Continuous Foam Fractionation: the Effect of Operating Variables on Separation

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Continuous foam fractionation has a great deal of promise as a chemical engineering separation technique; however more information is needed concerning the effect of operating variables upon the separation which may be obtained. An experimental investigation is presented of the influence of temperature, of liquid residence time, and of the position of feed introduction upon the foam fractionation of the ethylhexadecyldimethylammonium bromide-water system. The study involves three series of experiments and ninety foam separation runs. For a given air rate and feed stream concentration and rate, the drain stream concentration and rate increase linearly with temperature and the foam concentration and enrichment ratio are increasing functions of temperature. Equations derived from a multiple linear regression analysis enable the calculation of the drain stream concentration and rate from the feed concentration, air rate, and temperature.

Based upon experiments involving the variation in liquid residence time by two methods, changes in solution height have no influence upon the separation, indicating the rapid achievement of equilibrium. Changes in feed rate and air rate show that the volume of air employed per unit volume of feed treated is a prime variable affecting the separation.

Positioning the feed inlet at the solution-foam interface, compared with feeding into the solution, provides a significant increase in drain rate and decrease in drain concentration. Moving the feeder higher into the column of foam results in a continued decrease in drain concentration, but in the passage of the drain rate and foam concentration through maximum values at a height corresponding to approximately the midpoint of the column of foam.

Chemists, biologists, and engineers have used batch foam fractionation as a technique for the separation of liquid mixtures. Studies by Rogers et al. (*10, 14*) have been concerned with the transfer of surface-active organic solutes which have little or no foaming ability by the addition of foaming agents. Bacterial spores and vegetative cells have been separated and concentrated with a foaming process by Boyles and Lincoln (*3*). Kevorkian and Gaden (*13*) have conducted foaming studies on aqueous isobutanol solutions. The two major engineering applications of continuous foam fractionation have been the concentration of radioactive metal ions from aqueous solutions and the treatment of secondary sewage effluents. The separation of strontium and radium ions has been investigated by Schoen, et al. (*17, 18*) and by Gaden et al (*7*). Rubin and Everett (*15*) and Elidib (*5*) have reported on the removal of alkyl benzene sulfonate and chemical oxygen demand from secondary sewage effluents. The behavior and applications of foams in chemical technology have been discussed by Gaden and Kevorkian (*6*), and Bikerman (*2*) has made an extensive study of the theory and industrial applications of foams prior to 1953. A monograph by Schoen (*16*) dealing with new chemical engineering separation techniques contains an extensive review by Rubin and Gaden on foaming processes.

In spite of the large number of investigations which have been carried out, to date only a limited amount of work has been concerned with determining the significant operating variables and their effect on the separation obtained from a continuous foaming process. Kevorkian (*12*) studied the foam fractionation of aqueous solutions of Areskat-300, an anionic foaming agent, and was concerned with the influence of gas rate, gas bubble size, and foam column height and diameter on the separation of solutions of varying concentrations. Areskat-300 was also used by Brunner and Lemlich (*4*), who reported on the effect of foam reflux. Grieves et al. (*8, 11*) investigated the influence of gas rate and liquid feed rate on the fractionation of aqueous solutions of two anionic detergents, alkyl benzene sulfonate and dodecyl sodium sulfate. Batch data were obtained, and an equilibrium function was determined which could be used to predict the separations obtained from continuous experiments. For various concentrations and gas rates the effects of foam height and foam column diameter upon the separation of the ethylhexadecyldimethylammonium bromide-water system were determined by Grieves and Wood (*9*). This was the initial study of a cationic agent; all previous investigations of this type were limited to anionic surfactants.

These latter studies considered only a few of the significant operating variables of a continuous foaming process. In addition they were conducted with water-surfactant systems of limited commercial significance. It will not be possible to evaluate completely foam fractionation as a feasible chemical engineering separation technique until further information is provided on the factors which control the separations that are obtainable. This involves a large number of operating variables and equipment design parameters for a variety of surfactant-solvent systems. When sufficient information is available for a surfactant-solvent system of commercial significance, optimum conditions may be specified and the best separation for the desired throughput may be estimated.

In this connection three variables, considered to have a most significant effect upon continuous foam separation, were selected for study. They are temperature, including its influence on drain rate and composition for a given liquid feed composition and rate; liquid residence time, encompassing both the effect of the volume of liquid solution foamed and of liquid feed rate; and the position for the introduction of the feed, including the possibility of using the column of foam as an enricher, as a stripper, or as a combination of both.

