metric constraints of Equation (13), and the proposed mechanism can not be ruled out.

CONCLUSIONS

It has been shown that reaction systems with active intermediates are amenable to a straightforward analysis of the constraints imposed by stoichiometry and kinetics. These constraints yield considerable information about the structure of the general solution. Examples have been given of the application of the analysis to systems of varying complexity.

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NOTATION

$\mathbf{c}$ = vector of concentrations
$\mathbf{c}_1$, $\mathbf{c}_2$ = vectors of concentrations of stable and active species, respectively
$\mathbf{k}$ = vector of rate constants
$\mathbf{N}$ = basis for null space of $\boldsymbol{\beta}_2^T$
$\mathbf{r}$ = vector of rates of reaction
t = time
$\mathbf{x}$, $\mathbf{y}$ = state variables

Greek Letters

$\boldsymbol{\beta}$ = stoichiometric matrix
$\boldsymbol{\beta}_1$, $\boldsymbol{\beta}_2$ = partitioned stoichiometric matrix
δ, ϵ = small parameters
η = dimensionless extent of reaction
$\boldsymbol{\nu}$ = vectors in null space of $\boldsymbol{\beta}_2^T$

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A Method of Temperature Estimation in the Bubble Point Method of Iterative Distillation Calculations

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A general procedure for distillation calculation has been discussed by several authors, for example, Amundson et al. (1959), Holland (1963), Wang and Henke (1966), and Billingsley (1970). The procedure is summarized as follows: (1). assume an initial phase flow and temperature profiles; (2). calculate the vapor-liquid equilibrium constant of each component at each stage K_{ij}; (3). solve the material balance equations for the composition of each component at each stage. (4). The stage temperature is determined in a manner explained subsequently; (5). the phase flow rates are computed by the energy balance; and (6). steps (2) through (5) are repeated in order until $|(T_j)_n - (T_j)_{n-1}| < E_T$ for each stage where E_T is a prescribed tolerance.

Billingsley (1970) pointed out that the stage temperature determination is the least satisfactory part of any published scheme solving distillation problems. In the conventional bubble point method of iterative distillation calculation, the temperature profile in the column is estimated on the basis of the liquid composition at each stage by bubble point temperature calculation or the vapor composition by dew point temperature calculation. Wang and Henke (1966) used Muller's method to obtain the bubble point or dew point temperature, while most of the other investigators used the Newton-Raphson iterative method. Holland (1963) suggested that temperature for each stage can be approximated by the K_b method. Billingsley (1970) proposed an improvement in the K_b method.

The objective of this article is to present a new method, called the *hypothetical component method,* which provides a simple way to estimate the bubble point or dew point temperature for each stage.

HYPOTHETICAL COMPONENT METHOD

For convenience, we will delete the stage index; however, the reader should keep in mind that the derivation given is applicable to each stage. Let us assume that the mixture at any j^{th} stage is a hypothetical component, and

$$X_h = \sum_{i}^{NC} X_i \tag{1}$$

$$Y_h = \sum_{i}^{NC} Y_i \tag{2}$$

Further, let us assume that the well-known Clausius-Clapeyron equation prevails:

$$\ln P_v = \frac{A}{T} + B \tag{3}$$

where P_v is the vapor pressure of the hypothetical component at temperature T, and A and B are parameters.

BUBBLE POINT TEMPERATURE ESTIMATION

To estimate bubble point temperature, the liquid composition must be known; that is, $X_h = \Sigma_i X_i = 1$. The vapor pressure of the hypothetical component can be expressed as follows:

$$Y_h P = P_v \tag{4}$$

Note that Y_h is not equal to unity if the temperature is not at the bubble point. By substituting Equation (4) into Equation (3), the equation can be rewritten as follows:

$$\ln Y_h P = \frac{A}{T} + B \tag{5}$$

In most of the distillation calculations, total pressure is fixed. Hence, Equation (5) can be written as

$$\ln Y_h = \frac{A}{T} + B' \tag{6}$$

where

$$B' = B - \ln P$$

At the bubble point temperature T_b, the total pressure is equal to the vapor pressure $P = P_v$. Therefore, $\ln Y_h = 0$, and Equation (6) becomes

$$\frac{A}{T_b} + B' = 0 \tag{7}$$

Subtracting the left-hand side of Equation (7) from the right-hand side of Equation (6), one obtains

$$\ln Y_h = A\left(\frac{1}{T} - \frac{1}{T_b}\right) \tag{8}$$

Equation (8) can be rearranged as follows:

$$\begin{aligned} T_b &= T \frac{1}{1 - \dfrac{T}{A}\ln Y_h} \\ &= T \frac{1}{1 - \dfrac{T}{A}\ln \Sigma_i Y_i} \end{aligned} \tag{9}$$

