization of the reference component

$L_n$=Liquid flow rate from $n^{th}$ plate, moles/min

$l_n=L_n-\bar{L}_n$, deviation variable

$l_{N+1}=L_{N+1}-\bar{L}_{N+1}$, reflux perturbation

$L_{N+1}$=Reflux rate, moles/min

$M_n$=Liquid holdup on $n^{th}$ plate, moles

$M_0$=Liquid holdup in reboiler, moles

$q_1$=Liquid flow rate, $ft^3$/min

$r_i=\frac{\Delta H_i}{\Delta H_r}$, pseudo-molal weighting factor for component $i$

$T_1=\left(\frac{\partial M_n}{\partial L_n}\right)_{\bar{M}_n}$, liquid cascade time constant, min.

$T_{xn}=\frac{\bar{M}_n}{\bar{L}_n}$, liquid holdup time constant for plate $n$, min.

$V_H$=Liquid holdup in surge tank, moles

$V_n$=Vapor flow rate from $n^{th}$ plate, moles/min

$v_n=V_n-\bar{V}_n$, deviation variable

$V_0$=Vapor generation rate, moles/min

$v_0=V_0-\bar{V}_0$, deviation variable

$W$=Bottom product withdrawl rate, moles/min

$w=W-\bar{W}$, deviation variable

$X_{ni}$=Liquid composition on $n^{th}$ plate, mole fraction of component $i$

$x_{ni}=X_{ni}-\bar{X}_{ni}$, deviation variable

$X_F$=Feed composition, mole fraction of component $i$

$x_F=X_F\bar{X}_F$, deviation variable

$Y_{ni}$=Vapor composition on $n^{th}$ plate, mole fraction of component $i$

$y_{ni}=Y_{ni}-\bar{Y}_{ni}$, deviation variable

### GreekLetters

$\epsilon_n$=Slope of equilibrium line at $n^{th}$ plate

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