THE FOAM SEPARATION PROCESS

Foam fractionation utilizes the tendency of surface-active agents to accumulate at the gas-liquid interfaces

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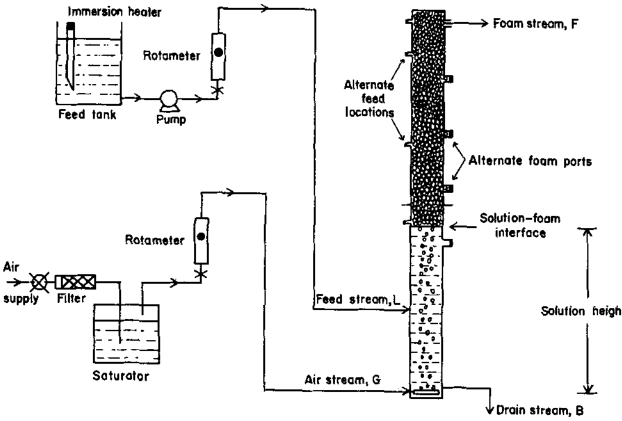

Fig. 1. Schematic flow diagram of experimental apparatus.

produced in a foam. An excellent description of the process has been presented in the literature (*16*). The process may be studied by means of a simple apparatus consisting of an aerator placed in a column which contains a solution of surfactant. For continuous feed to the column an overall material balance may be expressed as follows:

$$L = F + B \qquad (1)$$

A component balance involving the surfactant may also be made:

$$Lx_L = Fy_F + Bx_B \qquad (2)$$

For the foam fractionation of a specified surfactant from a solution of known concentration x_L, L may be selected and one additional composition and flow rate may be specified. B and x_B are likely to be specified if the objective is the stripping of a surface-active contaminant from a feed stream, while F and y_F are likely to be selected if the primary objective is the enrichment of the foam stream. In this study the response of B and x_B to changes in operating variables was followed.

A theoretical analysis of foam fractionation utilizing rate and equilibrium concepts of mass transfer has been carried out previously (*8*). A single contact was assumed to exist at the solution-foam interface with multiple contacts in the foam phase. A later investigation (9) showed that the height of foam above the solution-foam interface has an important effect upon the separation. The effect is most prominent near the interface, decreases with increasing distance from it, and becomes more pronounced as the air rate is increased. Based on these previous investigations it would appear that improved separations could be achieved by introducing the feed into the foam phase. Some indication of this has been reported in the literature (*16*). The effect of the position at which the feed is introduced should be most pronounced near the interface and should decrease with increasing distance from it. If one assumes that multiple contacts will be achieved in the foam phase, variation in feeder location should permit the foam column to be operated as an enriching column, as a stripping column, or as a combination of both.

Earlier investigations have not been concerned with the influence of the average residence time of liquid in the solution (below the interface). Liquid residence time may be varied in a column of specified cross section by changing the height of the solution at constant feed rate or by changing the feed rate at constant solution height. If equilibrium is rapidly achieved, variation in residence time by changing the solution height should have little effect; however variations in feed rate and thus in G/L, the volume of air employed per unit volume of feed treated, may have a most pronounced effect.

Temperature should have an important influence on the foam fractionation process. In accordance with the Gibbs' equation (*16*) the surface excess is inversely proportional to temperature; in addition foam stability is a strong function of temperature. For a given feed and fixed operating conditions both the drain rate and drain concentration should be significantly influenced by temperature, but not necessarily in a similar manner.

EXPERIMENTAL APPARATUS AND PROCEDURE

A schematic flow diagram of the apparatus is shown in Figure 1. The column consisted of two lengths of 4-in. I.D. polished Lucite tube, giving a total column 8 ft. in height. Foam was removed and feed was introduced through ¾-in. diameter holes drilled in the column at appropriate locations. The foam stream was taken from ports such that the removal was always 29 in. above the solution-foam interface. Previous studies (9) indicated that there was no difference in the separation obtained when high purity nitrogen or air was used, and therefore the latter was used in all of the experiments. The air was passed through a cotton filter, saturated to a relative humidity of 90%, and metered by a rotameter. The air was introduced into the solution by means of a 35-μ porous metal diffuser, 2⅜ in. in diameter. The aqueous feed solution was delivered by means of a small rotary pump, and the feed rate to the column was controlled by a rotameter. The drain rate from the bottom of the column was determined by timed, volumetric measurements.