When $\Sigma_i Y_i$ is very close to 1, $\ln \Sigma_i Y_i$ can be approximated as follows:

$$\ln \Sigma_i Y_i \approx \Sigma_i Y_i - 1 \tag{10}$$

Consequently, Equation (9) can be approximated as follows:

$$T_b \approx T \frac{1}{1 + \dfrac{T}{A}(1 - \Sigma_i Y_i)} \tag{11}$$

Usually, $T/A\ (1 - \Sigma_i Y_i)$ is very small when it is compared with 1. Therefore, Equation (11) can be further approximated as follows:

$$T_b \approx T\left(1 - \frac{T}{A}[1 - \Sigma_i Y_i]\right) \tag{12}$$

DEW POINT TEMPERATURE ESTIMATION

An equation similar to Equation (12) can be derived for dew point temperature estimation. In order to estimate the dew point temperature, the vapor composition must be known; that is, $Y_h = \Sigma_i Y_i = 1$. Replacing Equation (4) by the Raoult's law, one has

$$P = X_h P_v \tag{13}$$

Substituting Equation (13) into Equation (3) and rearranging, one obtains

$$-\ln X_h = \frac{A}{T} + B' \tag{14}$$

At dew point temperature T_d, the vapor pressure is equal to total pressure $P = P_v$. Therefore, $\ln X_h = 0$, and Equation (14) becomes

$$\frac{A}{T_d} + B' = 0 \tag{15}$$

Subtracting the left-hand side of Equation (15) from the right-hand side of Equation (14) and rearranging, one obtains

$$\begin{aligned} T_d &= T \frac{1}{1 + \dfrac{T}{A}\ln X_h} \\ &= T \frac{1}{1 + \dfrac{T}{A}\ln \Sigma_i X_i} \end{aligned} \tag{16}$$

Similar to Equation (9), Equation (16) can be approximated as follows:

$$T_d = T\left(1 + \frac{T}{A}[1 - \Sigma_i X_i]\right) \tag{17}$$

DISCUSSION

In Equations (12) and (17), A is the only parameter. The parameter A may vary from stage to stage. However, it has also been found that stability is not very sensitive to the parameter A. A constant value of A can be applied throughout the whole distillation column. A simple mixing rule is good enough to obtain the parameter A, that is

$$A = \Sigma_i X_{if} \cdot a_i \tag{18}$$

where X_{if} is the feed composition of i^{th} component, and a_i is the parameter in the Clausius-Clapeyron equation for i^{th} component

$$\ln P_{v,i} = \frac{a_i}{T} + b_i \tag{19}$$

where $P_{v,i}$ is the vapor pressure of i^{th} component.

In most cases, even if we replace the term $-T/A$ by a constant C, the iteration method is still stable. Equation (12) becomes

$$T_b \approx T(1 + C[1 - \Sigma_i Y_i]) \tag{20}$$

and Equation (17) becomes

$$T_d \approx T(1 - C[1 - \Sigma_i X_i]) \tag{21}$$

C usually is between 1/5 to 1/10. For most hydrocarbon mixtures, 1/7.5 is a good default value. The smaller the C constant, the slower the iteration scheme. However, if C is too large, the iteration will be oscillatory, and sometimes it might be divergent. The constant C should be adjusted to have good convergence. This method has been successfully applied to speed up iterative distillation calculation. It has also been successfully applied to calculate bubble point and dew point temperature under fixed pressure with a few cycles of iteration.

CONCLUSION

A new method, called the *hypothetical component method*, is presented as an alternative to the K_b method. This new method provides a simple way to estimate the bubble or dew point temperature for each stage and helps speed convergence of iterative distillation calculations.

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NOTATION

a_i, b_i = constants in Clausius-Clapeyron equation for i^{th} component
A, B = constants in Clausius-Clapeyron equation for the hypothetical component
C = constant
K_{ij} = vapor-liquid equilibrium constant of i^{th} component at j^{th} stage
NC = number of components
P = total pressure
P_v = vapor pressure
T = temperature
T_b = estimated bubble point temperature
T_d = estimated dew point temperature
T_j = temperature at j^{th} stage
$T_{j,n}$ = temperature at j^{th} stage during n^{th} trial
X_{ij} = liquid composition of i^{th} component at j^{th} stage
X_{if} = feed composition of i^{th} component
Y_{ij} = vapor composition of i^{th} component at j^{th} stage

Subscripts

f = feed
i = i^{th} component
j = j^{th} stage
n = n^{th} trial

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Extensional Viscosity and Recoil in Highly Dilute Polymer Solutions

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As one part of a current study of turbulent drag reduction with dilute polymer solutions, we have investigated the behavior of these materials in flow through an orifice. It is well known that for such a geometry many polymer melts and solutions adopt a "wine glass stem" appearance (Metzner, 1971; Bagley and Birks, 1960), consisting of a narrow rapidly converging central region, surrounded by large slowly recirculating eddies. Metzner, Uebler, and Chan Man Fong (1969) have analyzed the kinematics of this flow, arguing that large tensile stresses may arise within the converging section of the flow field. These stresses are reflected in the value of the pressure loss which may be significantly elevated relative to that of the solvent, even at extremely low polymer concentrations. Additional evidence of this effect is reported in the present note, along with a description of the recoil which occurs following sudden cessation of flow. This recoil effect offers a striking visual confirmation of the high extensional stresses which can develop in these systems.

EXPERIMENTAL

A 20 p.p.m. by weight solution of Separan AP 273 in deionized water was studied. Separan AP 273 is a polyacrylamide with a nominal molecular weight of 8 to 10 × 10^6, manufactured by Dow. The polymer has undergone approximately 30% hydrolysis and the resultant carboxyl groups converted to their sodium salt. Hence, in deionized water the solutions are slightly basic, with a *p*H of approximately 9 at 20 p.p.m. by weight. The flow setup consisted of a rectangular Plexiglas box, 30 cm long by 20 cm wide by 20 cm deep, fitted with a 0.35 cm long tube, 0.11 cm in diameter (hereafter referred to as the *orifice*). A distributor plate was located 23 cm upstream of the orifice. Pressure taps were mounted on the side walls, in the slowly recirculating region.

RESULTS AND DISCUSSION

Typical experimental data for the water and Separan solutions are tabulated in Table 1 vs. orifice velocity. The presence of the polymer leads to a marked elevation in