The effect of temperature was studied by preheating the feed, and the actual temperature of operation was determined by measurement in the column. In the liquid residence time experiments the solution height above the diffuser (bottom of the column) was varied from 4.5 to 50 in.; in the feed position experiments the feed was introduced to the column at heights above the diffuser ranging from 8 to 50 in. In the latter series the solution height was maintained at 20 in. Steady state operation was deemed to exist when the concentration of the drain stream and the drain and foam rates were constant. This required approximately 4 hr. of operation; after 6 hr. the foam and drain rates were accurately measured, and duplicate samples of the drain were taken for analysis. Random analyses of the foam stream were made for material balance verification.

Ethylhexadecyldimethylammonium bromide, a cationic surface-active agent, was used in all of the experiments. The concentrations of the surfactant were determined by means of the Volhard volumetric analysis for the bromide ion (*19*). The accuracy was ±0.0025 mg./ml.

THE EFFECT OF TEMPERATURE

A total of eighteen experiments were conducted at temperatures ranging from 75° to 100°F. and at air rates of 1,600 and 2,090 ml./min. (standard temperature and pressure). The feed rate was 100 ml./min., the solution height was maintained at 40 in., and the foam height above the interface was held constant at 29 in. Feed solutions of concentration 0.1, 0.2, and 0.4 mg./ml. were foamed at each air rate and at three different temperatures.

It was found that for fixed values of L, x_L, and G the drain stream concentration x_B and drain rate B increased linearly with temperature. Increases in both quantities would be expected, since foam stability decreases with temperature and the corresponding lower foam rate generally results in a higher concentration of surfactant in the drain stream. In addition the foam concentration y_F in every case was an increasing function of temperature, while F always decreased. The enrichment ratio y_F/x_B was also found to increase with temperature, thus indicating that the foam concentration is more temperature dependent than the drain concentration. The increasing enrichment probably is caused by improved contact in the less stable foam due to bubble breakage. With all of the temperature data utilized, a multiple linear regression analysis resulted in the following expressions for B and x_B; stand-

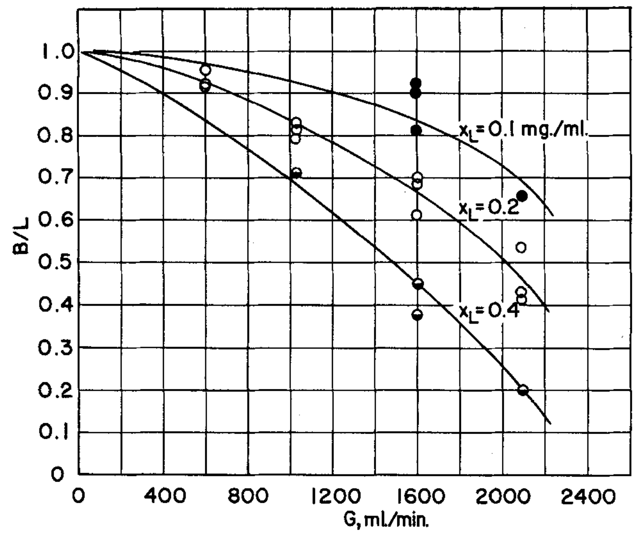

Fig. 2. Relationships between B/L and G from variable feed rate experiments.

ard deviations of estimate and multiple correlation coefficients are also given:

$$B = 33.60 - 109.8\,x_L + 1.399\,t - 0.03199\,G \quad (3)$$

Standard deviation: 6.3665
Correlation coefficient: 0.96016

$$x_B = -\,0.07165 + 0.7340\,x_L + 0.00104\,t - 0.00003\,G \quad (4)$$

Standard deviation: 0.00898
Correlation coefficient: 0.99633

As an example of the effect of temperature, for a feed of 0.3 mg./ml. and an air rate of 1,900 ml./min., B increases from 44.6 to 79.6 ml./min. and x_B increases from 0.169 to 0.195 mg./ml., corresponding to an increase in temperature from 75° to 100°F. Temperature has a most pronounced effect on drain rate, and for operation at a prescribed air rate the range of permissible operating temperatures may be extremely narrow. This would be particularly true if operation was desired with a very low foam rate. Although the ranges of air rates, feed concentrations, and temperatures employed in this study were somewhat limited, it is quite likely that the overall response should be similar. A linear temperature dependence should result for conditions other than those investigated.

THE EFFECT OF LIQUID RESIDENCE TIME

The second series of experiments was carried out in an effort to determine the effect of liquid residence time upon continuous foam separation. For 0.1, 0.2, and 0.4 mg./ml. feed solutions and feed rates of 25, 50, and 100 ml./min. experiments were conducted at solution heights (above the diffuser) ranging from 4.5 to 50 in. and air rates from 600 to 2,090 ml./min. (standard temperature and pressure). The temperature was held constant at 75°F., and the foam height above the solution-foam interface was maintained at 29 in.

Results showed that with all other variables held constant a variation in solution height had no effect upon the separation. At each of the four air rates and for the six solution heights used at each air rate the concentrations and rates of the effluent streams were independent of solution height. For example six runs at x_L = 0.2 mg./ml., L = 50 ml./min., and G = 1,030 ml./min. showed that x_B remained constant at 0.095 mg./ml. regardless of solution height, and B varied only from 40 to 42 ml./min. in a random manner. From these results it would appear that liquid residence time has no effect upon continuous foam separation. However experiments conducted with a fixed solution height and variable feed rate showed the separation to be a strong function of the feed rate.

In general it was found that at a fixed air rate the drain rate increased in direct proportion to an increase in feed rate, and the drain concentration also increased significantly. The results of the variable feed rate experiments are presented in Figures 2 and 3. Figure 2 relates the ratio of the drain rate to the feed rate to air rate, with parameters of feed concentration. The approximate, direct proportionality of the drain rate to the feed rate was exhibited at all air rates and concentrations employed. Figure 3 shows the relationship between the ratio of drain concentration to feed concentration and the ratio of air rate to feed rate. A single curve was found to represent all feed rates, air rates, and concentrations used; however the 0.4 mg./ml. feed solutions generally gave high results, indicating that it would be difficult to represent the data for more concentrated feed solutions on this basis. From Figure 3 it is clear that for a given feed concentration the drain concentration is fixed at a fixed volume of air delivered per unit volume of feed treated. Thus the same drain concentration should be obtained whether the feed is treated in a single large column or in several smaller columns in parallel, as long as the volumetric air rate employed is constant.

From the variable solution height data it can be concluded that equilibrium is rapidly achieved in the solution, and longer residence times do not influence the separation. Varying the feed rate at constant air rate has a pronounced effect on the separation; it may be hypothesized that G/L, the volume of air employed per unit volume of feed treated, is a prime variable, analogous to the heat input per unit weight of feed to a continuous still.

THE EFFECT OF THE POSITION OF FEED INTRODUCTION

The preceding series of experiments were conducted with the feed introduced into the liquid solution midway between the diffuser and the solution-foam interface. It was found that at a fixed solution height a change in the height of the feed inlet to the solution had no influence upon the separation, indicating that the solution was completely mixed. A third series of experiments was carried out to determine the effect of introducing the feed into the foam phase. For 0.2 and 0.4 mg./ml. feed solutions and air rates of 1,030, 1,600, and 2,090 ml./min. runs were made with the feeder located just above the solution-foam interface and at heights of 13, 25, and 28.5 in. above the interface. Feed was introduced into the foam phase by means of a nozzle which provided some constriction to the foam flow in the column. The feed rate was 50 ml./min., the column temperature was 75°F., the solution height was 20 in., and the foam height was 29 in.

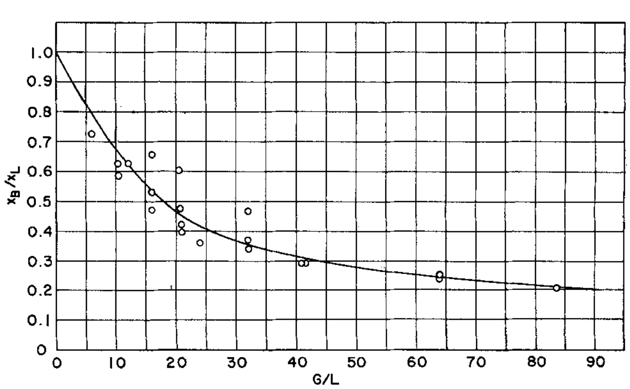

Fig. 3. Relationship between x_B/x_L and G/L from variable feed rate experiments.

The results of the variable feed position experiments are presented in Figures 4 and 5 for 0.2 and 0.4 mg./ml. feed solutions, respectively. x_B and B are plotted against the ratio of the height of the feeder above the interface to the foam height above the interface; H_F remained constant at 29 in., and negative values of H_L/H_F correspond to feed introduced into the liquid solution. Compared with placing the feeder in the solution a considerable improvement was achieved by introducing the feed at the solution-foam interface, resulting in both an increase in drain rate and decrease in drain concentration. The effect was maximized at the high feed concentration and at the higher air rates; for $x_L = 0.4$ mg./ml. and $G = 1{,}600$ ml./min. positioning the feeder at the interface provided an increase in the enrichment ratio y_F/x_B from 2.8 to 12.8. In all other tests y_F/x_B was at least doubled. It is possible that the constriction created in the column by the feed nozzle may account for a certain amount of the drain rate and enrichment ratio increase.

Raising the feeder to higher points in the foam column (above the interface) resulted in a continued decrease in drain concentration, while the drain rate passed through a maximum and then decreased. This behavior in all cases resulted in the foam concentrations y_F passing through maximum values at H_L/H_F approximately equal to 0.45. When one considers only the data for which H_L/H_F was greater than zero, feeding at the solution-foam interface utilized the foam phase as an enriching column giving a rich foam stream but not providing optimum removal from the drain stream. Moving the feed inlet higher up the column permitted the foam column to be utilized both as an enricher and a stripper, increasing y_F and decreasing x_B. Feeding at the top of the column provided excellent stripping of the drain stream but poor enrichment of the foam. If the major consideration is the reduction of x_B to a minimum value while maintaining B at a maximum value, the best feed location is at $H_L/H_F = 0.45$. At this location values of the enrichment ratio could be increased by as much as a factor of 15, compared with values with the feeder in the solution. By feeding at the top of the column a considerable saving in the volume of air delivered could be realized owing to the approach of x_B and B at all air rates; however a low drain rate would result.

CONCLUSIONS

From an experimental investigation of the ethylhexadecyldimethylammonium bromide-water system the following conclusions may be drawn:

1. For a given air rate and feed stream concentration and rate the drain stream concentration and rate increase linearly with temperature. The foam concentration and the enrichment ratio also are increasing functions of temperature. Equations derived from a multiple linear regression analysis enable the calculation of the drain stream rate and concentration from the air rate, feed concentration, and temperature.

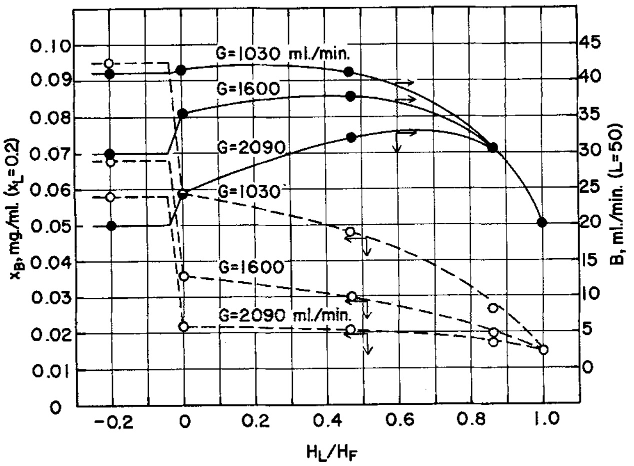

Fig. 4. Relationships between x_B, B, and ratio of feed location height to foam height for 0.2 mg./ml. feed solutions.

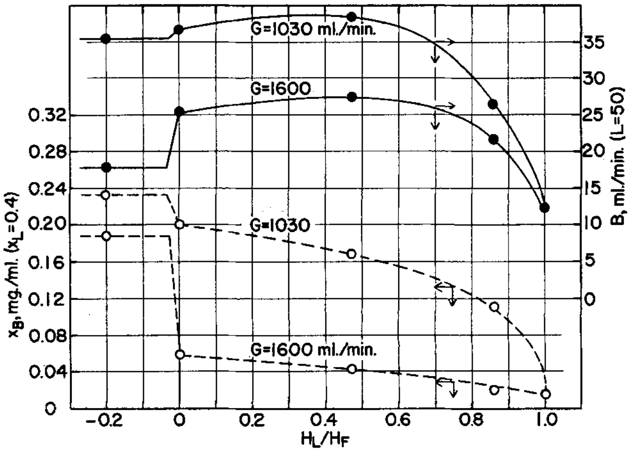

Fig. 5. Relationships between x_B, B, and ratio of feed location height to foam height for 0.4 mg./ml. feed solutions.

2. Based upon experiments involving the variation in liquid residence time by two methods it was found that there is no change in the separation with variable solution height but that there is a pronounced variation with liquid feed rate. When one considers the variable solution height data, it appears that an equilibrium separation is rapidly achieved in the solution and a rate approach to the mass transfer process is not valid. From the variable feed rate and air rate data it is clear that the volume of air employed per unit volume of feed treated is a prime factor influencing the separation, and an analogy may be made between the effect of G/L upon foam separation and the effect of the quantity of heat per unit weight of feed upon continuous distillation.

3. Positioning the feed inlet at the solution-foam interface, compared with feeding into the solution, provides a significant increase in drain rate and decrease in drain concentration. Moving the feeder higher into the column of foam results in a continued decrease in drain concentration but in the passage of the drain rate through a maximum value. The foam column may be operated as an enricher, as a stripper, or as a combination of both, with the optimum height for the feed at approximately the midpoint of the column of foam.

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NOTATION

B = drain rate, ml./min.
F = foam rate, ml./min.
G = air rate, ml./min.
H_F = height of foam above interface, in.
H_L = height of feed introduction to column above interface, in.
L = feed rate, ml./min.
t = temperature of column, °F.
x_B = concentration of drain stream, mg./ml.
x_L = concentration of feed stream, mg./ml.
y_F = concentration of foam stream, mg./ml.

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Solution of the Linearized Equations of Multicomponent Mass Transfer: II. Matrix Methods

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Solutions to the equations of multicomponent mass transfer may be written as matrix generalizations of the solution to the equivalent binary mass transfer equation when initial and boundary concentrations are constant, there are no homogeneous reactions, and all physical properties including the diffusion coefficient matrix are concentration independent.

The analogue of the binary mass transfer coefficient is a multicomponent mass transfer coefficient matrix which depends only upon the mass transfer coefficients of the equivalent binary system and the diffusion coefficient matrix of the multicomponent system.

When interphase transfer takes place, the inverse multicomponent mass transfer coefficient matrices of each phase are additive. Their sum yields an overall resistance to mass transfer which is the inverse of the overall multicomponent mass transfer coefficient matrix.

GENERAL THEORY

In Part I the linearized equations of multicomponent mass transfer were uncoupled, and solutions were obtained by an algebraic method.

In this part matrix methods are used to carry out the analysis. The present method is more efficient for systems of more than three components, gives solutions even if the diffusion equations cannot be uncoupled, and is advantageous in considering transfer between phases.

The starting equations for an $n + 1$ component system may be written as (*6*)

$$\frac{\partial C_i}{\partial \theta} + \nabla \cdot \{\underline{V} C_i\} = - \nabla \cdot \underline{j}_i + r_i, \; i = 1, \ldots, n \qquad (1')$$

$$\underline{j}_i = - \sum_j D_{ij} \nabla C_j, \; i = 1, \ldots, n \qquad (2')$$

and summations are always from 1 to n. A primed equation number indicates the scalar form of a matrix equation which will be written with the same number. The flux with respect to a coordinate moving at the reference velocity $\underline{V}$ has been written separately here to emphasize the fact that it is the coupling in Equation (2′) which gives rise to the basic difference between binary and multicomponent systems.

If the C_i are written as the elements of a column vector (C), the concentration vector; the $\underline{j}_i$ as the elements of a column vector $(\underline{j})$, the flux vector; the r_i as the elements of a column vector (r), the reaction vector; and the D_{ij} as the elements of a matrix $[D]$, the diffusion coefficient matrix; then in matrix notation Equations (1′) and (2′) become

$$\frac{\partial (C)}{\partial \theta} + \nabla \cdot \{\underline{V}(C)\} = - \nabla \cdot (\underline{j}) + (r) \qquad (1)$$

$$(\underline{j}) = - [D](\nabla C) \qquad (2)$$

It is noted that on thermodynamic grounds when all the n independent concentration gradients are zero all the n independent fluxes must be zero, and vice-versa. Hence $[D]$ must be nonsingular.

Equations (1) and (2) are now partially linearized as before (*6*) by assuming that the matrix $[D]$, which in

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